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Pim de Voogt *Editor*

Reviews of Environmental Contamination and Toxicology

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Reviews of Environmental Contamination and Toxicology Volume 250

Editor
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Coordinating Board of Editors

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Special Foreword

Almost 60 years ago now the Springer book series ‘Residue Reviews/Rückstands-Berichte’ was initiated in 1962 under the editorship of Francis A. Gunther, who wrote in the Preface to Volume 1, January 1962: ‘The justification for the preparation of any review for this book series is that it deals with some aspect of the many real problems arising from the presence of residues of foreign chemicals in foodstuffs. The scope of “Residue Reviews” is international. It encompasses those matters, in any country, which are involved in allowing pesticide and other plant-protecting chemicals to be used safely in producing, storing, and shipping crops. Added plant or animal pest-control chemicals or their metabolites that may persist into’ meat and other edible animal products. . .’.

One year later in January 1963, Gunther evaluated: ‘That residues of pesticides and other “foreign” chemicals in foodstuffs are of concern to everyone everywhere is attested by the reception accorded Volumes 1 and 2 of ‘Residue Reviews’, and by the gratifying enthusiasm, sincerity, and efforts shown by the individuals I have asked to prepare manuscripts. Many manuscripts on residue affairs are in preparation, but the field is so large and the non-polemical interests in it so varied that the editor and the Advisory Board will welcome suggestions for topics considered suitable and timely for review in this international book-series. There can be no serious question that pesticide and food-additive chemicals are essential to adequate food production, manufacture, marketing, and storage, yet without continuing surveillance and intelligent control some of those that persist could at times conceivably endanger the public health. The object of “Residue Reviews” is to provide concise, critical reviews of timely advances, philosophy, and significant areas of accomplished or needed endeavor in the total field of residues of these chemicals in foods, in feeds, and in transformed food products. These reviews are either general or specific, but properly they may lie in the domains of analytical chemistry and its methodology, biochemistry, human and animal medicine, legislation, pharmacology, physiology, regulation, and toxicology. . .’. Today, the words Gunther wrote are equally valid for the series when one substitutes ‘food’ or ‘foodstuffs’ by ‘environment’.

Gunther, later with the help of his wife Jane Davies Gunther, served for almost 25 years as the editor-in-chief of the book series. Volumes 1–97 of the book series were published bearing the title: ‘Residue Reviews. Residues of Pesticides and Other Contaminants in the Total Environment’. In 1986 (Volume 98), the title of the series was modified into ‘Reviews of Environmental Contamination and Toxicology’ (RECT) and George W. Ware took over the role of editor-in-chief. In 2008, David M. Whitacre succeeded Ware to become the editor-in-chief of RECT when Volume 194 was published. Whitacre served until Volume 235 (2015), when he invited me to become the next editor-in-chief. Gunther, Ware, and Whitacre were three editorial giants who turned out to be pivotal in the shaping of RECT into its present, highly successful status.

Apart from maintaining the original form of a book series, the publisher decided to also register RECT with an ISSN number, the series thus becoming also known as a regular journal with entries into the important publication databases, such as Web of Knowledge and PubMed. The change of the title that was effective as of 1986 reflected the wish felt by the editors and the publisher to widen the scope of the journal from food-focused research to reviews dedicated to environmental contamination and its consequences for the health of both humans and ecosystems. Together with the companion journals the Bulletin of Environmental Contamination and Toxicology (BECT) and the Archives of Environmental Contamination and Toxicology (AECT), the entire scope of article types a scientist may wish to publish, ranging from short communications to archival papers to lengthy reviews, is thus covered by a triumvirate of journals from the same publisher. The editors-in-chief of BECT, AECT, and RECT jointly with the publisher discuss on a regular basis the scopes of the three journals and the complementary editorial policies for each of the journals.

Over the almost 60 years that the book series now exists, RECT has become a concept in the scientific community dealing with the processes that underlie emissions, behaviour, fate, and effects of environmental contaminants and the methodologies to monitor and quantify these. To celebrate the publication of the 250th volume of the book series/journal, the members of the current Board of Associate Editors of RECT were invited to provide contributions from their own Institutes. These reviews were assembled for this special anniversary issue of RECT after being subjected to the common peer review protocol. The current volume illustrates both the width of RECT’s scope and the diverse scientific background of the members of its Editorial Board, without whom the success of the series would never have reached the standard it currently has achieved.

Pim de Voogt
Editor-in-Chief

Foreword

International concern in scientific, industrial, and governmental communities over traces of xenobiotics in foods and in both abiotic and biotic environments has justified the present triumvirate of specialized publications in this field: comprehensive reviews, rapidly published research papers and progress reports, and archival documentations These three international publications are integrated and scheduled to provide the coherency essential for nonduplicative and current progress in a field as dynamic and complex as environmental contamination and toxicology. This series is reserved exclusively for the diversified literature on "toxic" chemicals in our food, our feeds, our homes, recreational and working surroundings, our domestic animals, our wildlife, and ourselves. Tremendous efforts worldwide have been mobilized to evaluate the nature, presence, magnitude, fate, and toxicology of the chemicals loosed upon the Earth. Among the sequelae of this broad new emphasis is an undeniable need for an articulated set of authoritative publications, where one can find the latest important world literature produced by these emerging areas of science together with documentation of pertinent ancillary legislation.

Research directors and legislative or administrative advisers do not have the time to scan the escalating number of technical publications that may contain articles important to current responsibility. Rather, these individuals need the background provided by detailed reviews and the assurance that the latest information is made available to them, all with minimal literature searching. Similarly, the scientist assigned or attracted to a new problem is required to glean all literature pertinent to the task, to publish new developments or important new experimental details quickly, to inform others of findings that might alter their own efforts, and eventually to publish all his/her supporting data and conclusions for archival purposes.

In the fields of environmental contamination and toxicology, the sum of these concerns and responsibilities is decisively addressed by the uniform, encompassing, and timely publication format of the Springer triumvirate:

> *Reviews of Environmental Contamination and Toxicology* [Vol. 1 through 97 (1962–1986) as Residue Reviews] for detailed review articles concerned with any aspects of chemical contaminants, including pesticides, in the total environment with toxicological considerations and consequences.
>
> *Bulletin of Environmental Contamination and Toxicology* (Vol. 1 in 1966) for rapid publication of short reports of significant advances and discoveries in the fields of air, soil, water, and food contamination and pollution as well as methodology and other disciplines concerned with the introduction, presence, and effects of toxicants in the total environment.
>
> *Archives of Environmental Contamination and Toxicology* (Vol. 1 in 1973) for important complete articles emphasizing and describing original experimental or theoretical research work pertaining to the scientific aspects of chemical contaminants in the environment.

The individual editors of these three publications comprise the joint Coordinating Board of Editors with referral within the board of manuscripts submitted to one publication but deemed by major emphasis or length more suitable for one of the others.

Coordinating Board of Editors

Preface

The role of *Reviews* is to publish detailed scientific review articles on all aspects of environmental contamination and associated (eco)toxicological consequences. Such articles facilitate the often complex task of accessing and interpreting cogent scientific data within the confines of one or more closely related research fields.

In the 50+ years since *Reviews of Environmental Contamination and Toxicology* (formerly *Residue Reviews)* was first published, the number, scope, and complexity of environmental pollution incidents have grown unabated. During this entire period, the emphasis has been on publishing articles that address the presence and toxicity of environmental contaminants. New research is published each year on a myriad of environmental pollution issues facing people worldwide. This fact, and the routine discovery and reporting of emerging contaminants and new environmental contamination cases, creates an increasingly important function for *Reviews.* The staggering volume of scientific literature demands remedy by which data can be synthesized and made available to readers in an abridged form. *Reviews* addresses this need and provides detailed reviews worldwide to key scientists and science or policy administrators, whether employed by government, universities, nongovernmental organizations, or the private sector.

There is a panoply of environmental issues and concerns on which many scientists have focused their research in past years. The scope of this list is quite broad, encompassing environmental events globally that affect marine and terrestrial ecosystems; biotic and abiotic environments; impacts on plants, humans, and wildlife; and pollutants, both chemical and radioactive; as well as the ravages of environmental disease in virtually all environmental media (soil, water, air). New or enhanced safety and environmental concerns have emerged in the last decade to be added to incidents covered by the media, studied by scientists, and addressed by governmental and private institutions. Among these are events so striking that they are creating a paradigm shift. Two in particular are at the center of ever increasing media as well as scientific attention: bioterrorism and global warming. Unfortunately, these very worrisome issues are now superimposed on the already extensive list of ongoing environmental challenges.

The ultimate role of publishing scientific environmental research is to enhance understanding of the environment in ways that allow the public to be better informed or, in other words, to enable the public to have access to sufficient information. Because the public gets most of its information on science and technology from internet, TV news, and reports, the role for scientists as interpreters and brokers of scientific information to the public will grow rather than diminish. Environmentalism is an important global political force, resulting in the emergence of multinational consortia to control pollution and the evolution of the environmental ethic. Will the new politics of the twenty-first century involve a consortium of technologists and environmentalists, or a progressive confrontation? These matters are of genuine concern to governmental agencies and legislative bodies around the world.

For those who make the decisions about how our planet is managed, there is an ongoing need for continual surveillance and intelligent controls to avoid endangering the environment, public health, and wildlife. Ensuring safety-in-use of the many chemicals involved in our highly industrialized culture is a dynamic challenge, because the old, established materials are continually being displaced by newly developed molecules more acceptable to federal and state regulatory agencies, public health officials, and environmentalists. New legislation that will deal in an appropriate manner with this challenge is currently in the making or has been implemented recently, such as the REACH legislation in Europe. These regulations demand scientifically sound and documented dossiers on new chemicals.

Reviews publishes synoptic articles designed to treat the presence, fate, and, if possible, the safety of xenobiotics in any segment of the environment. These reviews can be either general or specific, but properly lie in the domains of analytical chemistry and its methodology, biochemistry, human and animal medicine, legislation, pharmacology, physiology, (eco)toxicology, and regulation. Certain affairs in food technology concerned specifically with pesticide and other food-additive problems may also be appropriate.

Because manuscripts are published in the order in which they are received in final form, it may seem that some important aspects have been neglected at times. However, these apparent omissions are recognized, and pertinent manuscripts are likely in preparation or planned. The field is so very large and the interests in it are so varied that the editor and the editorial board earnestly solicit authors and suggestions of underrepresented topics to make this international book series yet more useful and worthwhile.

Justification for the preparation of any review for this book series is that it deals with some aspect of the many real problems arising from the presence of anthropogenic chemicals in our surroundings. Thus, manuscripts may encompass case studies from any country. Additionally, chemical contamination in any manner of air, water, soil, or plant or animal life is within these objectives and their scope.

Manuscripts are often contributed by invitation. However, nominations for new topics or topics in areas that are rapidly advancing are welcome. Preliminary communication with the Editor-in-Chief is recommended before volunteered review manuscripts are submitted. *Reviews* is registered in WebofScience™.

Inclusion in the Science Citation Index serves to encourage scientists in academia to contribute to the series. The impact factor in recent years has increased from 2.5 in 2009 to 7.0 in 2017. The Editor-in-Chief and the Editorial Board strive for a further increase of the journal impact factor by actively inviting authors to submit manuscripts.

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Pim de Voogt

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Occurrence, Fate and Fluxes of Plastics and Microplastics in Terrestrial and Freshwater Ecosystems

Theresa Schell, Andreu Rico, and Marco Vighi

Contents

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Abbreviations

ATR	Attenuated total reflectance
ECHA	European Chemicals Agency
EEA	European Environment Agency
ERA	Ecological risk assessment
EVA	Ethylene-vinyl acetate
FTIR	Fourier transform infrared
MaP	Macroplastic
MP	Microplastic
NP	Nanoplastic
PA	Polyamide
PAH	Polycyclic aromatic hydrocarbons
PC	Polycarbonate
PCB	Polychlorinated biphenyl
PE	Polyethylene
PEC	Predicted environmental concentration
PES	Polyester
PET	Polyethylene terephthalate
PMMA	Polymethyl methacrylate
PNEC	Predicted no effect concentration
PP	Polypropylene
PS	Polystyrene
PUR	Polyurethane
PVC	Polyvinylchloride
Pyr-GC/MS	Pyrolysis-gas chromatography/mass spectrometry
SAPEA	Science Advice for Policy by European Academies
SEM	Scanning electron microscopy
WWTP	Wastewater treatment plant
XRF	X-ray fluorescence

1 Introduction

Over the past century, plastic has made the journey from being virtually non-existent to a ubiquitous and integral part of modern life. While plastic has numerous advantages compared to alternative materials, we are facing severe environmental, economic and ethical issues due to the vast plastic waste production and rapid disposal. Up until 2015, the total amount of plastic produced was 8300 million tons, 6300 million tons of which were discarded as waste (Geyer et al. 2017). Much of this waste (79%) is accumulated in landfills or the natural environment, and this amount is expected to increase significantly in the future (up to 12,000 million tons by 2050) if management actions are not immediately taken (Geyer et al. 2017).

Most macroplastics (MaPs) break down due to mechanical and chemical fragmentation into smaller pieces, which are commonly termed microplastics (particles <5 mm; MPs) or nanoplastics (particles <1 μm; NPs) (Gigault et al. 2018). The breakdown process may take between 50 and 600 years and usually depends on several factors such as the polymer composition and the environmental condition. MPs that are formed due to the breakdown of MaP are commonly referred to as secondary MPs, while MPs intentionally produced in this size range are referred to as primary MPs. Nowadays, MaPs, MPs and NPs can be found floating or in suspension in many water bodies, accumulated in sediments or in terrestrial ecosystems, and even can be transported and deposited in pristine environments due to wind and currents (Dris et al. 2015, 2016; Ballent et al. 2016; Fischer et al. 2016; Hurley and Nizzetto 2018).

The widespread distribution of plastic and its variability in size and shape allow the ingestion by organisms across many trophic levels and habitats (Wright et al. 2013; Kühn et al. 2015). Large plastic debris (MaPs) can cause adverse effects on coastal and marine animals (marine mammals, fish and seabirds) due to ingestion as well as to entanglement which impedes their mobility (Van Franeker et al. 2011; Knowlton et al. 2012; Schuyler et al. 2012; Kühn et al. 2015). Fishing gear, balloons, plastic bags and bottle caps have been identified to be the most harmful type of MaPs to marine organisms (Hardesty et al. 2015). Although most research has focused on the marine environment, freshwater and terrestrial organisms are expected to suffer from the same sort of effects. For example, cattle have been reported to suffocate and die due to the ingestion of plastic bags, which can block airways and stomachs (Ramaswamy and Sharma 2011).

Similar to MaPs, environmental exposure to MPs has raised concerns about their potentially adverse effects in smaller organisms. Ecotoxicological studies with MPs have been primarily conducted using marine organisms (77%), while freshwater organisms have been less researched (23%) (de Sá et al. 2018), and research involving terrestrial organisms is still in its beginnings (Chae and An 2018). MPs may cause physical effects such as internal and external abrasion or blockages of the digestive tract in small invertebrates and fish (Wright et al. 2013; Karami et al. 2016; Jovanović 2017). Research also shows that MPs ingested by freshwater organisms, either on purpose when they are confounded with preys or accidentally due to non-selective feeding strategies (i.e. water filtration or deposit feeding) (de Sá et al. 2018; Windsor et al. 2019), may reduce their feeding efficiency and lower the energy uptake, which often results in reduced growth, reproduction and survival (Foley et al. 2018). In addition, MPs may affect the growth, chlorophyll content, photosynthesis activity and reactive oxygen species of microalgae at high, currently not realistic, concentrations (Prata et al. 2019).

Although several cases evidence deleterious impacts of MaPs on aquatic and terrestrial organisms under laboratory conditions, the capacity of MPs or even NPs to pose a real threat for ecosystems and human health is disputable. This is because the majority of studies showing some impacts of MPs on terrestrial or freshwater organisms have been performed with very high exposure concentrations, while risk at environmentally relevant concentrations has yet to be disclosed (Lenz et al. 2016).

Despite physical effects, the release of additives such as phthalates, chlorinated paraffins and bisphenols present in some MaPs and MPs (Stenmarck et al. 2017) has been reported to induce endocrine-disrupting effects (Rochman et al. 2014). Furthermore, hydrophobic pollutants (e.g. some pesticides, PCBs, PAHs) can be adsorbed to plastics and may be released into the body of the organisms after ingestion, leading to the so-called Trojan Horse effect (Teuten et al. 2009; Koelmans et al. 2016; Crawford and Quinn 2017; Bouhroum et al. 2019). In contrast, it has been suggested that ingested clean MPs may reduce the concentration of bioaccumulated chemicals in the body of contaminated organisms (Lohmann 2017). Furthermore, MPs could not only act as carriers for chemicals but can also transport bacteria or pathogens attached to them (Keswani et al. 2016; Kirstein et al. 2016) across different environmental compartments and regions. In order to provide some responses to the concern produced by the perception of the potential risks for human health and the environment of MPs and of chemicals associated to them, Koelmans et al. (2017a) proposed adverse outcome pathways for assessing and comparing the risk of MaPs, MPs and NPs and highlighted the uncertainties that still exist in both, exposure and effect assessment.

The continuous emission patterns and the breakdown of plastic litter into smaller fractions in the environment may contribute to future concentrations that are orders of magnitude higher than the ones currently monitored (Everaert et al. 2018), thus contributing to a yet uncertain risk scenario. Policies dedicated to control emissions and manage risks of MaPs, MPs and NPs in the environment require a proper understanding of the main emission routes, the current exposure levels and the fluxes among environmental compartments. The available literature describing the exposure and impacts of plastics in the environment, providing a comparative assessment of the global occurrence, transport and fate, has so far mainly focused on the marine environment (see, e.g. GESAMP 2015; Auta et al. 2017). Although the freshwater environment is considered in some recent reviews (see, e.g. SAPEA 2018; Eerkes-Medrano et al. 2015), most studies consider specific emission routes and local monitoring campaigns.

Therefore, this study aimed to assess the state of the knowledge regarding the overall sources of plastic and its occurrence, fate, fluxes and loads into and within different environmental compartments of terrestrial and freshwater ecosystems. This study identifies data gaps that need to be addressed in order to understand the life cycle of the different plastic types in the environment, particularly in the soil-water interface, and provides relevant information to support research into the accumulation and ecotoxicological characterization of plastics to living organisms. Ultimately, this study provides guidance information to derive effective management measures aimed at reducing plastic discharges into the environment and attaining a more sustainable use and consumption of plastics in the nearby future.

2 Environmental Sources of Plastics

Nowadays, Asia is producing 50% of the world's plastic, followed by Europe and North America, producing 19% and 18%, respectively (PlasticsEurope 2018). The majority of plastics can be classified into the two main categories: thermoplastics (pellets that are remelted to manufacture the final product) and thermoset plastics (thermally produced into the commercial shape). Thermoplastics constitute 80% of the total plastic and are the main source of primary MPs. Thermoplastics are mainly formed by polyethylene (PE), polypropylene (PP) or polyvinylchloride (PVC), while thermoset plastics are formed, among others, by polyester (PES), polyurethane (PUR), silicone and polyamide (PA).

Sources of plastics can be classified in terms of the life expectancy of the produced plastics before disposal. Here we classify plastic sources into those with a short-term (single-use or very limited number of times with a useful lifespan up to 1 year), mid-term (up to 10 years), or long-term (more than 10 years) use expectancy.

2.1 Plastics with Short-Term Use Expectancy

Single-use items are mainly formed by packaging material, which is the biggest plastic sector worldwide (almost 36% in 2015; Fig. 1) and accounts for almost 50% of the generated plastic waste (Geyer et al. 2017). The vast majority of packaging plastics are PE, PP and polyethylene terephthalate (PET) (Geyer et al. 2017). Except for refillable PET bottles used in some countries, packaging is single-use with a lifespan of less than 6 months. Most foods are wrapped in plastic, and single-use plastic bags have been widely used all over the world due to their convenience, availability and low price. Plastic bags are known to cause severe environmental problems, especially in countries without proper waste management (Adane and Muleta 2009). Thus, many countries have put bans or levies in force to reduce their use or to encourage voluntary reductions (Xanthos and Walker 2017). Many African countries, for instance, have banned single-use plastic bags, while the EU Directive 2015/720 encourages member states to reduce the number of 'lightweight' carrier bags by 2025. Those bans and restrictions have already reduced the plastic bag use drastically in some countries (e.g. Ireland, England, Italy). Moreover, other single-use items like cutlery, plates, cups and straws are planned to be banned in Europe by 2021 (EC 2019).

Another important sector using single-use plastic is agriculture. Plastic films are used for plastic mulching, for the construction of greenhouses and tunnels, or to wrap silage to store animal fodder. The global plastic consumption in agricultural production is estimated to be about 2.5 million tons per year (Hussain and Hanid 2003). A variety of different plastic types are used in agriculture, including PE, PP, ethylene-vinyl acetate copolymer (EVA), PVC and polymethyl methacrylate (PMMA) (Scarascia-Mugnozza et al. 2012).

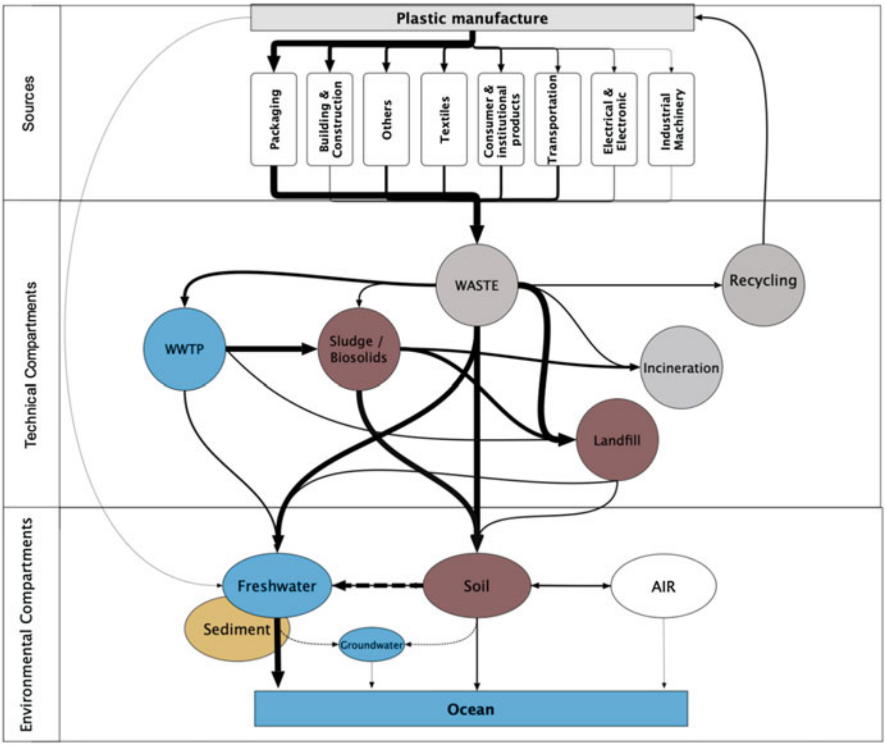

Fig. 1 Production and pathways of plastics into the different environmental compartments. Thickness of the different arrows is related to the quantitative relevance of the different mass flows. The relevance of the different plastic sources mass flows is based on Geyer et al. (2017), while the relevance of the technical compartments environmental flows is based on the reviewed literature or assumptions. Dashed lines indicate yet completely unexplored pathways with unknown relevance

MPs added to consumer products (e.g. as a component of personal care, cosmetic and cleaning products) are specially manufactured to be used once and then washed down the drain. They are often referred to as microbeads, even though they are mostly irregular in shape in order to obtain an abrasive effect (Fendall and Sewell 2009; Napper et al. 2015; Kalčíková et al. 2017). The majority of microbeads in facial and body scrubs are made of PE, with average concentrations of 4.82 g/ 100 mL body scrub and 0.74 g/100 mL facial scrub (Kalčíková et al. 2017; Gouin et al. 2015). Other plastic polymers used in cosmetic products include polylactic acid, PET, polyethylene isoterephthalate, nylon-12, nylon-6, PMMA, polytetrafluoroethylene and PUR (Leslie 2014; Rochman et al. 2015). Additionally, microbeads are used in industry as abrasives/scrubbers and sand-blasting media as well as in antislip, anti-blocking applications and for medical applications. It has been calculated that more than 4000 tons of PE microbeads were used in cosmetic products all over the EU (including Norway and Switzerland) in 2012 (Gouin et al.

2015), and the USA is emitting 263 tons of PE microbeads per year (2.4 mg per person per day; Gouin et al. 2011). A ban of microplastics intentionally added to products (i.e. microbeads) has been proposed in the EU (EC 2019), while the US Microbead-Free Waters Act of 2015 (US Congress 2015) prohibits the manufacturing, packaging and distribution of rinse-off cosmetics containing plastic microbeads already. This only applies to rinse-off products, while MPs are still permitted as a component in 'leave-on' products (e.g. lotions, sunscreens, make-ups and deodorants).

2.2 Plastics with Mid-Term Use Expectancy

Plastics with a mid-term lifespan are mainly found in the sectors of electronics, household, tyres and textiles. The production of electrical and electronic products counts to the fastest growing manufacturing and waste generation sectors (Geyer et al. 2017; Kumar et al. 2017), and as many textiles are made, entirely or to a certain extent, of synthetic plastic fibres (e.g. PA, PES, acrylic), also production rates of synthetic plastic fibres have increased over the last decade. Nowadays, two-thirds of the total fibre production is synthetic plastic fibres, and worldwide 59 tons of plastic textiles were produced in 2015 (Geyer et al. 2017; Gasperi et al. 2018).

Synthetic polymers with rubber-like characteristics are the principal component of vehicle tyres. They are composed of a mixture of natural and synthetic rubbers (styrene-butadiene rubber). While driving, tyre and road wear particles are formed which contain styrene-butadiene rubber in a mix with natural rubber, pavement parts and many other additives (Unice et al. 2013; Sundt et al. 2014). While tyres contain almost 50% of polymers, tyre wear particles, which are a mix of pavement part and polymers, contain only 16–23% of polymers (Kreider et al. 2010).

2.3 Plastics with Long-Term Use Expectancy

Plastics designed for long-term use belong to the following categories: parts of transportation (i.e. vehicle, plane and train parts), building and construction, industrial machinery, consumer products and institutional products. While plastics for the building and construction sector account for the second highest plastic consumption, only a small portion enters the waste stream directly (Fig. 1; Geyer et al. 2017). As these categories do not belong to the items that are usually littered, they are not expected to contribute significantly to the plastic load in the environment. However, their breakdown rate into MPs and NPs (due to exposure to light and weathering), also during their useful lifetime, is not clear.

3 Pathways of Plastic to the Environment

Hereafter plastic waste will refer to all plastic material that is discarded, while litter will include only those items that are not properly discarded. Packaging material is accounting for almost 50% of the generated plastic waste, followed by textiles (almost 14%; Geyer et al. 2017). Most plastic waste is generated in Asia, while America, Japan and the European Union are the world's largest producers of plastic packaging waste per capita.

3.1 Collected Solid Waste

Collected plastic waste is either landfilled, incinerated or recycled. In Europe, 27.3% is landfilled, 31.1% is recycled, and 41.6% is incinerated for energy recovery (PlasticsEurope 2018). The percentage of collected plastic waste varies strongly between different countries, depending on the applied waste management plans and policies. While, worldwide, the plastic recycling rate is still low, it has increased by almost 79% within the last 10 years in the EU, including Norway and Switzerland (PlasticsEurope 2018).

Large-scale industrial plastic production began in the 1950s, but plastic recycling was not established until the 1980s. It is estimated that only 9% of the total produced plastic waste up to 2015 has been recycled (Geyer et al. 2017). From this again only a small portion is submitted to primary recycling in which the recycled plastic is used to replace all or a least a proportion of the virgin polymer resins (Hopewell et al. 2009). While high-income countries have sorting and processing facilities, in low-income countries, plastic recycling is not well established. Moreover, certain types of plastic are difficult to recycle. For example, thermoset plastics, including textiles, are usually not recycled.

Plastic that is not recycled but still collected is landfilled or incinerated. In eight EU countries, Norway and Switzerland, a landfill ban for plastic is in force, leading to a very small percentage of plastic being used for landfill applications (PlasticsEurope 2018). On average, 27.3% of the generated plastic waste is landfilled in Europe. In contrast, in low-income countries, waste is mainly stored in open, poorly managed dumps, from where plastic can be transported by wind force. In middle-income countries, some controlled landfills are in place, but open dumping is still common practice. The advantages of combustion of plastic waste are that it can be used for energy recovery and the incinerated plastic cannot enter the environment anymore. At the same time, incineration results in the generation of air pollutants (Verma et al. 2016).

3.2 Wastewater

Both MPs, as well as MaP, enter wastewater either directly if products containing plastic are flushed down the drain (e.g. fibres detached during laundry of textiles, microbeads in consumer products, cotton buds or sanitary products) or in combined sewer systems from street dust and litter. MaPs escape wastewater treatment only on rare occasions and mainly enter the environment with untreated wastewater due to combined sewer overflows, e.g. after heavy rainfall events or snowmelts (Williams and Simmons 1999), or if untreated wastewater enters the environment because wastewater treatment plants (WWTPs) are not in place. Although high-income countries treat on average 70% of the wastewater, yet globally only 20% of the generated wastewater is treated (Sato et al. 2013). For MPs, the situation is different; due to their small size, they can escape the treatment and are also released with treated effluents (Ziajahromi et al. 2016). This pathway for MPs has been increasingly investigated. To date, 24 studies have measured MPs in wastewater (Table S1), from which three have not exclusively assessed MPs but included other litter items in the micro range (microlitter; HELCOM 2014; Michielssen et al. 2016; Talvitie et al. 2017b). Such studies were mainly carried out in northern and western Europe (14 studies), followed by North America (5 studies).

The number of MPs in raw wastewater varies greatly between WWTPs, from a few MPs/L to exceptional maximum values of more than 10,000 MP/L (Fig. 2). The data shown in Fig. 2 are described in more detail in Table S1 where the removal rate, identification method, particle shape and polymer composition are reported. Especially high concentrations have been observed in raw wastewaters in Denmark (Vollertsen and Hansen 2017; Simon et al. 2018). The Danish studies assessed MPs in the smaller size range (i.e. between 10 or 20 and 500 μm), while other studies assessing MPs down to 20 μm found much lower MP concentrations (Talvitie et al. 2015; Leslie et al. 2017).

WWTPs have, in general, a large retention potential for MPs, often higher than 95% (Table S1). However, in treated wastewater the number of MPs varies greatly too, from less than 1 MP/L (Browne et al. 2011; Carr et al. 2016; Murphy et al. 2016; Ziajahromi et al. 2017a) to several hundred (Simon et al. 2018) and up to several thousand MP/L (Vollertsen and Hansen 2017; Fig. 2). Larger MPs are usually better retained during the treatment, so the most frequently observed MPs in treated wastewater are smaller than 300 μm (Dris et al. 2015; Mintenig et al. 2017; Gündoğdu et al. 2018; Magni et al. 2019; Talvitie et al. 2017a; Lee and Kim 2018; Wolff et al. 2019; Liu et al. 2019b). For example, Magni et al. (2019) found that 94% of the MPs between 5 and 1 mm were retained by an Italian WWTP, while only 65% of the MPs between 0.1 and 0.01 mm were retained (Magni et al. 2019). Moreover, the number of MPs seems to be increasing with decreasing particle size. Wolff et al. (2019) reported the results of small-sized MPs measured in treated wastewater and indicated that 44% of the measured MPs are between 10 and 30 μm, while 51% are between 30 and 100 μm. Furthermore, current research indicates that the amount of MPs retained by WWTPs is not only influenced by the size but also by the particle shape. Usually, fibres are better retained in WWTPs as compared to

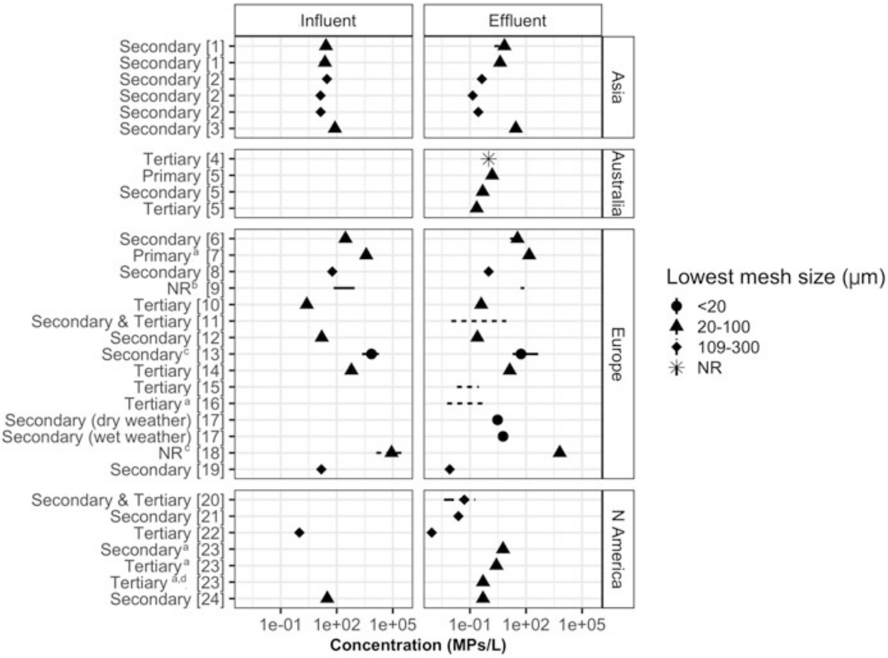

Fig. 2 Mean and/or minimum-maximum MP concentrations (MPs/L) in influent and effluent of municipal WWTPs with different treatment types. NR = not reported. N America = North America. Notes: [a]All anthropogenic litter in the micro range and not only MPs considered. [b]Range of mean concentrations between seven different WWTPs. [c]Upper size limit of 500 μm. [d]Pilot-scale anaerobic membrane bioreactor. References: [1] Gündoğdu et al. (2018), [2] Lee and Kim (2018), [3] Liu et al. (2019b), [4] Browne et al. (2011), [5] Ziajahromi et al. (2017), [6] Dris et al. (2015), [7] HELCOM (2014), [8] Lares et al. (2018), [9] Leslie et al. (2017), [10] Magni et al. (2019), [11] Mintening et al. (2017), [12] Murphy et al. (2016), [13] Simon et al. (2018), [14] Talvitie et al. (2015), [15] Talvitie et al. (2017a), [16] Talvitie et al. (2017b), [17] Wolff et al. (2019), [18] Vollertsen and Hansen (2017), [19] Magnusson and Noren (2014), [20] Mason et al. (2016), [21] Dyachenko et al. (2017), [22] Carr et al. (2016), [23] Michielssen et al. (2016), [24] Gies et al. (2018)

microbeads or other irregular particles (Magnusson and Norén 2014; Talvitie et al. 2017b; Gündoğdu et al. 2018). Fibres and fragments are the most frequently occurring MP types in WWTP effluents (Table S1). Regarding polymer composition, PE particles or PES fibres are the most common plastic types (Table S1). Although a huge amount of tyre debris is suspected to enter WWTPs (Kole et al. 2017), they have not been frequently reported in treated effluents (Table S1). Only Dyachenko et al. (2017) and Lee and Kim (2018) have reported the presence of black particles possibly being tyre fragments.

Concentrations of MPs in wastewaters show some seasonal and diurnal variations related to water consumption rates and human activity (Mintenig et al. 2017; Talvitie et al. 2017b; Lares et al. 2018). For instance, Talvitie et al. (2017b) reported that night time concentrations were slightly lower (average concentrations 476.7 and 0.8 μL/L in influent and effluent, respectively) compared to daytime concentrations

(584 and 1.7 μL/L in influent and effluent, respectively). Therefore, MP occurrence seems to be highly variable and depending on a variety of different environmental (weather, season) and behavioural variables but also methodological procedures (i.e. sampling method, including mesh sizes and sample volume), extraction method and determination method. Despite the high retention of MPs by WWTPs, considering the large volumes treated daily, it is considered that more than one million particles can enter the aquatic environment via this pathway per WWTP (Ziajahromi et al. 2017a; Gündoğdu et al. 2018), which constitutes one of the main sources of MPs into the environment.

3.3 Sludge and Other Agricultural Amendments

WWTPs retain the majority of MPs during pre- and primary treatment (mechanical treatment and sludge settling processes) and MPs are therefore concentrated in the grease or sludge phase (Murphy et al. 2016; Leslie et al. 2017; Talvitie et al. 2017b). While solids intercepted by grids and grease removal steps are disposed of in landfills, sludge is often reused as fertilizers in agriculture. The amount trapped in the sludge roughly constitutes 50–90% of the MPs present in raw wastewater (Table S2; Magnusson and Norén 2014; Carr et al. 2016; Lee and Kim 2018). MP concentrations measured in sludge range from 650 MPs/kg dw to more than 240,300 MPs/kg dw (Fig. S1, Table S2). Murphy et al. (2016) found significant bigger-sized MPs in the sludge phase compared to MPs in treated wastewater, confirming the differential retention potential of WWTPs regarding MP size. Furthermore, the sludge treatment process (thickening, digestion, drying, stabilization, dewatering) may affect the MP size (Mahon et al. 2017). Similar to wastewater, sludge samples usually show high numbers of fibres, followed by fragments (Table S2), and the main detected polymer is usually PES (particularly when there are many fibres present), followed by PE and PP.

Plastics can end up in compost used as agricultural amendment due to wrong recycling or separation of waste, e.g. if plastic food packaging is disposed of in the organic waste (Mercier et al. 2017; Weithmann et al. 2018). Weithmann et al. (2018) reported that organic fertilizers may contain up to 895 MPs/kg, and Fuller and Gautam (2016) found on average 23,000 mg MP/kg in composted waste materials.

4 Occurrence and Fluxes of Plastics in Environmental Compartments

It is reasonable to hypothesize that in different countries, relevant differences in the emissions of plastic waste and the presence of MaPs and MPs in environmental compartments exist. This may, in particular, originate from differences in waste management between high-income and low-income countries. In the following sections, some comparisons at the continental level are made. However, as the availability of information is not adequately balanced among countries and continents (e.g. data from Africa and South America are very scarce), the comparison is only partial.

4.1 Air

Studies assessing the occurrence of airborne plastic particles have identified mainly fibres (Dris et al. 2015; Abbasi et al. 2019). Atmospheric fallout of fibres in the area of Paris (France) showed a high variability, with values ranging between 2 and 355 fibres/m^2/day; however, half of those were natural (50%; cotton or wool), and only 17% were purely synthetic (mainly PET; Dris et al. 2016). Based on these samples, the same authors estimated that the fibre deposition rate in highly populated urban environments can roughly range between 1.2 and 4 kg/km^2/year and concluded that atmospheric fallout might constitute a relevant pathway of MPs. The limited data on atmospheric MPs deposition rates makes it difficult to draw conclusions on the relevance of this pathway for the environmental distribution of MPs. In the study by Dris et al. (2016), suburban fallout was found to be only about 50% of that observed in urban areas (53 particles/m^2/day compared to 110 particles/m^2/day), and thus it may be assumed that fibre fallout is even lower in natural and agricultural environments.

In addition to fibres, MPs in street dust are also likely to become airborne (Dall'Osto et al. 2014; Gasperi et al. 2018). According to Kole et al. (2017), 12% of the generated tyre dust (1040 tons/year) in the Netherlands ends up in the air. The particles are generated by the interaction of tyres with the road while driving and are generally found along roadside areas (Kreider et al. 2010). Wind and rainfall might influence the atmospheric transport and fallout of MPs, while deposited fibres and street dust in urban environments may be transported via water runoff into sewer systems or directly to terrestrial or aquatic ecosystems. However, studies properly describing such processes are lacking.

4.2 Soil

It has been suggested that agricultural soils could constitute larger MP sinks than marine ecosystems (Hurley and Nizzetto 2018). However, research on the quantification of plastics in soils (for both MaPs and MPs) is still very limited and mostly contracted to the last 4 years. We identified 12 studies reporting plastics in soil, from which 3 considered only a limited number of plastic types (Table S3). The available studies provide first indications of the scale of the pollution and suggest the ubiquitous presence of MPs in terrestrial ecosystems, also beyond agricultural areas. Most studies report plastic quantities in terms of particles, while some others provide concentrations based on mass measurements, which hampers to some extent direct comparisons among them. The highest MP concentration based on mass has been measured in soils from an industrial area in Australia, which was historically used to produce chlorinated plastic, containing 6700 mg MP/kg dw (Fuller and Gautam 2016). The highest concentration based on the number of MP particles was provided by Vollertsen and Hansen (2017), who described Danish agricultural soils containing about 145,000 MPs/kg, in the size range of 20–500 μm which was based on weight however only 12 mg/kg. Also Chinese farmland soils were found to contain a high MP content, ranging between 70 and 18,760 MPs/kg dw (Fig. S2; Liu et al. 2018; Zhang and Liu 2018; Zhang et al. 2018). In contrast, farmlands in Germany showed a much lower MP occurrence (0.34 MPs/kg dw; Piehl et al. 2018). This might be partly related to differences in the considered MP sizes during the study and due to differences in agricultural practices. While Piehl et al. (2018) assessed MPs of a size between 1 and 5 mm, the study by Vollertsen and Hansen (2017) considered MPs between 20 and 500 μm. However, the different ranges in concentrations may also be attributed to the presence of different input sources.

The application of sewage sludge as agricultural fertilizer (biosolids) is considered to be a major source of MPs to soils. Nizzetto et al. (2016) estimated that between 63,000–430,000 and 44,000–300,000 tons of MPs could be yearly added to agricultural land in Europe and North America, respectively. Corradini et al. (2019) found that an increasing number of sludge applications were positively correlated to increasing MP concentrations in soils. Zubris and Richards (2005) report up to 1210 fibres/kg in soils 5 years after sewage sludge application and detected fibres still 15 years after application, which is another indication for MPs accumulation in soil due to sludge application. On the other hand, almost twice the concentration of MPs was found in Danish fields not treated with sludge compared to treated fields (Vollertsen and Hansen 2017). Additional studies investigating the presence of MPs in soil after application of wastewater sludge are fundamental to estimate the importance of this pathway better.

Irrigation with reclaimed wastewater and the usage of plastic material in agriculture constitute additional sources of plastics in soil ecosystems. Based on studies from China, the latter one seems to be one of the most important plastic sources for elevated MP concentrations in soil in addition to sewage sludge application (Zhang and Liu 2018; Zhang et al. 2018). In contrast to those concentration hotspots, agricultural areas in Germany without plastic mulching or use of sewage sludge as fertilizer, the MP concentration seems much lower (i.e. on average 0.34 MP/kg dw soil; Piehl et al. 2018). As the frequency of the observed MaP polymer types was reflected by the types of MPs, MP particles in this study most likely come from the degradation of (littered) MaP (Piehl et al. 2018). The breakdown of MaP into MPs in terrestrial ecosystems may be dependent on their whereabouts in the soil and on soil cultivation. Williams and Simmons (1996) assessed low-density PE degradation over a period of 4 months in different environments (river beach, in trees at the river bench and buried by soil). They found that MaPs on the soil surface degrade faster as compared to buried plastics and assumed light to be the main influencing driver (although rainfall and other weathering processes may have affected degradation).

Littering, drift from landfills or spills from industry can also become important sources of plastics into soils. As described above, deposition of MPs from the air can additionally add MPs to soils. This seems, however, more relevant close to urban areas and streets with heavy traffic. Finally, during flood events, plastics from the aquatic environment can be deposited on the shores of rivers (Scheurer and Bigalke 2018). Therefore, based on the data that is available up to now, the primary inputs of MPs into soil seem to come from agricultural practices (sewage sludge, plastic mulching) and the fragmentation of plastic litter.

The most common polymer types reported in soils are PE and PP (Table S3). MaPs reported in terrestrial systems are PE films and bottles (Ramos et al. 2015; Huerta Lwanga et al. 2017b; Piehl et al. 2018). In a more remote place (desert in southern Arizona), plastics that are more mobile due to transportation by wind like plastic bags and balloons have been reported (Zylstra 2013).

The fate of MPs within the soil is not completely clear yet. MPs in soils may be transported along with water runoff and soil erosion into adjacent streams and rivers. So far, there is no knowledge of the importance of this pathway as it has not been experimentally proven. Translocation into deeper soil layers can occur through soil cultivation (Hurley and Nizzetto 2018) or transport by soil organisms. Earthworms and collembolans have been shown to ingest and transport MPs from the soil surface into deeper soil layers (Huerta Lwanga et al. 2017a; Maaß et al. 2017; Rillig et al. 2017). Also other animals, e.g. birds or domestic animals, which have been shown to take up MPs (Zhao et al. 2016; Huerta Lwanga et al. 2017b), can transport MPs over longer distances. To date, it is yet unclear whether low-sized MPs can be transported through soil pores into groundwater, but low concentrations of MPs (0–7 MPs/m^3) have been reported in raw drinking waters from groundwater wells (Mintenig et al. 2019). Uptake of plastics by plants is another potential source of mobilization of plastics from soil ecosystems, particularly for NPs; however no studies have investigated this using whole plants (Ng et al. 2018). The only study available in this respect is the one provided by Bandmann et al. (2012), who demonstrated uptake of 20 and 40 nm PS beads by tobacco BY-2 cells in cell culture via endocytosis, while 100 nm beads were excluded.

4.3 Freshwaters

Plastic pollution along rivers has been already observed and assessed in the 1990s (Williams and Simmons 1996, 1999). Nevertheless, few studies have reported plastic pollution in freshwaters until the whole environmental movement was initiated a few years ago. Some studies assessing litter in rivers have not exclusively focused on plastic but also included other litter items like glass, paper and wood. Those studies show that about 80% of the litter items are plastics, but do not provide concentrations or mass estimates (Crosti et al. 2018; González-Fernández et al. 2018; Castro-Jiménez et al. 2019).

Studies focusing on providing concentrations of MaPs in the environment are very limited (Table S4). MaPs concentrations have been reported, for example, for the Los Angeles River, in California (819 MaPs/m^3; Moore et al. 2011), the Yangtze River in China (8.74 × 10^3 MaPs/km^2; Xiong et al. 2019) and lakes (1800 MaPs/km^2) and rivers (0.012 MaPs/m^3) in Switzerland (Faure et al. 2015). It has been estimated that in the Seine River in France, 28,000 kg of floating plastic are trapped annually by floating debris retention booms (Gasperi et al. 2014), and floating MaPs in the Saigon River in Vietnam were estimated to range between 7500 and 13,700 tons per year (van Emmerik et al. 2018). As only buoyant plastics were considered in those studies, the total loads may be underestimated as plastic is also transported by sub-surface transport (Morritt et al. 2014). The most common MaPs reported in freshwater environments are plastic bottles, food packaging items, plastic bags and sewage-related plastic, like handles from buds of cotton wool and sanitary towels (Table S4). Regarding polymer composition, PP and PE are the plastic types that were omnipresent, and to a lesser extent, PS and PET have been reported (Table S4).

MPs in water have been assessed using different sampling methods and are reported in different units (i.e. particles per water volume or particles per area) (Fig. 3). To be able to compare the results of the different studies, we choose 38 studies which either reported the number of MPs per water volume or gave sufficient information to transform the reported unit. Like in other environmental

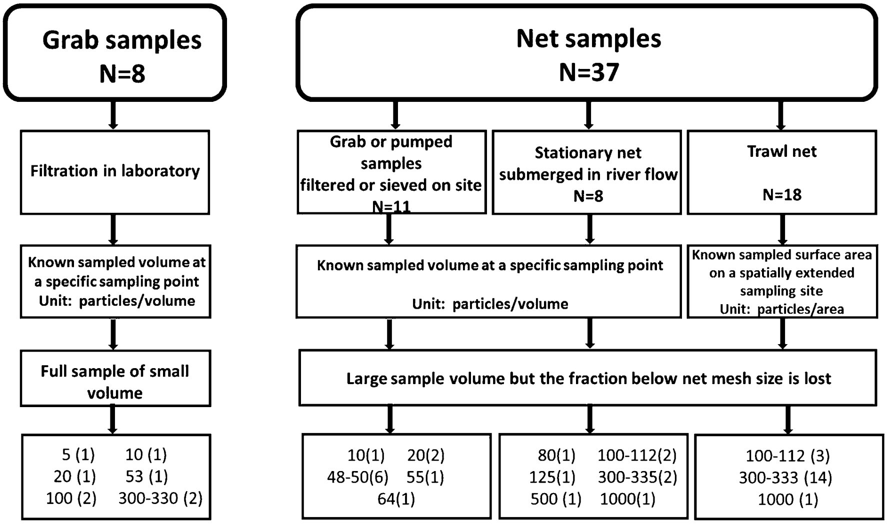

Fig. 3 Overview of the most common sampling methods used for freshwater MPs sampling. N is the number of studies that applied the respective sampling method. This does not correspond to the number of studies listed in Table S5 because some studies used more than one sampling method. In the last row of boxes, the minimum mesh size (μm) used in the different studies is reported (in bracket the number of studies)

compartments, the concentrations varied greatly among studies (Fig. 4). As for Fig. 2, the data shown in Fig. 4 are described in more detail in Table S5 where, besides the identification method, the particle shape, the polymer composition and the sampling methods are reported. Moreover, two additional studies are listed in Table S5, which are not included in the figure because they reported the MP concentration in weight per water volume instead of number per water volume, which hampers a direct comparison. Most studies in Europe found average concentrations of less than 1 to less than 100 MP/m^3, while the highest average concentration of 100,000 MPs/m^3 (with a maximum concentration of 187,000 MPs/m^3) was measured in the Amsterdam canals (Leslie et al. 2017). Furthermore, Liu et al. (2019a) reported up to 22,849 MPs/m^3 (average: 1409 MPs/m^3) in storm water ponds receiving urban runoff in Denmark. The highest peak concentration from all studies was found in the Snake River in North America and was as high as 5,405,000 MPs/m^3 (average: 91 MPs/m^2) (Kapp and Yeatman 2018). The second highest peak concentration was reported by Lahens et al. (2018) and corresponds to 519,223 MPs/m^3 (minimum 17,210 MPs/m^3) monitored in the Saigon River (Vietnam). Overall, reported concentrations of MPs appear to be higher in Asia, as compared to Europe and North America (Fig. 4). However, most of the studies carried out in Asia were performed in China and focused on assessing lower size classes than those studied in Europe. The only two studies conducted in Europe that considered a very small size (MPs below 20 μm) were the ones by Leslie et al. (2017) and Liu et al. (2019a), who observed by far the highest concentrations. Current research shows that smaller particles (<0.5 mm) are usually the most frequent ones (e.g. Leslie et al. 2017; Yan et al. 2019). Therefore, the higher concentrations found in Asia may be not exclusively related to higher pollution but also to the sampling methods used. The results of this overview are comparable with those reported by Li et al. (2018) on the occurrence of MPs in freshwater.

Studies assessing the concentration of MPs using different net sizes at the same sampling sites found substantial differences in the number of particles intercepted by plankton nets vs trawling nets (Dris et al. 2015; Xiong et al. 2019). Kapp and Yeatman (2018) used different sampling methods to assess the occurrence of particles larger than 100 μm and found that on average there were higher concentrations in grab samples (glass containers were filled with water from the surface) as compared to net samples (Table S5). Also, other differences in study design, such as sample volume, sample depth or sample location in the river, could influence the measured MP concentration. For example, Vermaire et al. (2017) found higher concentrations in grab samples close to the river shore, which were subsequently filtered through a 100 μm net compared to open water samples taken using a 100 μm manta trawl.

Although MPs have been found in remote locations and rural areas, there is evidence that MP concentration increases with proximity to cities (Wang et al. 2017b; Di and Wang 2018; Tibbetts et al. 2018). A modelling study identified the Yangtze River catchment as the catchment transporting the highest plastic loads into the ocean (Schmidt et al. 2017). The four case studies looking at MP concentrations in the Yangtze River found highly variable concentrations but were also among the

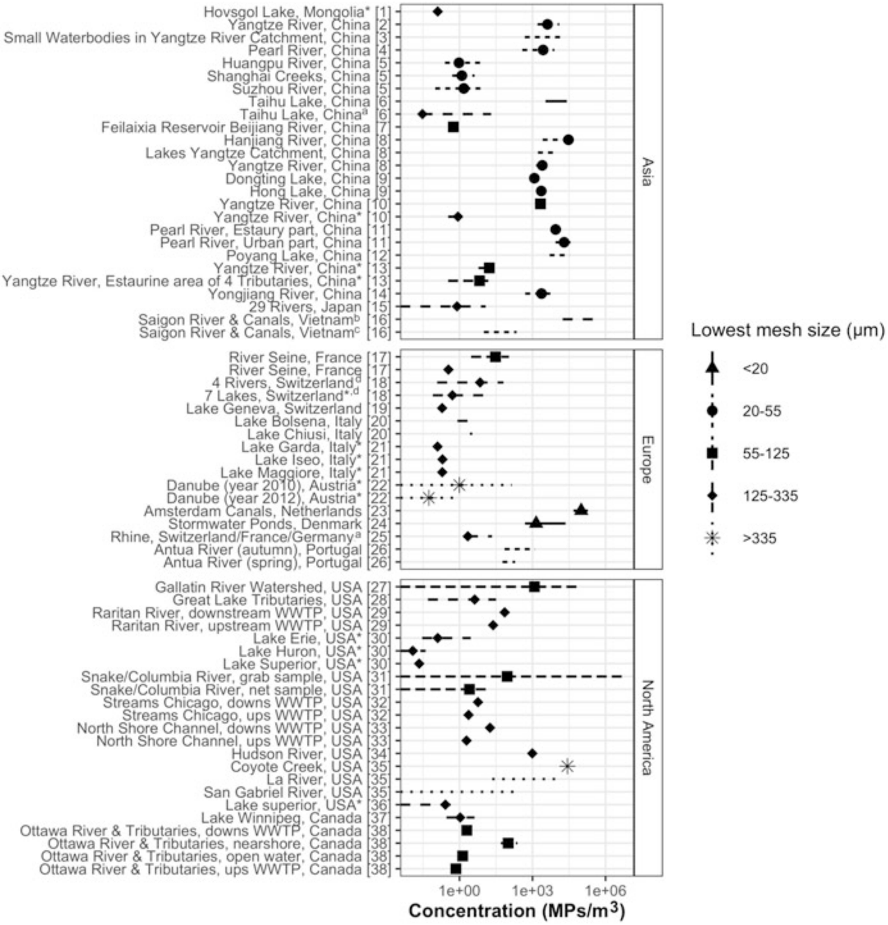

Fig. 4 Mean and/or minimum-maximum MP concentrations (MPs/m^3) in freshwater samples. Downs = downstream. Ups = upstream. Notes: *Concentration in MPs/m^3 was estimated by dividing the reported concentration in particles per area by the height of the net used for sampling. Notes: [a]Minimum concentration not specified. [b]Only fibres assessed. [c]Only fragments assessed. [d]Mean across all sample sites with minimum and maximum mean concentrations across sample sites. References: [1] Free et al. (2014), [2] Di and Wang (2018), [3] Hu et al. (2018), [4] Lin et al. (2018), [5] Luo et al. (2018), [6] Su et al. (2016), [7] Tan et al. (2019), [8] Wang et al. (2017a), [9] Wang et al. (2018), [10] Xiong et al. (2019), [11] Yan et al. (2019), [12] Yuan et al. (2019), [13] Zhang et al. (2015), [14] Zhang et al. (2019), [15] Kataoka et al. (2019), [16] Lahens et al. (2018), [17] Dris et al. (2015), [18] Faure et al. (2015), [19] Faure et al. (2012), [20] Fischer et al. (2016), [21] Sighicelli et al. (2018), [22] Lechner et al. (2014), [23] Leslie et al. (2017), [24] Liu et al. (2019a), [25] Mani et al. (2016), [26] Rodrigues et al. (2018), [27] Barrows et al. (2018), [28] Baldwin et al. (2016), [29] Estahbanati and Fahrenfeld (2016), [30] Eriksen et al. (2013), [31] Kapp and Yeatman (2018), [32] McCormick et al. (2016), [33] McCormick et al. (2014), [34] Miller et al. (2017), [35] Moore et al. (2011), [36] Hendrickson et al. (2018), [37] Anderson et al. (2017), [38] Vermaire et al. (2017)

highest observed (Zhang et al. 2015; Wang et al. 2017b; Di and Wang 2018; Xiong et al. 2019). However, concentrations in the same order of magnitude were also monitored in other rivers in China such as the Pearl River, which was also ranked under the top ten catchments transporting plastic into the ocean (Schmidt et al. 2017).

Not only spatial hotspots but temporal hotspots based on weather condition may exist in freshwater ecosystems. Storms and rainfall can increase plastic concentration in waters from both lateral (land-based) and sewage effluent discharge points (Fischer et al. 2016), and MPs that had been deposited on river beds can re-enter the water phase after flood events (Hurley et al. 2018a).

Fragments and fibres formed by PE and PP are the most frequently observed particles across all studies evaluating MP pollution in freshwater ecosystems, whereas pellets or beads are only rarely reported as the main occurring plastic types (Table S5). The latter are mainly found in studies along the rivers Rhine and Danube, in the proximity to plastic processing plants, and are thus assumed to be pre-production pellets (Lechner et al. 2014; Lechner and Ramler 2015; Mani et al. 2016). The prevalence of secondary MPs (fragments and fibres) suggests wastewater and runoff as sources for plastic pollution in freshwater ecosystems (Table S5). Several studies confirmed that by demonstrating that MP concentrations are higher downstream of WWTP as compared to sampling sites in upstream areas (McCormick et al. 2014; Estahbanati and Fahrenfeld 2016; Vermaire et al. 2017; Kay et al. 2018). For example, in the Ottawa River (Canada), 0.71 particles/m^3 were found upstream of WWTPs compared to 1.99 MPs/m^3 downstream. In the Raritan River and the North Shore Channel (USA), 24 MPs/m^3 and 1.94 MPs/m^3 were found upstream the WWTP, and 71.7 particles and 17.93 MPs/m^3 were detected downstream, respectively (McCormick et al. 2014; Estahbanati and Fahrenfeld 2016; Vermaire et al. 2017). As mentioned above, the majority of MPs in wastewater are smaller than 300 μm. Thus it may be presumed that larger MPs enter via different pathway like surface runoff or stem from the breakdown of MaPs directly in the aquatic environment. However, with untreated wastewater, for instance, during sewage overflows, large MPs and MaP can enter river ecosystems. For example, Morritt et al. (2014) identified pollution hotspots in the vicinity of WWTPs that were mainly constituted of sanitary products. MPs hotspots were also detected in areas with low population density but high agricultural use, also pointing to agricultural runoff as an important source (Kapp and Yeatman 2018). Finally, poor waste management likely increases plastic input into aquatic ecosystems (Lahens et al. 2018), where they can break down into smaller particles. Xiong et al. (2019), for example, found that the abundance of MPs is positively related to the presence of MaPs.

4.4 Sediments

Similar to MaP in surface waters, also MaPs in sediments are only rarely assessed, and the way MaP occurrence is reported is highly variable and difficult to compare (Table S6). MaPs along river banks have been observed while assessing buoyant litter in general (Williams and Simmons 1999; Rech et al. 2014), and river beach sediments in Switzerland contained on average 90 MaPs/m^2 (Faure et al. 2015). Across different lakeshores, MaPs concentrations have been shown to vary notably (Imhof et al. 2013; Fischer et al. 2016). While high MaPs concentrations have been observed at the south shore of Lake Garda (Italy; with an average concentration of 483 MaP/m^2), the occurrence at the north shore was significantly lower (i.e. 0–8.3 MaP/m^2; Imhof et al. 2013). Food packaging is among the most frequently observed MaPs, but also bottles, bags and ropes are described by several studies. Regarding the polymer composition, PE and PP, as well as styrofoam (PS), are reported (Table S6).

As for MaPs and the other compartments, the concentration of MPs in freshwater sediments has not been reported in consistent units across all studies. Therefore, we focused on studies that have reported the concentration in MPs/kg sediment. However, studies reporting MPs per sediment area, which gave sufficient information to estimate the concentration in MPs/kg, were also included. Therefore, from the 34 studies that were found during the literature search (Table S7), 30 were chosen for comparisons (Fig. 5). The data shown in Fig. 5 are described in more detail in Table S7 where the type of analysis, particle shapes and polymer composition are reported. The highest sediment concentration of 2071 MPs/kg dw has been found in the urban canals of Amsterdam, where also the highest water concentrations were observed (Leslie et al. 2017). This value is the average of six urban canals with high variability in MP concentration, particularly fibres, where the presence of a hotspot is evident. MP concentrations in river bed sediments seem, in general, higher than in river beach and shore sediments (Fig. 5; Table S7). Most studies on MPs in river bed sediments report concentrations between 100 MP/kg and a few thousands. Studies from Asia were exclusively carried out in China and reported similar concentration ranges as those described in Europe. Interestingly, the study on the Yangtze River (China), which has been estimated to be the highest contributor of plastic to the sea (Schmidt et al. 2017) and is among the highest MP concentrations reported in water (Fig. 4, Table S5), had a comparably low sediment concentration 7–66 MP/kg. The only study carried out in Africa (in a semi-arid South African basin) assessing the concentration of MPs in river sediment reports notable differences between concentrations in summer (1–14.6 MP/kg dw) and winter (13.3–563.8 MP/kg dw), which were related to a reduced flow condition in winter in the studied region (Nel et al. 2018). Subsequently, the hydrological variation shown by many rivers seems to be one of the main factors contributing to MPs deposition and remobilization from river beds. This was also demonstrated by Hurley et al. (2018a), who report that about 70% of the MPs in the sediments of the upper Mersey and Irwell catchments (UK) were exported after a flooding event. Several studies show that, after transportation with the river flows, MPs tend to (re)deposit in low-energy environments, such as meanders, deltas, dams, harbours and coastal lagoons (Claessens et al. 2011; Vianello et al. 2013; Shruti et al. 2019). The deposition of low-density polymers in sediment environments is also related to a density increase by biofouling (e.g. Ye and Andrady 1991; Andrady 2011; Zettler et al. 2013; McCormick et al. 2014).

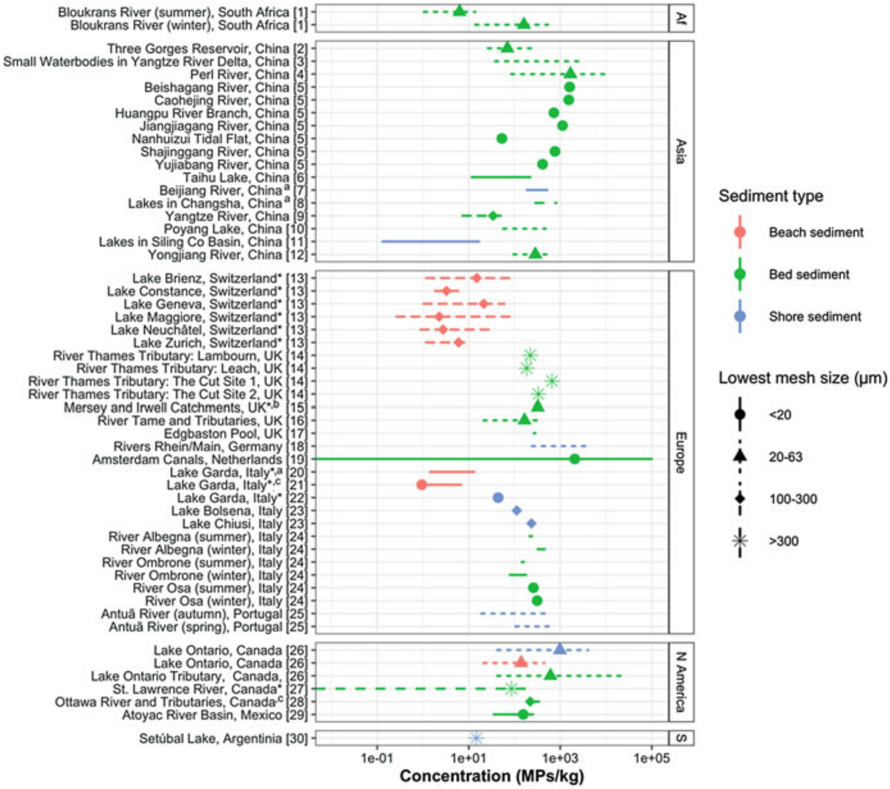

Fig. 5 MP concentrations in different types of sediment samples (MPs/kg). Notes: The sediment type for river sediment was categorized as bed sediment if the type was not clearly stated. *Concentration in MPs/kg was estimated by using the sample depth and assuming a density of 1.6 g/cm^3 for the sediment. [a]Range of mean concentrations across different sampling sites. [b]Maximum value is shown; [c]no lower value reported. Af = Africa. N America = North America. S = South America. References: [1] Nel et al. (2018), [2] Di and Wang (2018), [3] Hu et al. (2018), [4] Lin et al. (2018), [5] Peng et al. (2018), [6] Su et al. (2016), [7] Wang et al. (2017a), [8] Wen et al. (2018), [9] Xiong et al. (2019), [10] Yuan et al. (2019), [11] Zhang et al. (2016), [12] Zhang et al. (2019), [13] Faure et al. (2015), [14] Horton et al. (2017), [15] Hurley et al. (2018a), [16] Tibbetts et al. (2018), [17] Vaughan et al. (2017), [18] Klein et al. (2015), [19] Leslie et al. (2017), [20] Imhof et al. (2013), [21] Imhof et al. (2016), [22] Imhof et al. (2018), [23] Fischer et al. (2016), [24] Guerranti et al. (2017), [25] Rodrigues et al. (2018), [26] Ballent et al. (2016), [27] Castañeda et al. (2014), [28] Vermaire et al. (2017), [29] Shruti et al. (2019), [30] Blettler et al. (2017)

For lakes, mainly beach and shore sediment concentrations have been reported. In Europe, average concentrations for beach and shore sediments ranged between 0.94 and 44 MP/kg, while beach and shore sediments from Lake Ontario (Canada) contained much higher concentrations (20–27,830 MPs/kg; Fig. 5, Table S7). Several studies have noted that plastic concentrations differ strongly between different areas of the same lake (Zbyszewski and Corcoran 2011; Imhof et al. 2013;

Zbyszewski et al. 2014; Zhang et al. 2016), suggesting that accumulation is patchy and the formation of contamination hotspots is influenced by winds, waves and/or beach morphology (Imhof et al. 2016, 2018). Similar observations were made at Lake Huron (Canada), in which 94% of all monitored pellets were found to accumulate in one single beach (Zbyszewski and Corcoran 2011). In the Taihu Lake (China), MP concentrations ranged from 11 to 235 MP/kg in different bed areas, and the average MP abundance in sediments in the northwest area was approximately six times higher than the abundance of the south-east area (Su et al. 2016).

Fibres followed by fragments were usually the most common particle types monitored (Table S7). Spheres/beads or pellets were, in rare occasions, reported to be dominant, and mostly in the vicinity to plastic industries (Zbyszewski and Corcoran 2011; Zbyszewski et al. 2014; Corcoran et al. 2015; Hurley et al. 2018a; Peng et al. 2018). Based on polymer type, PE and PP were the most common, despite their buoyant properties, as well as PS (Table S7).

4.5 Marine

Rivers are estimated to be the main pathways for plastics entering the oceans. Estimations on the amount of plastic waste entering the ocean through this pathway range between 0.41 and 4 × 10^6 tons per year (Lebreton et al. 2017; Schmidt et al. 2017). From the top ten river catchments that transport 88–95% of the global plastic load into the oceans, eight are located in Asia (Schmidt et al. 2017). Oceans have been assumed to be the final sink for MaPs and MPs. As this review is focused on terrestrial and freshwater ecosystems, this compartment will not be discussed in detail. A number of articles and reviews have been published on the topic within the last few years which describe plastic occurrence in the oceans and its effects on marine life (see, e.g. Barboza and Gimenez 2015; Jambeck et al. 2015; Auta et al. 2017).

5 Discussion

We fully agree with the statement provided by the SAPEA (2018) report: 'The number of papers is growing exponentially in this field, but knowledge is not growing at the same rate – there is some redundancy and marginality in the papers'. Furthermore, many papers on plastic pollution do not assess and describe important plastic sources and flows. This review paper made an attempt to describe the available information regarding global environmental loads and the plastic life cycle and to show which further research studies are needed to fully understand specific plastic sources and pathways. This section describes the areas that need further research commitment and development to improve exposure assessments and to evaluate the long-term risks of plastics to terrestrial and freshwater ecosystems.

5.1 *The Need for Advancing and Standardizing Sampling and Analysis Techniques*

As indicated in several parts of this review, the sampling methods reported in the literature are extremely variable and, in many cases, difficult to compare. In marine monitoring studies, the most commonly used method for sampling is the so-called manta trawl, a device similar to a large plankton net with a mesh size usually larger than 300 µm (GESAMP 2015). Using a manta trawl allows to sample a thin layer of surface water, and, therefore, the results are generally reported as MPs (number or weight) per surface area (m^2 or km^2). The same device is frequently used also in freshwater, together with other sampling methods (Fig. 3), that produce results expressed as MPs per volume unit (e.g. L or m^3) and that may consider different size fractions, sometimes down to 20 µm. The results from studies considering the different sampling methods are hardly comparable. Data for surface units may be converted into data for unit volume, by calculating the mouth surface area of the manta trawl. However, this is a rough approximation because the trawl is not always fully immersed. Moreover, with the manta trawl, all particles below 300 µm are lost. This is shown by studies using both sampling methods (Kapp and Yeatman 2018; Lahens et al. 2018; Xiong et al. 2019). Small particles generally represent the largest share of the total amount of particles present in natural waters. Therefore, the manta trawl method largely underestimates the actual MP concentrations, at least in terms of particle numbers.

A recent report (GESAMP 2019) describes and compares methods for sampling MaPs and MPs, with particular focus on the marine environment. The report highlights advantages and disadvantages of the different sampling methods. However, particularly for MPs, precise indications or suggestions of the methods to be used for a better exposure and risk characterization are not provided. It should be noted that the impact of different size fractions may be extremely different on the various components of the aquatic ecosystem (e.g. small fishes, macro-invertebrates, micro-invertebrates, bacteria). Therefore, methods capable to provide quantitative samples of different fractions, including relatively small MPs (e.g. down to 20 µm, achievable with fine-meshed phytoplankton nets), should be used whenever possible.

The available data on soil and sediments is relatively scarce. This may be partly related to the complex and time-consuming procedure required to extract MPs from these matrices (Hurley et al. 2018b). Some studies report MP concentrations as the number of particles per kg, while others provide the weight of MPs per kg. In other cases, data is reported as MP number or weight per surface unit (e.g. mg/m^2). Therefore, the comparison of literature data is not straightforward.

Besides this, existing methods to identify and count MPs are quite variable. Until recently, it was common practice to solely rely on visual detection (using a microscope), which may lead to false positives or false negatives. In more recent studies, visual examination is usually combined with FTIR (Fourier transform infrared) or Raman spectroscopy, which allows polymer identification. This is, however, time-consuming, and thus frequently only a subsample is subjected to spectroscopic methods. Other studies use different methods like SEM (scanning electron microscopy), XRF (X-ray fluorescence) and Pyr-GC/MS (pyrolysis interfaced with gas chromatography/mass spectrometry) (Klein et al. 2017). It has been observed that MP abundance often varies with the methods used (Song et al. 2015; Mai et al. 2018; Picó et al. 2019), so analytical results may be difficult to compare across studies. The previously mentioned GESAMP report (GESAMP 2019) also compares methods for processing and analysing MPs but does not provide clear suggestions for standardization.

There is an urgent need for standardizing methodologies to be applied to the exposure assessment, which include those related to sample processing, MP extraction, identification and counting, as well as the units to be used for reporting data. The major gap refers to very small-sized MPs (below 20 μm) and NPs. Particularly the latter can currently not be included in monitoring programmes because suitable sampling methods are lacking and analytical methods, such as pyrolysis-GC/MS (Fischer and Scholz-Böttcher 2017), are exploratory (GESAMP 2019).

Most procedures commonly applied to date allow sampling, processing and measuring particles down to a minimum size of 20 μm. Only very few studies measured smaller particles, down to 10 μm (e.g. Leslie et al. 2017; Simon et al. 2018). In theory, very small particles and, especially, NPs should be more abundant in the environment, and their concentrations are expected to increase. The development of methods for the evaluation and quantification of small-sized MPs and NPs is one of the major research needs to assess the potential risks for human and environmental health. In particular, detection technologies to identify nano-sized plastic particles are still lacking (Mai et al. 2018). A promising approach, at least to quantify the mass and the composition (if not the number of particles), could be the use of Pyr-GC/MS (Hendrickson et al. 2018; Mintenig et al. 2018) coupled with methods of small-sized particle separation based on ultrafiltration membrane technologies (Mulder 1998; Judd and Jefferson 2003).

5.2 *Towards a Microplastic Mass Balance and Suitable Evaluation of Environmental Fluxes*

The difficulties in getting reliable and comparable results for the concentrations of MPs in the different environmental compartments and the limited information regarding some fluxes among compartments make the evaluation of a regional and global mass balance of plastics challenging. However, some first estimates can be made based on the available data, at least to give an approximate order of magnitude of the contribution of different sources to surface waters.

From the data reported in Fig. 2 and Table S1, it can be concluded that the range of particles in effluents from WWTPs that include secondary and tertiary treatments spans from 1 to 5800 MPs/L, with a geometric mean around 29 MPs/L. In

Table 1 Percentage of EU population connected to WWTPs in 2015 (EEA 2019)

	No treatment or no connection with sewerage	Primary treatment	Secondary treatment	Tertiary treatment
Northern	15.1	5.6	2.3	77
Central	3.4	0	16.5	80.1
Southern	23	2.2	21.3	53.4
Eastern	26	0.2	13.6	60.6
South-eastern	40	16.7	22.8	20.6
Weighted average with respect to population	13	2	18	67

non-treated wastewaters, the concentrations range from a few particles/L up to more than 100,000, with a geometric mean of about 242 MPs/L. These data are in reasonable agreement with the percentage of retention by WWTPs reported by several authors, which ranges from 80% to 99% of the number of inflowing particles (see Sect. 4.3).

The approximated per capita consumption of water in Europe is 140 L per day (EEA 2018). Although with some regional differences, it may be estimated that about 85% of the EU population (525 million in the EU plus Norway and Switzerland) is connected to WWTPs with secondary or tertiary treatment, while the remaining population (15%) is connected to WWTPs with only primary treatment or is not connected at all (Table 1).

From these data, it can be estimated that the daily input of MPs (in the range of 20–5000 μm) via wastewater into European surface waters is:

- From treated wastewater: an average value of 1800E+9 particles per day (possible range from 9E+9 to 130E+12 particles/day)
- From untreated wastewater: an average value of 2700E+9 particles per day (possible range from 27E+9 to 1400E+12 particles/day)

Transforming these data on a weight basis is challenging because, in general, only numbers of MPs are reported, while size/weight conversion factors are not readily available. Combined data on numbers and weight are reported in a Danish report (Vollertsen and Hansen 2017) assessing MP occurrence in ten different WWTPs and in the study by Simon et al. (2018). However, both studies took only MPs between 10 or 20 and 500 μm into account. Therefore, estimating the load on a weight basis from the particle numbers is not possible.

Despite their wide range of variability, these estimates give a first approximation of the load of MPs in surface waters from urban wastewater and allow the following observations. First, the load that may be attributed to the relatively small percentage of European untreated wastewaters is much higher than the load deriving from treated wastewater, which points towards a definite need of implementing secondary and tertiary WWTPs in areas that are still not connected to reduce total MPs emission. Taking into account that untreated wastewater is concentrated in south-eastern Europe, it may be hypothesized that some watersheds (e.g. lower Danube) are subjected to higher contamination than those located in other European regions (Lechner et al. 2014). Unfortunately, data on MP concentrations in surface waters of south-eastern Europe are not available. Siegfried et al. (2017) implemented a modelling approach based on estimations of mass-based per capita consumption rates of personal care products, plastic fibres from textiles, plastic fibres in household dust and tyre debris and concluded that the largest emitted mass from rivers to the sea occurs for tyre debris, followed by textile fibres. Furthermore, they estimated that the majority of plastic particles emitted in Europe flow into the Mediterranean and the Black sea as a result of different socio-economic development and technological status of sewage treatment facilities.

Due to the scarcity of data of water consumption and WWTP implementation, a comparable evaluation cannot be done for other continents. However, it may be hypothesized that the percentage of treated wastewater in Asia and Africa is much lower than in Europe or North America.

The problem is also complicated by the fact that only a relatively small part of the population is connected to sewerage systems. Data from the WHO/UNICEF Joint Monitoring Programme (JMP), referred to 2015, indicate that in Eastern, South-eastern and Central Asia, with a population of more than four billion inhabitants, only 25% of the population is connected with sewerage systems and in sub-Saharan Africa the percentage is lower than 6% (WHO/UNICEF 2019). The high concentrations of MPs in surface waters of Asia (mostly assessed in China), as compared to those measured in Europe (Fig. 4), support the hypothesis regarding the large influence of WWTP on surface water emissions. The dominant shape in WWTP effluents are fibres, followed by fragments. Only in one case a minor amount (<10%) of pellets that may be classified as primary microbeads was observed (Dyachenko et al. 2017).

Wastewater represents only one of the possible pathways of MPs into surface waters, and as discussed in this study, surface runoff from agricultural and urban soils may also represent a major source. Unfortunately, a comparable estimate of MPs emissions from soils due to water runoff is not possible due to field data limitations. On the other hand, this review shows that MP concentrations in WWTP sludge (mainly from Europe) range between 10E+3 and 10E+5 particles/kg dw. Nizzetto et al. (2016) estimated that the total yearly input of MPs from sewage sludge to farmland is about 63,000–430,000 tons in Europe and 44,000–300,000 tons in North America. Data on MP concentrations in soil are scarce and scattered (Fig. S2 and Table S3). The majority of data on agricultural soils refer to China and indicate a reduced range of variability (from about 60 to 200 particles/kg dw), except for a couple of higher values (more than 10,000 particles/kg dw) from soils sampled in a greenhouse. Overall this study shows that soil could be considered as a sink as well as a source of MPs to surface water. Therefore, further research is urgently required to assess fluxes of MPs from soils into surface water ecosystems and to assess the fate of MPs in the soil ecosystems, investigating its retention potential and the capacity of MPs to reach groundwater ecosystems. An additional source of MPs to soil and surface water may be atmospheric fallout (Dris et al. 2016). However, the information available to date does not yet allow a quantitative estimate (Wetherbee et al. 2019). An attempt to perform a quantitative evaluation of emissions to all environmental compartments (air, soil, WWTP, surface waters) has been made for tyre debris indicating that urban and road runoff, as well as atmospheric deposition, may represent relevant contributions (Kole et al. 2017).

The formation or disappearance of MPs within the compartments also has to be considered in an overall mass balance. MaP fragmentation in the different compartments is reasonably one of the major sources of MPs in the environment. However, the patterns of MaP fragmentation, their characterization and quantification in terms of amount produced and time to produce them are still largely unknown. The only fragmentation pattern that is sufficiently documented and quantified is the production of fibres during laundry of synthetic fabrics (Browne et al. 2011; Eerkes-Medrano et al. 2015). Although the amount of fibres may vary depending on the type of clothes (e.g. polymer composition, weave type, age), the type of washing machine and the washing condition, it has been estimated that several thousand fibres are generated per washing cycle (Hartline et al. 2016; Napper and Thompson 2016; Pirc et al. 2016; Carney Almroth et al. 2018).

For any other type of plastic breakdown process, reliable experimental quantitative information is not yet available, although a modelling approach to predict the contribution of MaP breakdown to the MPs bulk in the ocean has been proposed (Koelmans et al. 2017b). Plastic fragmentation in the environment may be extremely variable in function of factors like light intensity, temperature, erosion and other physical impacts. The number and weight of MPs and NPs that may be produced by a MaP item (e.g. a bag or a bottle) in a given time under environmental conditions are still largely unknown. This is an important knowledge gap that must be investigated in depth and may be somewhat inferred based on the amount and type of polymers of MaP litter in the environment and their documented half-lives.

Although plastic polymers are persistent compounds, some polymers can undergo biodegradation (Albertsson et al. 1987). Scientific evidence of biodegradation through bacterial activity and invertebrate digestion mechanisms has increased recently (Briassoulis et al. 2015; Yoshida et al. 2016; Yang et al. 2018). Compared to MaPs, MPs and NPs may be more prone to form complex structures with organic matter particles and be readily attacked by bacteria and invertebrates. Therefore, a real possibility of their complete disappearance exists. Nevertheless, to date, the extent of these degradation processes in environmental compartments, their time scale as well as the patterns and the end products are relatively unknown (SAPEA 2018). Although plastic polymers are practically inert molecules, with low biological and toxicological activity, many monomers, which can be formed during the degradation of plastic, are not. Monovinylchloride (the monomer of PVC), for instance, is a recognized carcinogenic compound (Brandt-Rauf et al. 2012).

5.3 Microplastics in Environmental Compartments: What Does It Mean in Terms of Risks for Living Organisms?

As discussed above, information on the presence of MPs in environmental compartments is often biased by the inconsistency of units (e.g. n/L, n/m^2, mg/L, n/kg, mg/kg), by the variability in size classes sampled and measured and by the complexity in shape and composition that are often not clearly reported. These inconsistencies make the assessment of their possible impact on living organisms rather complex, so the actual environmental risks of different plastics and their associated chemicals remain largely unknown (Koelmans et al. 2017a). It is important to highlight that quantifying the effects of MPs on living organisms by a simple concentration-response relationship of the whole mass of MPs of a certain type found in environmental samples is more complicated than for most chemical contaminants. Their impacts on aquatic organisms depend on a number of factors such as:

- The shape: the physical effect determined by long and thin fibres may be completely different from those determined by microspheres or by irregular fragments (Au et al. 2015; Lambert et al. 2017).
- The size range: the definition of MPs in terms of size is extremely wide (from 5 mm to 1 μm), and the living organisms that may be affected by MPs are also extremely variable in size, for example, in the aquatic environment, from fish to zooplankton; for any type and size of organism, different MP size classes may be ingested, including small sizes (below 20 μm) and NPs, that are practically never measured.
- The composition: for most MP polymers, being the effects mainly physical, it may be hypothesized that the response is not related to the polymer composition; however, for some particular MP particles, such as for tyre debris, the composition is much more complex, and the effects may also be determined by the leaching of non-polymeric chemicals.

Some recent effect studies took these parameters into account, used exposure conditions in relation to the traits of the organisms (i.e. feeding type; substrate preference) or provided dose-response relationships (e.g. Au et al. 2015; Redondo Hasselerharm et al. 2018; Scherer et al. 2017; Ziajahromi et al. 2017b). This allows to conduct an ecological risk assessment with preliminary data for a range of species based on a comparison between an environmental exposure (e.g. a PEC – predicted environmental concentration) and an effect level (e.g. a PNEC – predicted no effect concentration). So far five studies carried out a provisional ecological risk assessment for MPs (Adam et al. 2019; Besseling et al. 2019; Burns and Boxall 2018; Everaert et al. 2018; Zhang et al. 2019). Burns and Boxall (2018) did not identify any ecological risk for measured concentrations in water or sediment. Adam et al. (2019) conducted risk assessment for different continents and found that although no risk is expected for Europe and North America, 'a risk cannot completely be excluded in Asia', where the highest MP pollution occurred. These findings are supported by a case study in the Youngjiang River in south China (Zhang et al. 2019). The authors calculated a risk quotient for each of their sample sites by dividing the measured MP concentrations by PNEC values derived from species sensitivity distribution based on literature toxicity data. They found that for most sites, a risk threshold was not exceeded, except for the two most contaminated sites, which were close to the urban centre of Nanning City (Zhang et al. 2019). Besseling et al. (2019) concluded that hazardous MP concentrations do not occur for freshwaters, while hotspot locations of nearshore marine surface waters may exceed safe concentrations. Similarly, Everaert et al. (2018) derived for the marine environment that at current average concentrations, no risk is expected but that a risk cannot be excluded for heavily polluted sites. As MP concentrations in the environment are usually reported in particle numbers while effect data is based on mass, a transformation was necessary in these studies to be able to compare effect and exposure data. To perform a refined ecological risk assessment of MPs will require much more detailed information on MP exposure with a precise assessment of number (or weight) of particles per size classes, shape and composition. Considering that current methods for the analysis of MPs are complex, expensive and time-consuming, this level of detail is, to date, difficult to achieve. Further research should be devoted to both areas, to refine exposure assessments including areas that are expected to be heavily polluted but on which information is still completely missing such as the Ganges in India or the Amazon in South America (Adam et al. 2019). Moreover, effect assessments should be performed taking into account ecologically relevant combinations of organisms and MP sizes, shapes and types. It is most likely that future risk assessments need to consider MP particle mixtures taking into account different polymer types, shapes and sizes and that exposure and risk indicators are derived taking all these variables into account.

For NPs, risk assessment is currently not feasible as they cannot be detected in environmental samples thus far. Also, regarding the effect assessment, the major unknown issues are related to small and very small particles (Koelmans 2019). NPs are particularly interesting because they may cross cellular membranes and enter into cells if they are below a given size. Within the cells, NPs can possibly interact with the cellular content, structure and function. This represents a substantial difference in comparison with MaPs or MPs. Indeed MPs cannot be accumulated in biological organs and tissues and may produce mainly physical stress on living organisms, although the consequences of that may result in physiological and metabolic alterations. The size threshold below which small plastic particles may enter in the cells is still unknown. Recent studies on NPs performed with reference materials labeled with fluorescent dye demonstrate their capacity to be taken up, enter tissues and accumulate in small organisms (Cui et al. 2017; Lee et al. 2019). However, some authors discuss that this can be an artefact either created by the leaching of those dye paints, which can be taken up into cells or due to the autofluorescence of the evaluated biological tissues (Catarino et al. 2019; Schür et al. 2019).

5.4 How Can MP Inputs into the Environment Be Controlled?

From all the considerations mentioned above, it is evident that the precautionary principles strongly push towards the control of MPs and NPs. From the available literature on MP presence in the environment, it appears that primary MPs represent a relatively small amount of the total bulk of MPs detected, being secondary MPs the largest majority. It is difficult to quantify the percentage of primary MPs in the environment precisely. However, in general, it seems to be never higher than 10%, and in most cases, the percentage is much lower, sometimes almost negligible. For example, in urban wastewater, the majority of MPs is represented by textile fibres (see, e.g. Dris et al., 2015; Vollertsen and Hansen 2017; Wang et al. 2017b), while in runoff water the most abundant particles are fragments from MaP breakdown (see, e.g. Liu et al. 2019a). Therefore, the recent proposal of ECHA (2019) for a ban or restriction of primary MPs may have a limited relevance and effectiveness for the reduction of the presence of MPs in the environment.

Based on the information available to date, the most plausible solution to reduce the environmental emission and exposure to MPs seems to be the control of MaPs. The restrictions on single-use plastic items that will be active in Europe starting from 2021 (EC 2019) seem to be an excellent starting point. Comparable restrictions should be applied in the short term on food and other kinds of packaging, which represent the largest amount of plastic wastes. In addition to restrictions, a more efficient recycling strategy and improvement of the circular economy related to plastic products would be beneficial (Barra and Leonard 2018). However, in some cases, different types of measures should be developed. As shown above, fibres represent the most abundant type of MPs present in wastewater. Since it is almost impossible to ban synthetic fabrics that today make up the majority of our clothing, the solution should be sought in another direction (e.g. by means of retaining fibres in washing machines, water treatment procedures, etc.).

Finally, the substitution of traditional plastic polymers, based on the petrochemical industry, with new-generation polymers, based on biological resources (e.g. PLA, polylactic acid; PHA, polyhydroxyalkanoates) is often proposed as a suitable solution. However, present knowledge on the toxicological properties of these new compounds and of their degradation products must be improved (Lambert and Wagner 2017; Picó and Barceló 2019). Understanding possible biodegradation patterns of traditional and emerging plastic polymers is important for future management and remediation of plastics in the environment.

6 Conclusions

In this study we have described the state of the knowledge regarding the occurrence of MaPs and MPs in different environmental compartments. It has been highlighted that some data gaps still exist in order to better understand their life cycle, to develop a precise mass balance and to quantitatively assess the contribution of the different main sources of MaPs, MPs and NPs in the environment. The emission of MPs from WWTPs into aquatic ecosystems is the environmental pathway that has been most researched. However, there are other pathways that may have similar or even larger contributions and that require further investigation. Those pathways are, for example, the fluxes of plastics from landfills and agricultural soils towards surface and groundwater ecosystems by water runoff or deep-horizon infiltration, or the transport and deposition of plastic particles from the atmosphere. Moreover, quantitative evaluations of the occurrence of large-sized plastics in natural environments need to be performed, and their breakdown rates into MPs and NPs still need to be assessed under different environmental conditions (i.e. temperature and light intensities, water currents).

There is enough experimental evidence demonstrating that the presence of MaPs in aquatic ecosystems represents an environmental risk, particularly for large animals. Regarding MPs, a risk for human and environmental health has not been demonstrated. Available toxicological evidence indicates that some effects on aquatic and terrestrial organisms, vertebrates and invertebrates, have been observed only at concentrations that are orders of magnitude higher than the maximum levels measured in the environment. Other possible effects, such as a potential increase in the bioaccumulation of chemicals due to their transport into the organisms adsorbed on MPs (the 'Trojan Horse effect'), seem to be context dependent and negligible in comparison with direct accumulation from the surrounding environment (e.g. from water) or from food (Koelmans et al. 2013, 2014; Lohmann 2017; Mohamed Nor and Koelmans 2019). However, research still needs to demonstrate this experimentally. An additional gap is represented by the toxicological risks of NPs that has to be investigated in further detail, taking into account their bioaccumulative and reactive potential in biological tissues, organs and cells.

Current knowledge gaps regarding environmental fluxes and breakdown of MPs and NPs are still too large in order to assess future risks for man and the environment. Furthermore, the bias on sampling and analysis makes a precise quantification challenging. This is particularly difficult for small MPs and NPs, which are probably the more concerning particles from a toxicological point of view. Moreover, although present exposure seems to be far away from levels of concern, it is difficult to predict future emission patterns since they will be closely related to plastic use and management policies. This review shows that the construction of wastewater treatment facilities and the proper management of sludge applications in agriculture are efficient means to reduce MPs emissions. Moreover, the ban of single-use plastics, the substitution of some plastic polymers with biodegradable compounds and the reduction of MPs emission at a source are key to control plastic pollution. From now onwards, we expect technological solutions to be developed and implemented in this direction. There is no doubt that plastics changed our life in the middle of the last century and the control of plastics will again change our life in the near future.

7 Summary

This study assessed the current knowledge regarding the industrial sources of plastics and MPs, their environmental pathways and load rates and their occurrence and fate in different environmental compartments. Existing data limitations regarding the global environmental cycle and exposure sources of MaPs, MPs and NPs to aquatic and terrestrial ecosystems are highlighted. While the presence of MPs in wastewater and freshwater is relatively well studied, data on sediments and especially soil ecosystems are too limited. Moreover, the overall occurrence of large-sized plastics, the patterns of MP and NP formation from them, the presence and deposition of plastic particles from the atmosphere and the fluxes of all kinds of plastics from soils towards aquatic environments (e.g. by surface water runoff, soil infiltration) are still poorly understood. Finally, this study discussed several research areas that need urgent development in order to better understand the potential ecological risks of plastic pollution and provides some recommendations to improve management and control of plastic and MP inputs into the environment.

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References

Abbasi S, Keshavarzi B, Moore F et al (2019) Distribution and potential health impacts of microplastics and microrubbers in air and street dusts from Asaluyeh County, Iran. Environ Pollut 244:153–164. https://doi.org/10.1016/j.envpol.2018.10.039

Adam V, Yang T, Nowack B (2019) Toward an ecotoxicological risk assessment of microplastics: comparison of available hazard and exposure data in freshwaters. Environ Toxicol Chem 38:436–447. https://doi.org/10.1002/etc.4323

Adane L, Muleta D (2009) Survey on the usage of plastic bags, their disposal and adverse impacts on environment: a case study in Jimma City, Southwestern Ethiopia. J Toxicol Environ Heal Sci 3:234–248

Albertsson A-C, Andersson SO, Karlsson S (1987) The mechanism of biodegradation of polyethylene. Polym Degrad Stab 18:73–87. https://doi.org/10.1016/0141-3910(87)90084-X

Anderson PJ, Warrack S, Langen V et al (2017) Microplastic contamination in Lake Winnipeg, Canada. Environ Pollut 225:223–231. https://doi.org/10.1016/j.envpol.2017.02.072

Andrady AL (2011) Microplastics in the marine environment. Mar Pollut Bull 62:1596–1605. https://doi.org/10.1016/j.marpolbul.2011.05.030

Au SY, Bruce TF, Bridges WC, Klaine SJ (2015) Responses of Hyalella azteca to acute and chronic microplastic exposures. Environ Toxicol Chem 34:2564–2572

Auta HS, Emenike CU, Fauziah SH (2017) Distribution and importance of microplastics in the marine environment: a review of the sources, fate, effects, and potential solutions. Environ Int 102:165–176. https://doi.org/10.1016/j.envint.2017.02.013

Baldwin AK, Corsi SR, Mason SA (2016) Plastic debris in 29 Great Lakes tributaries: relations to watershed attributes and hydrology. Environ Sci Technol 50:10377–10385. https://doi.org/10.1021/acs.est.6b02917

Ballent A, Corcoran PL, Madden O et al (2016) Sources and sinks of microplastics in Canadian Lake Ontario nearshore, tributary and beach sediments. Mar Pollut Bull 110:383–395. https://doi.org/10.1016/j.marpolbul.2016.06.037

Bandmann V, Müller JD, Köhler T, Homann U (2012) Uptake of fluorescent nano beads into BY2-cells involves clathrin-dependent and clathrin-independent endocytosis. FEBS Lett 586:3626–3632. https://doi.org/10.1016/j.febslet.2012.08.008

Barboza LGA, Gimenez BCG (2015) Microplastics in the marine environment: current trends and future perspectives. Mar Pollut Bull 97:5–12. https://doi.org/10.1016/j.marpolbul.2015.06.008

Barra R, Leonard SA (2018) Plastics and the circular economy. https://www.thegef.org/sites/default/files/publications/PLASTICS for posting.pdf

Barrows APW, Christiansen KS, Bode ET, Hoellein TJ (2018) A watershed-scale, citizen science approach to quantifying microplastic concentration in a mixed land-use river. Water Res 147:382–392. https://doi.org/10.1016/j.watres.2018.10.013

Besseling E, Redondo-Hasselerharm P, Foekema EM et al (2019) Quantifying ecological risks of aquatic micro- and nanoplastic. Crit Rev Environ Sci Technol 49:32–80. https://doi.org/10.1080/10643389.2018.1531688

Blettler MCM, Ulla MA, Rabuffetti AP, Garello N (2017) Plastic pollution in freshwater ecosystems: macro-, meso-, and microplastic debris in a floodplain lake. Environ Monit Assess 189:581. https://doi.org/10.1007/s10661-017-6305-8

Bouhroum R, Boulkamh A, Asia L et al (2019) Concentrations and fingerprints of PAHs and PCBs adsorbed onto marine plastic debris from the Indonesian Cilacap coast and the North Atlantic gyre. Reg Stud Mar Sci 29:100611. https://doi.org/10.1016/J.RSMA.2019.100611

Brandt-Rauf P, Long C, Kovvali G et al (2012) Plastics and carcinogenesis: the example of vinyl chloride. J Carcinog 11:5. https://doi.org/10.4103/1477-3163.93700

Briassoulis D, Babou E, Hiskakis M, Kyrikou I (2015) Analysis of long-term degradation behaviour of polyethylene mulching films with pro-oxidants under real cultivation and soil burial conditions. Environ Sci Pollut Res 22:2584–2598. https://doi.org/10.1007/s11356-014-3464-9

Browne MA, Crump P, Niven SJ et al (2011) Accumulations of microplastic on shorelines worldwide: sources and sinks. Environ Sci Technol 45(21):9175–9179. https://doi.org/10.1021/es201811s

Burns EE, Boxall ABA (2018) Microplastics in the aquatic environment: evidence for or against adverse impacts and major knowledge gaps. Environ Toxicol Chem 37:2776–2796. https://doi.org/10.1002/etc.4268

Carney Almroth BM, Åström L, Roslund S et al (2018) Quantifying shedding of synthetic fibers from textiles; a source of microplastics released into the environment. Environ Sci Pollut Res 25:1191–1199. https://doi.org/10.1007/s11356-017-0528-7

Carr SA, Liu J, Tesoro AG (2016) Transport and fate of microplastic particles in wastewater treatment plants. Water Res 91:174–182. https://doi.org/10.1016/j.watres.2016.01.002

Castañeda RA, Avlijas S, Simard MAA et al (2014) Microplastic pollution in St. Lawrence River sediments. Can J Fish Aquat Sci 71:1767–1771. https://doi.org/10.1139/cjfas-2014-0281

Castro-Jiménez J, González-Fernández D, Fornier M et al (2019) Macro-litter in surface waters from the Rhone River: plastic pollution and flows to the NW Mediterranean Sea. Mar Pollut Bull 146:60–66. https://doi.org/10.1016/j.marpolbul.2019.05.067

Catarino AI, Frutos A, Henry TB (2019) Use of fluorescent-labelled nanoplastics (NPs) to demonstrate NP absorption is inconclusive without adequate controls. Sci Total Environ 670:915–920. https://doi.org/10.1016/j.scitotenv.2019.03.194

Chae Y, An Y-J (2018) Current research trends on plastic pollution and ecological impacts on the soil ecosystem: a review. Environ Pollut 240:387–395. https://doi.org/10.1016/j.envpol.2018.05.008

Claessens M, De Meester S, Van Landuyt L et al (2011) Occurrence and distribution of microplastics in marine sediments along the Belgian coast. Mar Pollut Bull 62:2199–2204. https://doi.org/10.1016/j.marpolbul.2011.06.030

Corcoran PL, Norris T, Ceccanese T et al (2015) Hidden plastics of Lake Ontario, Canada and their potential preservation in the sediment record. Environ Pollut 204:17–25. https://doi.org/10.1016/j.envpol.2015.04.009

Corradini F, Meza P, Eguiluz R et al (2019) Evidence of microplastic accumulation in agricultural soils from sewage sludge disposal. Sci Total Environ 671:411–420. https://doi.org/10.1016/j.scitotenv.2019.03.368

Crawford CB, Quinn B (2017) The interactions of microplastics and chemical pollutants. In: Crawford CB, Quinn B (Eds.) Microplastic Pollutants, pp. 131–157. Elsevier. https://doi.org/10.1016/b978-0-12-809406-8.00006-2

Crosti R, Arcangeli A, Campana I et al (2018) 'Down to the river': amount, composition, and economic sector of litter entering the marine compartment, through the Tiber river in the Western Mediterranean Sea. Rend Lincei 29:859–866. https://doi.org/10.1007/s12210-018-0747-y

Cui R, Kim SW, An YJ (2017) Polystyrene nanoplastics inhibit reproduction and induce abnormal embryonic development in the freshwater crustacean Daphnia galeata. Sci Rep 7:1–10. https://doi.org/10.1038/s41598-017-12299-2

Dall'Osto M, Beddows DCS, Gietl JK et al (2014) Characteristics of tyre dust in polluted air: studies by single particle mass spectrometry (ATOFMS). Atmos Environ 94:224–230. https://doi.org/10.1016/j.atmosenv.2014.05.026

de Sá LC, Oliveira M, Ribeiro F et al (2018) Studies of the effects of microplastics on aquatic organisms: what do we know and where should we focus our efforts in the future? Sci Total Environ 645:1029–1039. https://doi.org/10.1016/j.scitotenv.2018.07.207

Di M, Wang J (2018) Microplastics in surface waters and sediments of the Three Gorges Reservoir, China. Sci Total Environ 616–617:1620–1627. https://doi.org/10.1016/j.scitotenv.2017.10.150

Dris R, Gasperi J, Rocher V et al (2015) Microplastic contamination in an urban area: a case study in Greater Paris. Environ Chem 12:592–599. https://doi.org/10.1071/EN14167

Dris R, Gasperi J, Saad M et al (2016) Synthetic fibers in atmospheric fallout: a source of microplastics in the environment? Mar Pollut Bull 104:290–293. https://doi.org/10.1016/j.marpolbul.2016.01.006

Dyachenko A, Mitchell J, Arsem N (2017) Extraction and identification of microplastic particles from secondary wastewater treatment plant (WWTP) effluent. Anal Methods 9:1412–1418. https://doi.org/10.1039/c6ay02397e

EC (Euopean Commission) (2019) Press release database. http://europa.eu/rapid/press-release_STATEMENT-19-1873_en.htm

ECHA (2019) Proposal for a restriction on intentionally added microplastics. Version n. 1.1. 20 March 2019, European Chemicals Agency (ECHA), Helsinki, Finland

EEA (European Environment Agency) (2019) Urban waste water treatment. https://www.eea.europa.eu/data-and-maps/indicators/urban-waste-water-treatment. Accessed 10 June 2019

EEA (European Environmental Agency) (2018) Water is life. EEA Signals, Copenhagen 2018. https://www.eea.europa.eu//publications/eea-signals-2018-water-is-life

Eerkes-Medrano D, Thompson RC, Aldridge DC (2015) Microplastics in freshwater systems: a review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. Water Res 75:63–82. https://doi.org/10.1016/j.watres.2015.02.012

Eriksen M, Mason S, Wilson S et al (2013) Microplastic pollution in the surface waters of the Laurentian Great Lakes. Mar Pollut Bull 77:177–182. https://doi.org/10.1016/j.marpolbul.2013.10.007

Estahbanati S, Fahrenfeld NL (2016) Influence of wastewater treatment plant discharges on microplastic concentrations in surface water. Chemosphere 162:277–284. https://doi.org/10.1016/j.chemosphere.2016.07.083

Everaert G, Van Cauwenberghe L, De Rijcke M et al (2018) Risk assessment of microplastics in the ocean: modelling approach and first conclusions. Environ Pollut 242:1930–1938. https://doi.org/10.1016/j.envpol.2018.07.069

Faure F, Corbaz M, Baecher H, De Alencastro LF (2012) Pollution due to plastics and microplastics in lake Geneva and in the Mediterranean Sea. Arch des Sci 65:157–164. https://doi.org/10.1071/EN14218

Faure F, Demars C, Wieser O et al (2015) Plastic pollution in Swiss surface waters: nature and concentrations, interaction with pollutants. Environ Chem 12:582–591. https://doi.org/10.1071/EN14218

Fendall LS, Sewell MA (2009) Contributing to marine pollution by washing your face: microplastics in facial cleansers. Mar Pollut Bull 58:1225–1228. https://doi.org/10.1016/j.marpolbul.2009.04.025

Fischer M, Scholz-Böttcher BM (2017) Simultaneous trace identification and quantification of common types of microplastics in environmental samples by pyrolysis-gas chromatography−mass spectrometry. Environ Sci Technol 51:5052–5060

Fischer EK, Paglialonga L, Czech E, Tamminga M (2016) Microplastic pollution in lakes and lake shoreline sediments – a case study on Lake Bolsena and Lake Chiusi (central Italy). Environ Pollut 213:648–657. https://doi.org/10.1016/j.envpol.2016.03.012

Foley CJ, Feiner ZS, Malinich TD, Höök TO (2018) A meta-analysis of the effects of exposure to microplastics on fish and aquatic invertebrates. Sci Total Environ 631–632:550–559. https://doi.org/10.1016/j.scitotenv.2018.03.046

Free CM, Jensen OP, Mason SA et al (2014) High-levels of microplastic pollution in a large, remote, mountain lake. Mar Pollut Bull 85:156–163. https://doi.org/10.1016/j.marpolbul.2014.06.001

Fuller S, Gautam A (2016) A procedure for measuring microplastics using pressurized fluid extraction. Environ Sci Technol 50:5774–5780. https://doi.org/10.1021/acs.est.6b00816

Gasperi J, Dris R, Bonin T et al (2014) Assessment of floating plastic debris in surface water along the Seine River. Environ Pollut 195:163–166. https://doi.org/10.1016/j.envpol.2014.09.001

Gasperi J, Wright SL, Dris R et al (2018) Microplastics in air: are we breathing it in? Curr Opin Environ Sci Heal 1:1–5. https://doi.org/10.1016/j.coesh.2017.10.002

GESAMP (2015) Sources, fate and effects of microplastic in the marine environment: a global assessment. In: Kershaw PJ (ed) (IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP/ISA Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). Rep Stud GESAMP No. 93, 220 p

GESAMP (2019) Guidelines or the monitoring and assessment of plastic litter and microplastics in the ocean. Kershaw PJ, Turra A, Galgani F (eds) (IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP/ISA Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). Rep. Stud. GESAMP No. 99, 130 p. https://environmentlive.unep.org/media/docs/marine_plastics/une_science_dvision_gesamp_reports.pdf. Accessed 6 Jun 2019

Geyer R, Jambeck JR, Law KL (2017) Production, use, and fate of all plastics ever made. Sci Adv 3:e1700782. https://doi.org/10.1126/sciadv.1700782

Gies EA, Lenoble JL, Noël M et al (2018) Retention of microplastics in a major secondary wastewater treatment plant in Vancouver, Canada. Mar Pollut Bull 133:553–561. https://doi.org/10.1016/j.marpolbul.2018.06.006

Gigault J, Halle AT, Baudrimont M et al (2018) Current opinion: what is a nanoplastic? Environ Pollut 235:1030–1034. https://doi.org/10.1016/j.envpol.2018.01.024

González-Fernández D, Hanke G, The RiLON Network (2018) Floating macro litter in European rivers – top items. Publ Off Eur Union EUR 29383. https://doi.org/10.2760/316058

Gouin T, Roche N, Lohmann R, Hodges G (2011) A thermodynamic approach for assessing the environmental exposure of chemicals absorbed to microplastic. Environ Sci Technol 45:1466–1472. https://doi.org/10.1021/es1032025

Gouin T, Avalos J, Brunning I et al (2015) Use of micro-plastic beads in cosmetic products in Europe and their estimated emissions to the North Sea environment. SOFW J 141:40–46

Guerranti C, Cannas S, Scopetani C et al (2017) Plastic litter in aquatic environments of Maremma Regional Park (Tyrrhenian Sea, Italy): contribution by the Ombrone river and levels in marine sediments. Mar Pollut Bull 117:366–370. https://doi.org/10.1016/j.marpolbul.2017.02.021

Gündoğdu S, Çevik C, Güzel E, Kilercioğlu S (2018) Microplastics in municipal wastewater treatment plants in Turkey: a comparison of the influent and secondary effluent concentrations. Environ Monit Assess 190:626. https://doi.org/10.1007/s10661-018-7010-y

Hardesty BD, Good TP, Wilcox C (2015) Novel methods, new results and science-based solutions to tackle marine debris impacts on wildlife. Ocean Coast Manag 115:4–9. https://doi.org/10.1016/j.ocecoaman.2015.04.004

Hartline NL, Bruce NJ, Karba SN et al (2016) Microfiber masses recovered from conventional machine washing of new or aged garments. Environ Sci Technol 50:11532–11538. https://doi.org/10.1021/acs.est.6b03045

HELCOM (2014) Preliminary study on synthetic microfibers and particles at a municipal waste water treatment plant. Balt Mar Environ Prot Comm HELCOM 14 p. http://www.helcom.fi/Lists/Publications/Microplastics%20at%20a%20municipal%20waste%20water%20treatment%20plant.pdf. Accessed 20 Apr 2019

Hendrickson E, Minor EC, Schreiner K (2018) Microplastic abundance and composition in western Lake Superior as determined via microscopy, Pyr-GC/MS, and FTIR. Environ Sci Technol 52:1787–1796. https://doi.org/10.1021/acs.est.7b05829

Hopewell J, Dvorak R, Kosior E (2009) Plastics recycling: challenges and opportunities. Philos Trans R Soc B Biol Sci 364:2115–2126. https://doi.org/10.1098/rstb.2008.0311

Horton AA, Svendsen C, Williams RJ et al (2017) Large microplastic particles in sediments of tributaries of the River Thames, UK – abundance, sources and methods for effective quantification. Mar Pollut Bull 114:218–226. https://doi.org/10.1016/j.marpolbul.2016.09.004

Hu L, Chernick M, Hinton DE, Shi H (2018) Microplastics in small waterbodies and tadpoles from Yangtze River Delta, China. Environ Sci Technol 52:8885–8893. https://doi.org/10.1021/acs.est.8b02279

Huerta Lwanga E, Gertsen H, Gooren H et al (2017a) Incorporation of microplastics from litter into burrows of Lumbricus terrestris. Environ Pollut 220:523–531. https://doi.org/10.1016/j.envpol.2016.09.096

Huerta Lwanga E, Vega JM, Quej VK et al (2017b) Field evidence for transfer of plastic debris along a terrestrial food chain. 7(1):14071. https://doi.org/10.1038/s41598-017-14588-2

Hurley RR, Nizzetto L (2018) Fate and occurrence of micro(nano)plastics in soils: knowledge gaps and possible risks. Curr Opin Environ Sci Heal 1:6–11. https://doi.org/10.1016/j.coesh.2017.10.006

Hurley R, Woodward J, Rothwell JJ (2018a) Microplastic contamination of river beds significantly reduced by catchment-wide flooding. Nat Geosci 11:251–257. https://doi.org/10.1038/s41561-018-0080-1

Hurley RR, Lusher AL, Olsen M, Nizzetto L (2018b) Validation of a method for extracting microplastics from complex, organic-rich, environmental matrices. Environ Sci Technol 52(13):7409–7417. https://doi.org/10.1021/acs.est.8b01517

Hussain I, Hamid H (2003) Plastic in agriculture. In: Andrady AL (Ed.), Plastics and the Environment. John Wiley & Sons, Inc., Hoboken, NJ, pp. 185–209. https://doi.org/10.1002/0471721557.ch5

Imhof HK, Ivleva NP, Schmid J et al (2013) Contamination of beach sediments of a subalpine lake with microplastic particles. Curr Biol 23:867–868. https://doi.org/10.1016/j.cub.2013.09.001

Imhof HK, Laforsch C, Wiesheu AC et al (2016) Pigments and plastic in limnetic ecosystems: a qualitative and quantitative study on microparticles of different size classes. Water Res 98:64–74. https://doi.org/10.1016/j.watres.2016.03.015

Imhof HK, Wiesheu AC, Anger PM et al (2018) Variation in plastic abundance at different lake beach zones – a case study. Sci Total Environ 613–614:530–537. https://doi.org/10.1016/j.scitotenv.2017.08.300

Jambeck JR, Geyer R, Wilcox C et al (2015) Plastic waste inputs from land into the ocean. Science 347(6223):768–771. https://doi.org/10.1126/science.1260352

Jovanović B (2017) Ingestion of microplastics by fish and its potential consequences from a physical perspective. Integr Environ Assess Manag 13:510–515. https://doi.org/10.1002/ieam.1913

Judd S, Jefferson B (2003) Membrane for industrial wastewater recovery and re-use. Elsevier, Oxford

Kalčíková G, Alič B, Skalar T et al (2017) Wastewater treatment plant effluents as source of cosmetic polyethylene microbeads to freshwater. Chemosphere 188:25–31. https://doi.org/10.1016/j.chemosphere.2017.08.131

Kapp KJ, Yeatman E (2018) Microplastic hotspots in the Snake and Lower Columbia rivers: a journey from the Greater Yellowstone Ecosystem to the Pacific Ocean. Environ Pollut 241:1082–1090. https://doi.org/10.1016/j.envpol.2018.06.033

Karami A, Romano N, Galloway T, Hamzah H (2016) Virgin microplastics cause toxicity and modulate the impacts of phenanthrene on biomarker responses in African catfish (Clarias gariepinus). Environ Res 151:58–70. https://doi.org/10.1016/j.envres.2016.07.024

Kataoka T, Nihei Y, Kudou K, Hinata H (2019) Assessment of the sources and inflow processes of microplastics in the river environments of Japan. Environ Pollut 244:958–965. https://doi.org/10.1016/j.envpol.2018.10.111

Kay P, Hiscoe R, Moberley I et al (2018) Wastewater treatment plants as a source of microplastics in river catchments. Environ Sci Pollut Res 25:20264–20267. https://doi.org/10.1007/s11356-018-2070-7

Keswani A, Oliver DM, Gutierrez T, Quilliam RS (2016) Microbial hitchhikers on marine plastic debris: human exposure risks at bathing waters and beach environments. Mar Environ Res 118:10–19. https://doi.org/10.1016/j.marenvres.2016.04.006

Kirstein IV, Kirmizi S, Wichels A et al (2016) Dangerous hitchhikers? Evidence for potentially pathogenic Vibrio spp. on microplastic particles. Mar Environ Res 120:1–8. https://doi.org/10.1016/j.marenvres.2016.07.004

Klein S, Worch E, Knepper TP (2015) Occurrence and spatial distribution of microplastics in river shore sediments of the rhine-main area in Germany. Environ Sci Technol 49:6070–6076. https://doi.org/10.1021/acs.est.5b00492

Klein S, Dimzon IK, Eubeler J, Knepper TP (2017) Analysis, occurrence, and degradation of microplastics in the aqueous environment. In: Wagner M, Lambert S (eds) Freshwater microplastics. emerging environmental contaminants? Springer, Cham. https://doi.org/10.1007/798-3-319-61615-5

Knowlton AR, Hamilton PK, Marx MK et al (2012) Monitoring North Atlantic right whale Eubalaena glacialis entanglement rates: a 30 yr retrospective. Mar Ecol Prog Ser 466:293–302. https://doi.org/10.3354/meps09923

Koelmans AA (2019) Proxies for nanoplastic. Nat Nanotechnol 14:307–308. https://doi.org/10.1038/s41565-019-0416-z

Koelmans AA, Besseling E, Wegner A, Foekema EM (2013) Plastic as a carrier of POPs to aquatic organisms: a model analysis. Environ Sci Technol 47:7812–7820. https://doi.org/10.1021/es401169n

Koelmans AA, Besseling E, Foekema EM (2014) Leaching of plastic additives to marine organisms. Environ Pollut 187:49–54. https://doi.org/10.1016/j.envpol.2013.12.013

Koelmans AA, Bakir A, Burton GA, Janssen CR (2016) Microplastic as a vector for chemicals in the aquatic environment: critical review and model-supported reinterpretation of empirical studies. Environ Sci Technol 50:3315–3326. https://doi.org/10.1021/acs.est.5b06069

Koelmans AA, Besseling E, Foekema E et al (2017a) Risks of plastic debris: unravelling fact, opinion, perception, and belief. Environ Sci Technol 51:11513–11519. https://doi.org/10.1021/acs.est.7b02219

Koelmans AA, Kooi M, Lavender LK, van Sebille E (2017b) All is not lost: deriving a top-down mass budget of plastic at sea. Environ Res Lett 12(11):114028. https://doi.org/10.1088/1748-9326/aa9500

Kole PJ, Löhr AJ, Van Belleghem FGAJ, Ragas AMJ (2017) Wear and tear of tyres: a stealthy source of microplastics in the environment. Int J Environ Res Public Health 14(10). pii: E1265. https://doi.org/10.3390/ijerph14101265

Kreider ML, Panko JM, McAtee BL et al (2010) Physical and chemical characterization of tire-related particles: comparison of particles generated using different methodologies. Sci Total Environ 408:652–659. https://doi.org/10.1016/j.scitotenv.2009.10.016

Kühn S, Bravo Rebolledo EL, van Franeker JA (2015) Deleterious effects of litter on marine life. In: Bergmann M, Gutow L, Klages M (eds) Marine anthropogenic litter. Springer, Cham, pp 75–116

Kumar A, Holuszko M, Espinosa DCR (2017) E-waste: an overview on generation, collection, legislation and recycling practices. Resour Conserv Recycl 122:32–42. https://doi.org/10.1016/j.resconrec.2017.01.018

Lahens L, Strady E, Kieu-Le TC et al (2018) Macroplastic and microplastic contamination assessment of a tropical river (Saigon River, Vietnam) transversed by a developing megacity. Environ Pollut 236:661–671. https://doi.org/10.1016/j.envpol.2018.02.005

Lambert S, Wagner M (2017) Environmental performance of bio-based and biodegradable plastics: the road ahead. Chem Soc Rev 46:6855–6871. https://doi.org/10.1039/C7CS00149E

Lambert S, Scherer C, Wagner M (2017) Ecotoxicity testing of microplastics: considering the heterogeneity of physicochemical properties. Integr Environ Assess Manag 13:470–475. https://doi.org/10.1002/ieam.1901

Lares M, Ncibi MC, Sillanpää M, Sillanpää M (2018) Occurrence, identification and removal of microplastic particles and fibers in conventional activated sludge process and advanced MBR technology. Water Res 133:236–246. https://doi.org/10.1016/j.watres.2018.01.049

Lebreton LCM, Van Der Zwet J, Damsteeg JW et al (2017) River plastic emissions to the world's oceans. Nat Commun 8:1–10. https://doi.org/10.1038/ncomms15611

Lechner A, Ramler D (2015) The discharge of certain amounts of industrial microplastic from a production plant into the River Danube is permitted by the Austrian legislation. Environ Pollut 200:159–160. https://doi.org/10.1016/j.envpol.2015.02.019

Lechner A, Keckeis H, Lumesberger-Loisl F et al (2014) The Danube so colourful: a potpourri of plastic litter outnumbers fish larvae in Europe's second largest river. Environ Pollut 188:177–181. https://doi.org/10.1016/j.envpol.2014.02.006

Lee H, Kim Y (2018) Treatment characteristics of microplastics at biological sewage treatment facilities in Korea. Mar Pollut Bull 137:1–8. https://doi.org/10.1016/j.marpolbul.2018.09.050

Lee WS, Cho H-J, Kim E et al (2019) Bioaccumulation of polystyrene nanoplastics and their effect on the toxicity of Au ions in zebrafish embryos. Nanoscale 11:3173–3185. https://doi.org/10.1039/C8NR09321K

Lenz R, Enders K, Gissel T (2016) Microplastic exposure studies should be environmentally realistic. Proc Natl Acad Sci U S A 113:2–3. https://doi.org/10.1073/pnas.1606615113

Leslie HA (2014) Review of microplastics in cosmetics. IVM Inst Environ Stud 476(33)

Leslie HA, Brandsma SH, van Velzen MJM, Vethaak AD (2017) Microplastics en route: Field measurements in the Dutch river delta and Amsterdam canals, wastewater treatment plants, North Sea sediments and biota. Environ Int 101:133–142. https://doi.org/10.1016/j.envint.2017.01.018

Li J, Liu H, Paul Chen J (2018) Microplastics in freshwater systems: a review on occurrence, environmental effects, and methods for microplastics detection. Water Res 137:362–374. https://doi.org/10.1016/j.watres.2017.12.056

Lin L, Zuo LZ, Peng JP et al (2018) Occurrence and distribution of microplastics in an urban river: a case study in the Pearl River along Guangzhou City, China. Sci Total Environ 644:375–381. https://doi.org/10.1016/j.scitotenv.2018.06.327

Liu M, Lu S, Song Y et al (2018) Microplastic and mesoplastic pollution in farmland soils in suburbs of Shanghai, China. Environ Pollut 242:855–862. https://doi.org/10.1016/j.envpol.2018.07.051

Liu F, Olesen KB, Borregaard AR, Vollertsen J (2019a) Microplastics in urban and highway stormwater retention ponds. Sci Total Environ 671:992–1000. https://doi.org/10.1016/j.scitotenv.2019.03.416

Liu X, Yuan W, Di M et al (2019b) Transfer and fate of microplastics during the conventional activated sludge process in one wastewater treatment plant of China. Chem Eng J 362:176–182. https://doi.org/10.1016/j.cej.2019.01.033

Lohmann R (2017) Microplastics are not important for the cycling and bioaccumulation of organic pollutants in the oceans – but should microplastics be considered POPs themselves? Integr Environ Assess Manag 13:460–465. https://doi.org/10.1002/ieam.1914

Luo W, Su L, Craig NJ et al (2018) Accepted manuscript comparison of microplastic pollution in different water bodies from urban creeks to coastal waters. Environ Pollut 246:174–182. https://doi.org/10.1016/j.envpol.2018.11.081

Maaß S, Daphi D, Lehmann A, Rillig MC (2017) Transport of microplastics by two collembolan species. Environ Pollut 225:456–459. https://doi.org/10.1016/j.envpol.2017.03.009

Magni S, Binelli A, Pittura L et al (2019) The fate of microplastics in an Italian wastewater treatment plant. Sci Total Environ 652:602–610. https://doi.org/10.1016/j.scitotenv.2018.10.269

Magnusson K, Norén F (2014) Screening of microplastic particles in and down-stream a wastewater treatment plant. IVL Swedish Environ Res Inst C 55. https://urn.kb.se/resolve?urn=urn:nbn:se:naturvardsverket:diva-2226

Mahon AM, O'Connell B, Healy MG et al (2017) Microplastics in sewage sludge: effects of treatment. Environ Sci Technol 51:810–818. https://doi.org/10.1021/acs.est.6b04048

Mai L, Bao LJ, Shi L et al (2018) A review of methods for measuring microplastics in aquatic environments. Environ Sci Pollut Res 25:11319–11332. https://doi.org/10.1007/s11356-018-1692-0

Mani T, Hauk A, Walter U, Burkhardt-Holm P (2016) Microplastics profile along the Rhine River. Sci Rep 5:17988. https://doi.org/10.1038/srep17988

Mason SA, Garneau D, Sutton R et al (2016) Microplastic pollution is widely detected in US municipal wastewater treatment plant effluent. Environ Pollut 218:1045–1054. https://doi.org/10.1016/j.envpol.2016.08.056

McCormick A, Hoellein TJ, Mason SA et al (2014) Microplastic is an abundant and distinct microbial habitat in an urban river. Environ Sci Technol 48:11863–11871. https://doi.org/10.1021/es503610r

McCormick AR, Hoellein TJ, London MG et al (2016) Microplastic in surface waters of urban rivers: concentration, sources, and associated bacterial assemblages. Ecosphere 7(11):e01556. https://doi.org/10.1002/ecs2.1556

Mercier A, Gravouil K, Aucher W et al (2017) Fate of eight different polymers under uncontrolled composting conditions: relationships between deterioration, biofilm formation, and the material surface properties. Environ Sci Technol 51:1988–1997. https://doi.org/10.1021/acs.est.6b03530

Michielssen MR, Michielssen ER, Ni J, Duhaime MB (2016) Fate of microplastics and other small anthropogenic litter (SAL) in wastewater treatment plants depends on unit processes employed. Environ Sci Water Res Technol 2:1064–1073. https://doi.org/10.1039/C6EW00207B

Miller RZ, Watts AJR, Winslow BO et al (2017) Mountains to the sea: river study of plastic and non-plastic microfiber pollution in the northeast USA. Mar Pollut Bull 124:245–251. https://doi.org/10.1016/j.marpolbul.2017.07.028

Mintenig SM, Int-Veen I, Löder MGJ et al (2017) Identification of microplastic in effluents of waste water treatment plants using focal plane array-based micro-Fourier-transform infrared imaging. Water Res 108:365–372. https://doi.org/10.1016/j.watres.2016.11.015

Mintenig SM, Bäuerlein PS, Koelmans AA et al (2018) Closing the gap between small and smaller: towards a framework to analyse nano- and microplastic in aqueos environmental samples. Environ Sci Nano 5:1640–1649. https://doi.org/10.1039/C8EN00186C

Mintenig SM, Löder MGJ, Primpke S, Gerdts G (2019) Low numbers of microplastics detected in drinking water from ground water sources. Sci Total Environ 648:631–635. https://doi.org/10.1016/j.scitotenv.2018.08.178

Mohamed Nor NH, Koelmans AA (2019) Transfer of PCBs from microplastics under simulated gut fluid conditions is biphasic and reversible. Environ Sci Technol 53:1874–1883. https://doi.org/10.1021/acs.est.8b05143

Moore CJ, Lattin GL, Zellers AF (2011) Quantity and type of plastic debris flowing from two urban rivers to coastal waters and beaches of Southern California. Rev Gestão Costeira Integr 11:65–73. https://doi.org/10.5894/rgci194

Morritt D, Stefanoudis PV, Pearce D et al (2014) Plastic in the thames: a river runs through it. Mar Pollut Bull 78:196–200. https://doi.org/10.1016/j.marpolbul.2013.10.035

Mulder M (1998) Basic principle of membrane technology. Kluwer, Dordrecht

Murphy F, Ewins C, Carbonnier F, Quinn B (2016) Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment. Environ Sci Technol 50:5800–5808. https://doi.org/10.1021/acs.est.5b05416

Napper IE, Thompson RC (2016) Release of synthetic microplastic plastic fibres from domestic washing machines: effects of fabric type and washing conditions. Mar Pollut Bull 112:39–45. https://doi.org/10.1016/j.marpolbul.2016.09.025

Napper IE, Bakir A, Rowland SJ, Thompson RC (2015) Characterisation, quantity and sorptive properties of microplastics extracted from cosmetics. Mar Pollut Bull 99:178–185. https://doi.org/10.1016/j.marpolbul.2015.07.029

Nel HA, Dalu T, Wasserman RJ (2018) Sinks and sources: assessing microplastic abundance in river sediment and deposit feeders in an Austral temperate urban river system. Sci Total Environ 612:950–956. https://doi.org/10.1016/j.scitotenv.2017.08.298

Ng EL, Huerta Lwanga E, Eldridge SM et al (2018) An overview of microplastic and nanoplastic pollution in agroecosystems. Sci Total Environ 627:1377–1388. https://doi.org/10.1016/j.scitotenv.2018.01.341

Nizzetto L, Futter M, Langaas S (2016) Are agricultural soils dumps for microplastics of urban origin? Environ Sci Technol 50:10777–10779. https://doi.org/10.1021/acs.est.6b04140

Peng G, Xu P, Zhu B et al (2018) Microplastics in freshwater river sediments in Shanghai, China: a case study of risk assessment in mega-cities. Environ Pollut 234:448–456. https://doi.org/10.1016/j.envpol.2017.11.034

Picó Y, Barceló D (2019) Analysis and prevention of microplastics pollution in water: current perspectives and future directions. ACS Omega 4:6709–6719. https://doi.org/10.1021/acsomega.9b00222

Picó Y, Alfarhan A, Barceló D (2019) Nano- and microplastic analysis: focus on their occurrence in freshwater ecosystems and remediation technologies. Trends Anal Chem 113:409–425. https://doi.org/10.1016/j.trac.2018.08.022

Piehl S, Leibner A, Löder MGJ et al (2018) Identification and quantification of macro- and microplastics on an agricultural farmland. Sci Rep 8:17950. https://doi.org/10.1038/s41598-018-36172-y

Pirc U, Vidmar M, Mozer A, Kržan A (2016) Emissions of microplastic fibers from microfiber fleece during domestic washing. Environ Sci Pollut Res 23:22206–22211. https://doi.org/10.1007/s11356-016-7703-0

PlasticsEurope (2018) Plastics – the facts. https://www.plasticseurope.org/application/files/6315/4510/9658/Plastics_the_facts_2018_AF_web.pdf

Prata JC, da Costa JP, Lopes I et al (2019) Effects of microplastics on microalgae populations: a critical review. Sci Total Environ 665:400–405. https://doi.org/10.1016/j.scitotenv.2019.02.132

Ramaswamy V, Sharma HR (2011) Research article plastic bags – threat to environment and cattle health: a retrospective study from Gondar city of Ethiopia. IIOAB J 2:7–12

Ramos L, Berenstein G, Hughes EA et al (2015) Polyethylene film incorporation into the horticultural soil of small periurban production units in Argentina. Sci Total Environ 523:74–81. https://doi.org/10.1016/j.scitotenv.2015.03.142

Rech S, Macaya-Caquilpán V, Pantoja JF et al (2014) Rivers as a source of marine litter – a study from the SE Pacific. Mar Pollut Bull 82:66–75. https://doi.org/10.1016/j.marpolbul.2014.03.019

Redondo Hasselerharm PE, Falahudin D, Peeters E, Koelmans AA (2018) Microplastic effect thresholds for freshwater benthic macroinvertebrates. Environ Sci Technol 52(4):2278–2286. https://doi.org/10.1021/acs.est.7b05367

Rillig MC, Ziersch L, Hempel S (2017) Microplastic transport in soil by earthworms. Sci Rep 7:1362. https://doi.org/10.1038/s41598-017-01594-7

Rochman CM, Kurobe T, Flores I, Teh SJ (2014) Early warning signs of endocrine disruption in adult fish from the ingestion of polyethylene with and without sorbed chemical pollutants from the marine environment. Sci Total Environ 493:656–661. https://doi.org/10.1016/j.scitotenv.2014.06.051

Rochman CM, Kross SM, Armstrong JB et al (2015) Scientific evidence supports a ban on microbeads. Environ Sci Technol 49:10759–10761. https://doi.org/10.1021/acs.est.5b03909

Rodrigues MO, Abrantes N, Gonçalves FJM et al (2018) Spatial and temporal distribution of microplastics in water and sediments of a freshwater system (Antuã River, Portugal). Sci Total Environ 633:1549–1559. https://doi.org/10.1016/j.scitotenv.2018.03.233

SAPEA, Science Advice for Policy by European Academies (2018) A scientific perspective on microplastics in nature and society. SAPEA, Berlin. https://doi.org/10.26356/microplastics

Sato T, Qadir M, Yamamoto S et al (2013) Global, regional, and country level need for data on wastewater generation, treatment, and use. Agric Water Manag 130:1–13. https://doi.org/10.1016/j.agwat.2013.08.007

Scarascia-Mugnozza G, Sica C, Russo G (2012) Plastic materials in European agriculture: actual use and perspectives. J Agric Eng 42:15. https://doi.org/10.4081/jae.2011.3.15

Scherer C, Brennholt N, Reifferscheid G, Wagner M (2017) Feeding type and development drive the ingestion of microplastics by freshwater invertebrates. Sci Rep 7:1–9. https://doi.org/10.1038/s41598-017-17191-7

Scheurer M, Bigalke M (2018) Microplastics in Swiss floodplain soils. Environ Sci Technol 52:3591–3598. https://doi.org/10.1021/acs.est.7b06003

Schmidt C, Krauth T, Wagner S (2017) Export of plastic debris by rivers into the sea. Environ Sci Technol 51:12246–12253. https://doi.org/10.1021/acs.est.7b02368

Schür C, Rist S, Baun A et al (2019) When fluorescence is not a particle: the tissue translocation of microplastics in Daphnia magna seems an artIfact. Environ Toxicol Chem 38(7):1495–1503. https://doi.org/10.1002/etc.4436

Schuyler Q, Hardesty BD, Wilcox C, Townsend K (2012) To eat or not to eat? Debris selectivity by marine turtles. PLoS One 7(10). https://doi.org/10.1371/journal.pone.0040884

Shruti VC, Jonathan MP, Rodriguez-Espinosa PF, Rodríguez-González F (2019) Microplastics in freshwater sediments of Atoyac River basin, Puebla City, Mexico. Sci Total Environ 654:154–163. https://doi.org/10.1016/j.scitotenv.2018.11.054

Siegfried M, Koelmans AA, Besseling E, Kroeze C (2017) Export of microplasticsfrom land to sea. A modelling approach. Water Res 127:249–257. https://doi.org/10.1016/j.watres.2017.10.011

Sighicelli M, Pietrelli L, Lecce F et al (2018) Microplastic pollution in the surface waters of Italian Subalpine Lakes. Environ Pollut 236:645–651. https://doi.org/10.1016/j.envpol.2018.02.008

Simon M, van Alst N, Vollertsen J (2018) Quantification of microplastic mass and removal rates at wastewater treatment plants applying Focal Plane Array (FPA)-based Fourier Transform Infrared (FT-IR) imaging. Water Res 142:1–9. https://doi.org/10.1016/j.watres.2018.05.019

Song YK, Hong SH, Jang M, et al (2015) A comparison of microscopic and spectroscopic identification methods for analysis of microplastics in environmental samples. Mar Pollut Bull 93:202–209. https://doi.org/10.1016/j.marpolbul.2015.01.015

Stenmarck Å, Belleza EL, Fråne A et al (2017) Hazardous substances in plastics: ways to increase recycling. Nordisk Ministerråd, Copenhagen. https://doi.org/10.6027/TN2017-505

Su L, Xue Y, Li L et al (2016) Microplastics in Taihu Lake, China. Environ Pollut 216:711–719. https://doi.org/10.1016/j.envpol.2016.06.036

Sundt P, Schulze P-E, Syversen F (2014) Sources of microplastic-pollution to the marine environment Project report. Norweg Environ Agency. M-321|2015

Talvitie J, Heinonen M, Pääkkönen JP et al (2015) Do wastewater treatment plants act as a potential point source of microplastics? Preliminary study in the coastal Gulf of Finland, Baltic Sea. Water Sci Technol 72:1495–1504. https://doi.org/10.2166/wst.2015.360

Talvitie J, Mikola A, Koistinen A, Setälä O (2017a) Solutions to microplastic pollution – removal of microplastics from wastewater effluent with advanced wastewater treatment technologies. Water Res 123:401–407. https://doi.org/10.1016/j.watres.2017.07.005

Talvitie J, Mikola A, Setälä O et al (2017b) How well is microlitter purified from wastewater? – A detailed study on the stepwise removal of microlitter in a tertiary level wastewater treatment plant. Water Res 109:164–172. https://doi.org/10.1016/j.watres.2016.11.046

Tan X, Yu X, Cai L et al (2019) Microplastics and associated PAHs in surface water from the Feilaixia Reservoir in the Beijiang River, China. Chemosphere 221:834–840. https://doi.org/10.1016/j.chemosphere.2019.01.022

Teuten EL, Saquing JM, Knappe DRU et al (2009) Transport and release of chemicals from plastics to the environment and to wildlife. Philos Trans R Soc B Biol Sci 364:2027–2045. https://doi.org/10.1098/rstb.2008.0284

Tibbetts J, Krause S, Lynch I, Smith GHS (2018) Abundance, distribution, and drivers of microplastic contamination in urban river environments. Water 10(11):1597. https://doi.org/10.3390/w10111597

Unice KM, Kreider ML, Panko JM (2013) Comparison of tire and road wear particle concentrations in sediment for watersheds in France, Japan, and the United States by quantitative pyrolysis GC/MS analysis. Environ Sci Technol 47:8138–8147. https://doi.org/10.1021/es400871j

US Congress (2015) Microbead-Free Waters Act of 2015. Public Law 114–231 114th Congress An Act. Public Law 114–144. https://www.congress.gov/bill/114th-congress/house-bill/1321/text. Accessed 26 May 2019

van Emmerik T, Kieu-Le T-C, Loozen M et al (2018) A methodology to characterize riverine macroplastic emission into the ocean. Front Mar Sci 5:1–11. https://doi.org/10.3389/fmars.2018.00372

Van Franeker JA, Blaize C, Danielsen J et al (2011) Monitoring plastic ingestion by the northern fulmar Fulmarus glacialis in the North Sea. Environ Pollut 159:2609–2615. https://doi.org/10.1016/j.envpol.2011.06.008

Vaughan R, Turner SD, Rose NL (2017) Microplastics in the sediments of a UK urban lake. Environ Pollut 229:10–18. https://doi.org/10.1016/j.envpol.2017.05.057

Verma R, Vinoda KS, Papireddy M, Gowda ANS (2016) Toxic pollutants from plastic waste – a review. Procedia Environ Sci 35:701–708. https://doi.org/10.1016/j.proenv.2016.07.069

Vermaire JC, Pomeroy C, Herczegh SM et al (2017) Microplastic abundance and distribution in the open water and sediment of the Ottawa River, Canada, and its tributaries. Facets 2:301–314. https://doi.org/10.1139/facets-2016-0070

Vianello A, Boldrin A, Guerriero P et al (2013) Microplastic particles in sediments of Lagoon of Venice, Italy: first observations on occurrence, spatial patterns and identification. Estuar Coast Shelf Sci 130:54–61. https://doi.org/10.1016/j.ecss.2013.03.022

Vollertsen J, Hansen AA (eds) (2017) Microplastic in Danish wastewater: sources, occurrences and fate. Danish Environmental Protection Agency, Odense C

Wang J, Peng J, Tan Z et al (2017a) Microplastics in the surface sediments from the Beijiang River littoral zone: composition, abundance, surface textures and interaction with heavy metals. Chemosphere 171:248–258. https://doi.org/10.1016/j.chemosphere.2016.12.074

Wang W, Ndungu AW, Li Z, Wang J (2017b) Microplastics pollution in inland freshwaters of China: a case study in urban surface waters of Wuhan, China. Sci Total Environ 575:1369–1374. https://doi.org/10.1016/j.scitotenv.2016.09.213

Wang W, Yuan W, Chen Y, Wang J (2018) Microplastics in surface waters of Dongting Lake and Hong Lake, China. Sci Total Environ 633:539–545. https://doi.org/10.1016/j.scitotenv.2018.03.211

Weithmann N, Möller JN, Löder MGJ et al (2018) Organic fertilizer as a vehicle for the entry of microplastic into the environment. Sci Adv 4:1–8. https://doi.org/10.1126/sciadv.aap8060

Wen X, Du C, Xu P et al (2018) Microplastic pollution in surface sediments of urban water areas in Changsha, China: abundance, composition, surface textures. Mar Pollut Bull 136:414–423. https://doi.org/10.1016/j.marpolbul.2018.09.043

Wetherbee GA, Baldwin AK, Ranville JF (2019) It is raining plastic. U.S. Geological Survey Open-File Report 2019–1048, 1 sheet. https://doi.org/10.3133/ofr20191048

WHO/UNICEF (2019) Joint Monitoring Programme for water supply, sanitation and hygiene (JMP). https://ec.europa.eu/knowledge4policy/online-resource/whounicef-joint-monitoring-programme-water-supply-sanitation-hygiene-jmp_en?pages=1

Williams AT, Simmons SL (1996) The degradation of plastic litter in rivers: implications for beaches. J Coast Conserv 2:63–72. https://doi.org/10.1007/BF02743038

Williams AT, Simmons SL (1999) Sources of riverine litter: the river Taff, South Wales. UK Water Air Soil Pollut 112:197–216. https://doi.org/10.1023/A:1005000724803

Windsor FM, Tilley RM, Tyler CR, Ormerod SJ (2019) Microplastic ingestion by riverine macroinvertebrates. Sci Total Environ 646:68–74. https://doi.org/10.1016/j.scitotenv.2018.07.271

Wolff S, Kerpen J, Prediger J et al (2019) Determination of the microplastics emission in the effluent of a municipal waste water treatment plant using Raman microspectroscopy. Water Res X 2:100014. https://doi.org/10.1016/J.WROA.2018.100014

Wright SL, Thompson RC, Galloway TS (2013) The physical impacts of microplastics on marine organisms: a review. Environ Pollut 178:483–492. https://doi.org/10.1016/j.envpol.2013.02.031

Xanthos D, Walker TR (2017) International policies to reduce plastic marine pollution from single-use plastics (plastic bags and microbeads): a review. Mar Pollut Bull 118:17–26. https://doi.org/10.1016/j.marpolbul.2017.02.048

Xiong X, Wu C, Elser JJ et al (2019) Occurrence and fate of microplastic debris in middle and lower reaches of the Yangtze River – from inland to the sea. Sci Total Environ 659:66–73. https://doi.org/10.1016/j.scitotenv.2018.12.313

Yan M, Nie H, Xu K et al (2019) Microplastic abundance, distribution and composition in the Pearl River along Guangzhou city and Pearl River estuary, China. Chemosphere 217:879–886. https://doi.org/10.1016/j.chemosphere.2018.11.093

Yang S-S, Brandon AM, Andrew Flanagan JC et al (2018) Biodegradation of polystyrene wastes in yellow mealworms (larvae of Tenebrio molitor Linnaeus): factors affecting biodegradation rates and the ability of polystyrene-fed larvae to complete their life cycle. Chemosphere 191:979–989. https://doi.org/10.1016/j.chemosphere.2017.10.117

Ye S, Andrady AL (1991) Fouling of floating plastic debris under biscayne bay exposure conditions. Mar Pollut Bull 22(12):608–613

Yoshida S, Hiraga K, Takanaha T et al (2016) A bacterium that degrades and assimilates poly (ethyleneterephthalate). Science 351:1196–1199. https://doi.org/10.1126/science.aad6359

Yuan W, Liu X, Wang W et al (2019) Microplastic abundance, distribution and composition in water, sediments, and wild fish from Poyang Lake, China. Ecotoxicol Environ Saf 170:180–187. https://doi.org/10.1016/j.ecoenv.2018.11.126

Zbyszewski M, Corcoran PL (2011) Distribution and degradation of fresh water plastic particles along the beaches of Lake Huron, Canada. Water Air Soil Pollut 220:365–372. https://doi.org/10.1007/s11270-011-0760-6

Zbyszewski M, Corcoran PL, Hockin A (2014) Comparison of the distribution and degradation of plastic debris along shorelines of the Great Lakes, North America. J Great Lakes Res 40:288–299. https://doi.org/10.1016/j.jglr.2014.02.012

Zettler ER, Mincer TJ, Amaral-Zettler LA (2013) Life in the "Plastisphere": microbial communities on plastic marine debris. Environ Sci Technol 47:7137–7146. https://doi.org/10.1021/es401288x

Zhang GS, Liu YF (2018) The distribution of microplastics in soil aggregate fractions in southwestern China. Sci Total Environ 642:12–20. https://doi.org/10.1016/j.scitotenv.2018.06.004

Zhang K, Gong W, Lv J et al (2015) Accumulation of floating microplastics behind the Three Gorges Dam. Environ Pollut 204:117–123. https://doi.org/10.1016/j.envpol.2015.04.023

Zhang K, Su J, Xiong X et al (2016) Microplastic pollution of lakeshore sediments from remote lakes in Tibet plateau, China. Environ Pollut 219:450–455. https://doi.org/10.1016/j.envpol.2016.05.048

Zhang S, Yang X, Gertsen H et al (2018) A simple method for the extraction and identification of light density microplastics from soil. Sci Total Environ 616–617:1056–1065. https://doi.org/10.1016/j.scitotenv.2017.10.213

Zhang X, Leng Y, Liu X et al (2019) Microplastics' pollution and risk assessment in an Urban River: a case study in the Yongjiang River, Nanning City, South China. Expo Heal. https://doi.org/10.1007/s12403-018-00296-3

Zhao S, Zhu L, Li D (2016) Microscopic anthropogenic litter in terrestrial birds from Shanghai, China: not only plastics but also natural fibers. Sci Total Environ 550:1110–1115. https://doi.org/10.1016/j.scitotenv.2016.01.112

Ziajahromi S, Neale PA, Leusch FDLL (2016) Wastewater treatment plant effluent as a source of microplastics: review of the fate, chemical interactions and potential risks to aquatic organisms. Water Sci Technol 74:2253–2269. https://doi.org/10.2166/wst.2016.414

Ziajahromi S, Neale PA, Rintoul L, Leusch FDL (2017a) Wastewater treatment plants as a pathway for microplastics: development of a new approach to sample wastewater-based microplastics. Water Res 112:93–99. https://doi.org/10.1016/j.watres.2017.01.042

Ziajahromi S, Kumar A, Neale PA, Leusch FDL (2017b) Impact of microplastic beads and fibers on water flea (Ceriodaphnia dubia) survival, growth, and reproduction: implications of single and mixture exposures. Environ Sci Technol 51:13397–13406. https://doi.org/10.1021/acs.est.7b03574

Zubris KAV, Richards BK (2005) Synthetic fibers as an indicator of land application of sludge. Environ Pollut 138:201–211. https://doi.org/10.1016/j.envpol.2005.04.013

Zylstra ER (2013) Accumulation of wind-dispersed trash in desert environments. J Arid Environ 89:13–15. https://doi.org/10.1016/j.jaridenv.2012.10.004

A Methodology for Data-Driven Decision-Making in the Monitoring of Particulate Matter Environmental Contamination in Santiago of Chile

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1 Introduction

The main components of air are nitrogen (approximately 78%), oxygen (21%) and argon, carbon dioxide, helium, hydrogen, neon, and water vapor (together ~1%). Atmospheric pollution is the lasting presence in the air of these and other chemicals at concentrations above their natural levels, which could potentially lead to adverse health effects. It derives mainly from anthropogenic activities that use combustion. Effects of air contamination are important if climatological and geographical factors reduce its dissipation, especially in areas with huge anthropogenic activity. Due to this, many people breathe contaminated air, and the World Health Organization (WHO) has estimated that 4.2 million deaths every year are a result of poor air quality, with 91% of the world's population being exposed to air pollutants by living in places where air quality exceeds WHO safety guidelines (https://www.who.int/airpollution/en/).

It is a fact that meteorological and climatic variables play an important role in the determination of air pollution patterns and the global climate change is foreseen to cause an increase in the concentration of some pollutants (Kinney 2008). Santiago, the capital city of Chile, is among the cities with higher air pollution levels in the world. Its location and weather, when combined with high anthropological emissions, create critical air pollution conditions. A recent model explained elevated particulate matter (PM) concentrations during high pollution events in Santiago, as a function of weather conditions in central Chile and in Argentina, which at the local level generate a depression at the base of the inversion layer, an increase in the vertical thermal stability, lower humidity and low-wind conditions. Pollutant dispersion is thus decreased leading to poor ventilation of contaminated air (Toro et al. 2019).

Due to its geography, people in the city of Santiago experience dry and hot summers and damp winters, which contribute to the air pollution episodes that put younger and older people at risk of respiratory and cardiovascular diseases. Henríquez and Urrea (2017) showed a rise in daily emergency visits in winter compared to summer (odds ratio of 2.2646), which were associated with higher daily concentrations of PM, carbon monoxide, and sulfur and nitrogen oxide during winter. Noteworthy, the press has recently covered the news that Chile has nine of the ten more air-contaminated cities in South America (https://bit.ly/2ovYLiu).

The effects on health of air pollution vary according to type of pollutants, their concentration, and duration of exposure. It is generally accepted that air contamination causes cardiovascular and pulmonary morbidity in addition to increased mortality after exposure, but other epidemiological associations have also been described, including cancer as well as reproductive and immunological toxicity (https://www.who.int/airpollution/en/). Due to the multicomponent aspect of contaminated air, it is hard to establish what component of the contaminant mixture produces a specific health problem. However, there is a growing amount of evidence that indicates that PM plays a key role in the induction of cardiovascular and respiratory diseases (Kim et al. 2015).

Data analytics may be employed to generate information of air quality within the context of data-driven decision-making (DDDM), a process associated with big data and data science (Baesen 2014; Dietrich 2015; Aykroyd et al. 2019). DDDM allows us to study the impact of atmospheric contaminants on human health and the urban environment. In epidemiological studies, average air contaminant concentrations are employed as indicators of air pollutant levels. However, since concentrations of air pollutants vary with geographical and meteorological conditions, they are treated as random variables taking values greater than zero. Then, these random variables are described by a statistical distribution, which is frequently asymmetrical with a positive skewness (Marchant et al. 2013). Note that pollutant concentrations are expressed as number of units of mass of a certain substance (or agent) per a defined unit of mass in the set, so it can never take negative values (Ott 1990). Thus, the popular normal or Gaussian distribution is not applicable and authors resort to data transformation which has limitations. Alternatively, one can avoid data transformation by modeling with a suitable distribution (Leiva et al. 2015; Marchant et al. 2019) such as Birnbaum-Saunders.

The Birnbaum-Saunders distribution has positive skewness (asymmetry). It has been defined over a range of continuous values greater than zero, allowing its use to describe random variables with positive support such as atmospheric pollutant concentrations. This distribution was derived from physical considerations of material failure due to fatigue (Leiva 2016) and has been successfully applied to describe air pollutant concentrations (Leiva et al. 2008, 2015; Vilca et al. 2010; Ferreira et al. 2012; Marchant et al. 2018, 2019). Leiva et al. (2015) provided a mathematical formulation based on the proportionate-effect law (also known as the Gibrat law) to justify the use of the Birnbaum-Saunders model as environmental contaminant statistical distribution, justification which was previously associated also with the lognormal distribution (Ott 1990). According to Leiva et al. (2015), a contaminant concentration follows the proportionate-effect law if the growth in the concentration at any step of the contamination process is a random proportion of the previous value of the concentration. The Birnbaum-Saunders distribution has properties that are similar to those of the lognormal distribution (Aitchison and Brown 1973; Leiva 2016), including the relationship with the proportionate-effect law and contamination processes (Aitchison and Brown 1973, p. 22; Ott 1990; Leiva et al. 2015). In addition, in both Birnbaum-Saunders and lognormal distributions, their parameter estimation is sensitive to atypical (extreme or outliers) data; a situation frequently found when one analyzes air contaminant concentrations. Díaz-García and Leiva (2005) derived an extension of the Birnbaum-Saunders distribution which is known as the generalized Birnbaum-Saunders distribution. These distributions are a flexible general family based on the Birnbaum-Saunders distribution, which contains several particular cases. One of these cases is the Birnbaum-Saunders-Student-t distribution, from now on Birnbaum-Saunders-t distribution (Athayde et al. 2019), whose estimation of its parameters is not sensitive (robust) to the presence of atypical observations, which are common in environmental contamination data. It is important to mention this issue of robustness to be kept in mind when using the Birnbaum-

Saunders-t distribution, due to the relevant role that the Birnbaum-Saunders distribution and its extensions are taking in environmental modeling.

Air chemical pollutants can be broadly grouped into four classes: gaseous compounds; heavy metals; persistent organic pollutants; and suspended particles or PM. Given the importance of PM in air pollution toxicity and that the Birnbaum-Saunders and Birnbaum-Saunders-t models are adequate to statistically describe pollutant distributions, the objectives of this article are (1) to provide a notion of the serious threat of PM10 and PM2.5 for human health; (2) to describe the air contamination problem in Santiago, Chile; and (3) to propose a data science methodology that can be applied for modeling air quality. We exemplify this methodology using air contamination real data from the city of Santiago, Chile.

2 Particulate Matter and Contamination in Santiago of Chile

2.1 Adverse Effects of Particulate Matter

PM is a complex mixture of particles and liquid droplets that get into the air (Adams et al. 2015; Hime et al. 2018). It is classified according to its diameter, which is important for risk evaluation, as particle size determines site of deposition within the respiratory tract. Thus, particles with a diameter over 10 μm do not penetrate into airways. Hence, these particles are usually considered to be of low risk, as they are deposited in the upper respiratory tract (on the nose and throat epithelium, above the larynx) and are cleared by mucociliary function. On the contrary, particles with a diameter smaller than 10 μm (PM10) are considered to be inhalable, that is, they get past the larynx, and, according to their size, they are deposited either on lower airways (particles between 2.5 and 10 μm) or on the alveoli of the lungs (particles smaller than 2.5 μm, PM2.5). Particles smaller than 0.1 μm are called ultrafine particles (UFPs) and easily reach the lung, where they are absorbed into the blood (WHO 2000, 2013).

PM is very complex as it varies greatly in source and composition. Coarser particles (those between 2.5 and 10 μm) are formed by the breakup of larger particles and usually contain minerals as well as carbon. Finer particles (<2.5 μm and including UFPs) derive mainly from combustion and may be either a carbon core with adsorbed hydrocarbons, such as polycyclic aromatic hydrocarbons and metals or secondary particles formed from sulfur and nitrogen oxides. Coarser particles may also include biological material such as mold, pollen, endotoxins, and bacteria (WHO 2000; Adams et al. 2015; Falcon-Rodriguez et al. 2016; Thompson 2018).

Anthropogenic activities, such as public transportation and industrial combustion, are the main contributors to the pollution of air in urban environments. The health effects of inhalable PM, after both acute and chronic exposure, have been described in the scientific literature. For instance, a 1953 article describes how the London Fog

Incident in December 1952 led to the death of at least 4000 people mainly from respiratory and cardiovascular conditions (Logan 1953). Nowadays, it is greatly accepted that toxicity from exposure to air pollution results in great part from the action of airborne PM. In addition, these health effects generally include not only respiratory and cardiovascular diseases but also cancer (WHO 2013). Furthermore, there is some evidence that PM may also cause or contribute to neurotoxicity and developmental toxicity (Thompson 2018). Animal and human studies have reported that PM causes systemic inflammation increasing respiratory and cardiovascular morbidity, as well as mortality from respiratory and cardiovascular diseases and cancer (WHO 2013; Wu et al. 2018). In fact, outdoor air pollution and PM in outdoor air pollution are both classified by the International Agency for Research on Cancer (IARC) as carcinogenic to humans (Group 1). The IARC concluded that PM not only is associated with an increase in genetic damage predictive of cancer but that it also may promote cancer progression by inducing oxidative stress and sustained inflammation (IARC 2016).

2.2 Geography, Topography, and Location of Santiago and Its Air Monitoring Stations

Santiago, the capital of Chile, is the largest city in the country, with an area of 867.75 km^2 and a population of about 7.1 million people, which is approximately 40.5% of the Chilean population (according to the information obtained from the Population and Housing Census 2017 conducted by the Chilean government). Santiago city is located in subtropical South America (33°27′S, 70°40′W), between a coastal mountain range to the West (with an altitude close to 1000 m above sea level) and the Andes mountain range to the East (with an altitude of around 3000 m above sea level). Santiago has been facing air pollution problems for more than three decades, becoming one of the cities with the highest levels of air pollution in the world (Ostro 2003). Its poor air quality is believed to be the result of the growing industrial sector, fast-growing population, and increased number of motor vehicles, worsened by geophysical constraints for pollutant dispersion in Santiago's basin (Préndez et al. 2011; Mendoza et al. 2019). In fall and winter seasons, subsidence conditions induce thermal inversion layers that increase levels of pollutant concentrations, creating a characteristic seasonality of air quality in the city (Villalobos et al. 2015).

Santiago has eleven (11) monitoring stations (which make the air quality assessment network for the Metropolitan Region of Santiago, denominated MACAM), located at different zones in the Metropolitan region of Chile. Figure 1 shows these stations which are named as (MS1) Independencia; (MS2) La Florida; (MS3) Las Condes; (MS4) Santiago city; (MS5) Pudahuel; (MS6) Cerrillos; (MS7) El Bosque; (MS8) Cerro Navia; (MS9) Puente Alto; (MS10) Talagante; and (MS11) Quilicura. The monitoring stations are geographically located with their respective numbers on the map of Fig. 1.

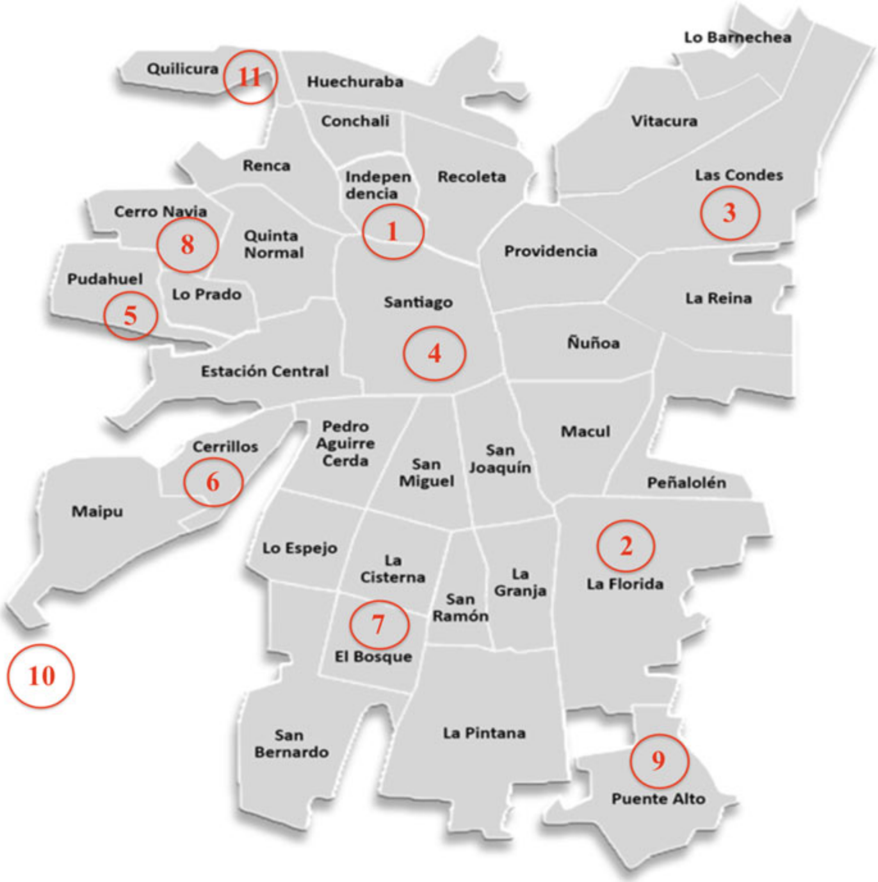


Fig. 1 Map of MACAM network of Santiago (Source: Metropolitan Regional Secretariat of the Chilean Ministry of Health)

2.3 Local Air Quality Guidelines

The current official methodology used by the Chilean authority in Santiago to predict PM10 concentrations is based on a multiple regression model (Morales et al. 2012). It helps to forecast the maximum value of the 24 h average concentration of PM10 in μg/normalized cubic meters (Nm^3) for the period from 00:00 to 24:00 h of the next day. In 2015, through Supreme Decree number 15/2015 and resolution number 9664/2015, it was instructed by the Chilean Ministry of Health to declare sanitary alert based on PM2.5 concentrations. Chilean guidelines for PM2.5 and PM10 concentrations are established at maximum values of 50 and 150 (in $\mu g/Nm^3$), during 24 h, respectively (CONAMA 1998; MMA 2011).

2.4 Health Effects of PM in Santiago

Several studies indicate that people living in Santiago are at risk due to the poor air quality of the city (Préndez et al. 2011; Romieu et al. 2012; Requia et al. 2018; Perez-Padilla and Menezes 2019). Ilabaca et al. (1999) evaluated the impact of daily variation of PM2.5 and other pollutants on the number of daily respiratory emergency visits to an important pediatric hospital of Santiago. The authors concluded that atmospheric air pollutant mixtures, especially fine PM, adversely affected the respiratory health of children residing in Santiago, evidenced by an increase in the number of daily respiratory emergency visits. Cifuentes et al. (2000) studied the effect of concentrations of inhalable PM, as well as of other gaseous pollutants, finding an association with increased daily mortality. Traffic combustion-related particles were found to be associated with emergency visits in Santiago (Cakmak et al. 2009). Franck et al. (2014, 2015) provided evidence for increased hospital admissions related to respiratory and cardiovascular diseases, after critical air pollution events in Santiago, showing the influence of combined exposure to airborne pollutants. Recently, Matus and Oyarzún (2019) indicated that an increase of 10 μg/m^3 of PM2.5 with 1 and 2 days of lag was associated with an increase of near 2% in children's hospitalizations due to respiratory diseases. This percentage increased to 5% when the exposure was with 8 days of lag, reflecting synergism between PM and respiratory viruses.

3 Data Science Methodology for Monitoring Urban Environmental Contamination

3.1 Birnbaum-Saunders np Control Charts

An np-chart is an adaptation of the control chart for nonconforming fraction when samples of equal size (n) are taken from the process (Leiva et al. 2015; Aykroyd et al. 2019). The np-chart is based on the binomial distribution as detailed below. In quality monitoring processes, one could be concerned about a random variable corresponding to the number (D) of times that the quality variable (X) exceeds a fixed value (x) established for the process, given an exceedance probability (p). Here, p can be computed by means of a continuous statistical distribution of the quality variable X as $p = \mathrm{P}(X > x) = 1 - F_X(x)$, where F_X is the cumulative distribution function of X. Thus, D follows a binomial distribution with parameters n and p. Based on this distribution, an np-chart is proposed with lower control limit (LCL), central line (CL), and upper control limit (UCL) given by

$$\text{LCL} = \max\left\{0, np_0 - k(np_0(1-p_0))^{1/2}\right\}, \quad \text{CL} = np_0, \quad \text{UCL} = np_0 + k(np_0(1-p_0))^{1/2},$$

where k is a control coefficient such that $k = 2$ indicates a warning level and $k = 3$ a dangerous level; p_0 is the nonconforming fraction corresponding to a target mean ${\mu_X}^{(0)}$ of the quality variable X, when the process is in control; and n is the size of each subgroup to be monitored. Note that the nonconforming fraction is the probability that the random variable X exceeds a dangerous concentration (x_0), and therefore, this probability is $P(X > x_0) = 1 - F_X(x_0)$. The Birnbaum-Saunders distribution has as one of its parameters the median (Leiva 2016). One can reparameterize the Birnbaum-Saunders distribution switching its median to its mean μ_X (Santos-Neto et al. 2014), with μ_X being the mean of the quality variable X previously defined. Note that this mean-based reparameterization of the Birnbaum-Saunders distribution allows us to have a similar setting as the Gaussian or normal distribution. Therefore, considering x_0 as proportional to ${\mu_X}^{(0)}$, that is, $x_0 = a{\mu_X}^{(0)}$, this permit us to establish a monitoring criterion, where $a > 0$ is a proportionality constant. Note that the target mean ${\mu_X}^{(0)}$ and the dangerous level x_0 can be taken from process specifications. Thus, when a monitoring process is in control ($\mu_X = {\mu_X}^{(0)}$) for a quality variable X following a Birnbaum-Saunders distribution (Leiva et al. 2015), the nonconforming fraction is given by $p_0 = 1 - F_X(x_0)$. Note that the specification of the point x_0 is equivalent to specifying the inspection point $a > 0$, because $x_0 = a{\mu_X}^{(0)}$, in which ${\mu_X}^{(0)}$ is the target mean, which is assumed to be known. Algorithm 1 provides a criterion for monitoring processes using an np-chart for a quality variable X following a Birnbaum-Saunders distribution.

Algorithm 1 np Control Chart Based on the Birnbaum-Saunders Distribution

1. Consider N subgroups of size n.
2. Collect n data $x_1, \ldots, x_n$ of the random variable of interest X for each subgroup.
3. Set the target mean ${\mu_X}^{(0)}$, the inspection constant a, and the control coefficient k.
4. Count in each subgroup of n data the number d of times that x_i exceeds $x_0 = a{\mu_X}^{(0)}$, for $i = 1,\ldots,n$.
5. Compute $\text{LCL} = \max\{0, np_0 - k(n\widehat{p}_0(1 - \widehat{p}_0))^{1/2}\}$, $\text{CL} = n\widehat{p}_0$, and $\text{UCL} = n\widehat{p}_0 + k(n\widehat{p}_0(1 - \widehat{p}_0))^{1/2}$, where $\widehat{p}_0$ is the maximum likelihood estimate of $p_0 = 1 - F_X(x_0)$, where F_X is the cumulative distribution function of the random variable X defined in step 2.
6. Declare the process as out-of-control if $d > \text{UCL}$ or $d < \text{LCL}$ or as in-control if $\text{LCL} \leq d \leq \text{UCL}$.

3.2 *Standard Bivariate Control Charts*

The standard Hotelling T^2 chart (Jackson 1985) is a useful tool for bivariate process control under a normal distribution. Specifically, it assumes that the vector summarizing the quality characteristics, (X_1, X_2), namely, follows a bivariate normal distribution. To monitor a bivariate process, the following statistical hypotheses are considered:

$$\mathrm{H}_0 : (\mu_1, \mu_2) = \left({\mu_1}^{(0)}, {\mu_2}^{(0)}\right) \text{ versus } \mathrm{H}_1 : (\mu_1, \mu_2) \neq \left({\mu_1}^{(0)}, {\mu_2}^{(0)}\right), \qquad (1)$$

where (${\mu_1}^{(0)}$, ${\mu_2}^{(0)}$) is the target mean vector of an in-control process. Then, the standard T^2 statistic for testing the hypotheses above under a normal distribution is used. In general, the construction of a bivariate control chart considers two phases. In Phase I, a data set of size $N = m \times n$ is obtained from an in-control status of the underlying process, where m is the number of subgroups and n is the size of each subgroup. This data set is used (a) to estimate the parameters of interest; (b) to verify the distributional assumption with goodness-of-fit techniques; (c) to calculate LCL and UCL; and (d) to detect bivariate outliers. Note that a bivariate outlier is considered to be atypical by considering the whole bivariate data and not the value of one given random variable (Marchant et al. 2019). In Phase II, LCL and UCL obtained in Phase I are used to assess whether a data sample for a new subgroup from the process is in control or not. Hence, in Phase II, LCL and UCL are used to detect deviations of the new data set for a target mean value, (${\mu_1}^{(0)}$, ${\mu_2}^{(0)}$), namely, or another target parameter of interest. In particular, for standard bivariate control charts, in Phase I, considering a number $m \geq 20$ of subgroups and a size of subgroups greater than one ($n > 1$), the distribution of the standard T^2 test statistic has a closed mathematically form. Then, the corresponding LCL and UCL obtained from T^2 are used (Lowry and Montgomery 1995; Montgomery 2009). Next, in Algorithm 2, we detail how to compute the LCL and UCL of a standard bivariate control chart. The average run length (ARL) is the mean number of points that must be plotted before one of them to indicate an out-of-control status. ARL can be used to evaluate the performance of a control chart. The probability that an observation is considered as out of control, if the process is actually in control, indicates a false alarm rate (FAR) η, which often is in the range 0.01–0.05 (1–5%).

Algorithm 2 Computation of Control Limits in Phase I for Standard Hotelling T^2 Charts

1. Consider two quality characteristics ($X_{1\mathrm{i}}$, $X_{2\mathrm{i}}$) ~ $\mathrm{N}_2((\mu_1, \mu_2), \sum)$ and the data vector (x_{1hi}, x_{2hi}), containing the observations of these two quality characteristics from an in-control process, where $h = 1,\ldots, m$ and $i = 1,\ldots, n$.
2. Obtain the maximum likelihood estimates of (μ_1, μ_2) and $\sum$ using the data of the pooled sample of size $N = m \times n$.
3. Verify the distributional assumption, as well as the presence of bivariate outliers. If the distributional assumption is verified and no bivariate outliers are detected, go to Step 4; otherwise, non-normal and/or robust control charts must be considered.
4. Calculate T^2 assuming a target (${\mu_1}^{(0)}$, ${\mu_2}^{(0)}$).
5. Obtain the LCL and UCL for the bivariate control chart of FAR η.

Now, the LCL and UCL obtained in Phase I are used to monitor the process in Phase II, that is, to observe whether the process remains in control as the data of new subgroups are obtained. In Phase II, the T^2 statistic is now denoted by T^2_{new}. Thus, we plot the sequence of values for T^2_{new} in the bivariate control chart corresponding to r subgroups generated in this phase. Next, in Algorithm 3, we indicate how the control chart based on the bivariate normal distribution is utilized to monitor the underlying process.

Algorithm 3 Process Monitoring Using the Standard Hotelling T^2 Chart in Phase II

1. Obtain the new data vector (x_{1hi}, x_{2hi}), for $h = 1,\ldots, r$ and $i = 1,\ldots, n$, but, in this case, it is not necessary that the new data are collected from an in-control process.
2. Obtain the maximum likelihood estimates of (μ_1, μ_2) and $\sum$ with the data of Step 1.
3. Compute T^2_{new} for each sample of new data generated in the hth subgroup, with $h = 1,\ldots,r$, for regular time intervals, obtaining the sequence $t^2_{\text{new}1},\ldots, t^2_{\text{new}r}$.
4. Plot the points $t^2_{\text{new}1},\ldots, t^2_{\text{new}r}$ in the bivariate control chart with LCL and UCL obtained in Phase I.
5. Establish that the process is in control if all points $t^2_{\text{new}1},\ldots,t^2_{\text{new}r}$ fall between LCL and UCL; otherwise, if any of the points $t^2_{\text{new}1},\ldots, t^2_{\text{new}r}$ falls below the LCL or above the UCL, the process is in an out-of-control condition.

Bivariate control charts under a normal distribution use mean vector and variance-covariance matrix estimates, which are sensitive to outliers in Phase I. Bivariate outliers can influence parameter estimates and cause out-of-control conditions not be detected. The identification of outliers is usually based on the Mahalanobis distance (MD. Note that the MD is useful to test goodness of fit in regression models (Marchant et al. 2016b). However, sometimes outliers do not have a large MD, which is known as masking effect (Ben-Gal 2005). This effect is because the maximum likelihood estimators of the model parameters employed to generate the MD are statistically non-robust. Masking effects occur when a group of outliers distorts the estimates of the mean vector and/or variance-covariance matrix, resulting in a small difference from the outlier to the mean. For details on the masking effect, see Marchant et al. (2018) and references therein.

3.3 *Bivariate Birnbaum-Saunders Control Charts (Phase I)*

There are many practical applications where the normality assumption is not fulfilled, because the data exhibit asymmetrical behavior or heavy tails, as in the case of environmental pollution data. In this perspective, the bivariate Birnbaum-Saunders and Birnbaum-Saunders-t distributions are a good alternative to the bivariate normal distribution. In addition, as mentioned, these distributions have attractive properties, including robustness and a theoretical justification for modeling environmental data (Leiva et al. 2015). Thus, bivariate control charts based on Birnbaum-Saunders and

Birnbaum-Saunders-t distributions can provide a useful methodology for monitoring urban environmental pollution and particularly PM2.5 and PM10. In order to present the methodology to be used, the type Hotelling chart for bivariate process control is considered under Birnbaum-Saunders and Birnbaum-Saunders-t distributions. Specifically, we assume that the vector summarizing the quality characteristics (X_{1i}, X_{2i}) follows a bivariate Birnbaum-Saunders or Birnbaum-Saunders-t distribution, for $i = 1,\ldots, n$. The observed values (data) of these characteristics are (x_{1hi}, x_{2hi}), corresponding to the ith case in the hth subgroup, for $h = 1,\ldots,m$ and $i = 1,\ldots,n$, with $m \geq 20$ and $n > 1$, as mentioned. In addition, suppose that the underlying process is in control and the vectors (X_{1i}, X_{2i}) are independent over time. Now, in practice, we work with the observations (y_{1hi}, y_{2hi}), where $y_{j\mathrm{hi}} = \log(x_{j\mathrm{hi}})$, for the hth subgroup of the random vector (Y_{1i}, Y_{2i}), which follows a bivariate log-Birnbaum-Saunders and log-Birnbaum-Saunders-t distribution, with $h = 1,\ldots,m$, $i = 1,\ldots, n$ and $j = 1, 2$. For details on the bivariate log-Birnbaum-Saunders and log-Birnbaum-Saunders-t distributions, see Marchant et al. (2016b).

Such as in (1), to monitor a bivariate process control, the following statistical hypotheses are considered:

$$H_0 : (\mu_{Y1}, \mu_{Y2}) = \left(\mu_{Y1}^{(0)}, \mu_{Y2}^{(0)}\right) \quad \text{versus} \quad H_1 : (\mu_{Y1}, \mu_{Y2}) \neq \left(\mu_{Y1}^{(0)}, \mu_{Y2}^{(0)}\right) \tag{2}$$

where $\left(\mu_{Y1}^{(0)}, \mu_{Y2}^{(0)}\right) = \left(\log\left(\beta_1^{(0)}\right), \log\left(\beta_2^{(0)}\right)\right)$ is the target mean vector of an in-control process in logarithmic scale (see details in Marchant et al. 2018), with $\beta_j^{(0)}$ being the jth element of the target median vector $\left(\beta_1^{(0)}, \beta_2^{(0)}\right)$. Note that, differently from the normal case, the distribution of the T^2 statistic adapted ($T^2{}_{\mathrm{a}}$) to the case of bivariate Birnbaum-Saunders distributions does not have a closed mathematically form. Then, we use the parametric bootstrap technique to determine its distribution (Hall 2013). After this distribution is obtained, we compute its quantiles, and then the LCL and UCL of the bivariate quality control chart used in this work are obtained in Phase I. Next, in Algorithms 4 and 5, we detail how to compute the LCL and UCL of bivariate Birnbaum-Saunders (with no outliers) and bivariate Birnbaum-Saunders-t (with outliers) control charts, respectively, with the parametric bootstrap distribution of the $T^2{}_{\mathrm{a}}$ statistic.

Algorithm 4 Computation of Bivariate Birnbaum-Saunders Control Chart Limits in Phase I

1. Consider two positive quality characteristics (X_{1i}, X_{2i}) which follow a bivariate Birnbaum-Saunders distribution and their data vector (t_{1hi}, t_{2hi}) contains the observations of these quality characteristics, where $h = 1,\ldots,m$ and $i = 1,\ldots,n$, with $m \geq 20$ subgroups of size $n > 1$ from an in-control process, as mentioned.
2. Generate the data vector (y_{1hi}, y_{2hi}) containing the logarithms of the data collected in Step 1, where (y_{1hi}, y_{2hi}) can be considered as an observation of (Y_{1i}, Y_{2i}), which follows a bivariate log-Birnbaum-Saunders distribution, with $h = 1,\ldots, m$, $i = 1,\ldots, n$ and $j = 1, 2$.

3. Obtain the maximum likelihood estimates of the corresponding parameters using the data of Step 2 with the pooled sample of size $N = m \times n$, and verify the distributional assumption. If the bivariate Birnbaum-Saunders distributional assumption is verified and no bivariate outliers are detected, go to Step 4; otherwise, non-normal and/or robust control charts must be considered, for example, as that proposed in Algorithm 5.
4. Produce a parametric bootstrap sample $((y^*_{1h1}, y^*_{2h1}),\ldots, (y^*_{1hn}, y^*_{2hn}))$ of size n from a bivariate log-Birnbaum-Saunders distribution using the maximum likelihood estimates computed in Step 3.
5. Calculate T^2_{a} with the bootstrap sample generated in Step 4, denoted by T^{2*}_{a}, assuming a target mean $\left(\mu_{Y1}^{(0)}, \mu_{Y2}^{(0)}\right)$ from the process.
6. Repeat Steps 4–5 a number B of times (for example B = 10,000) and compute B values of the bootstrap statistic of T^2_{a}, denoted by $t^{2*}_{\mathrm{a}1},\ldots, t^{2*}_{\mathrm{aB}}$.
7. Set the desired FAR η of the control chart.
8. Use the B values of the bootstrap statistic obtained in Step 6 to find out the $100 \times (\eta/2)$th and $100 \times (1 - \eta/2)$th quantiles of the distribution of T^2_{a}, which represent the LCL and UCL for the bivariate Birnbaum-Saunders control chart of FAR η, respectively.

Algorithm 5 Computation of Bivariate Birnbaum-Saunders-t Control Chart Limits in Phase I

1. Consider two positive quality characteristics $(X_{1\mathrm{i}}, X_{2\mathrm{i}})$ which follow a bivariate Birnbaum-Saunders-t distribution and their data vector (t_{1hi}, t_{2hi}) which contains the observations of these quality characteristics, where $h = 1,\ldots,m$ and $i = 1,\ldots, n$, with $m \geq 20$ subgroups of size $n > 1$ from an in-control process, as mentioned.
2. Generate the data vector (y_{1hi}, y_{2hi}) containing the logarithms of the data collected in Step 1, where (y_{1hi}, y_{2hi}) can be considered as an observation of (Y_{1i}, Y_{2i}), which follows a bivariate log-Birnbaum-Saunders-t distribution, with $h = 1,\ldots, m$, $i = 1,\ldots,n$ and $j = 1, 2$.
3. Obtain the maximum likelihood estimates of the corresponding parameters using the data of Step 2 with the pooled sample of size $N = m \times n$, and verify the distributional assumption. If the bivariate Birnbaum-Saunders-t distributional assumption is verified, go to Step 4; otherwise, another robust non-normal control charts must be considered.
4. Produce a parametric bootstrap sample $((y^*_{1h1}, y^*_{2h1}),\ldots, (y^*_{1hn}, y^*_{2hn}))$ of size n from a bivariate log-Birnbaum-Saunders-t distribution using the maximum likelihood estimates computed in Step 3.
5. Calculate T^2_{a} with the bootstrap sample generated in Step 4, denoted by T^{2*}_{a}, assuming a target mean $\left(\mu_{Y1}^{(0)}, \mu_{Y2}^{(0)}\right)$ from the process.
6. Repeat Steps 4–5 a number B of times (for example B = 10,000) and compute B values of the bootstrap statistic of T^2_{a}, denoted by $t^{2*}_{\mathrm{a}1},\ldots, t^{2*}_{\mathrm{aB}}$.
7. Set the desired FAR η of the control chart.

8. Use the B values of the bootstrap statistic obtained in Step 6 to find out the $100 \times (\eta/2)$th and $100 \times (1 - \eta/2)$th quantiles of the distribution of T^2_{a}, which represent the LCL and UCL for the bivariate Birnbaum-Saunders-t control chart of FAR η, respectively.

3.4 Bivariate Birnbaum-Saunders Control Charts (Phase II)

Note that, in Phase I, it is also necessary to verify the distribution assumption by using goodness-of-fit techniques and evaluate bivariate outliers with appropriate methods. Subsequently, the LCL and UCL of the bivariate Birnbaum-Saunders or Birnbaum-Saunders-t control charts obtained in Phase I, and summarized in Algorithms 4 and 5, are used to monitor the process in Phase II, that is, to assess whether the underlying process remains in control as the data of new subgroups are obtained. Therefore, the monitoring process using the bivariate Birnbaum-Saunders control charts is carried out in Phase II and summarized in Algorithm 6, with the adapted Hotelling statistic being denoted by T^2_{anew}.

Algorithm 6 Process Monitoring Using the Bivariate Birnbaum-Saunders and Birnbaum-Saunders-t Chart in Phase II

1. Repeat Steps 1–2 of Algorithms 4 and 5, obtaining the data vector (y_{1hi}, y_{2hi}), for $h = 1,\ldots,r$ and $i = 1,\ldots,n$, but, as mentioned, in this case, it is not necessary that the new data are collected from an in-control process.
2. Calculate the T^2_{anew} statistic for each sample of the new data obtained in Step 1, generated in the hth subgroup, with $h = 1,\ldots, r$, for regular time intervals, generating the sequence $t^2_{\mathrm{anew}1},\ldots, t^2_{\mathrm{anew}r}$.
3. Plot the points $t^2_{\mathrm{anew}1},\ldots, t^2_{\mathrm{anew}r}$ in the bivariate Birnbaum-Saunders and Birnbaum-Saunders–t control charts, with LCL and UCL obtained in Phase I.
4. Establish that the process is in control if all points $t^2_{\mathrm{anew}1},\ldots, t^2_{\mathrm{anew}r}$ fall between LCL and UCL; otherwise, if any of the points $t^2_{\mathrm{anew}1},\ldots, t^2_{\mathrm{anew}r}$ falls below the LCL or above the UCL, the process is in an out-of-control condition.

4 Case Study in Santiago of Chile

4.1 Data and Air Monitoring Stations in Santiago

We use data collected by the Chilean Metropolitan Environmental Health Service corresponding to the random variables: PM2.5 (X_1) and PM10 (X_2) concentrations, both of them measured in μg/Nm^3. These data are available at https://sinca.mma.gob.cl/ and were collected in 2015 as 1 h (hourly) average values. PM2.5 and

PM10 concentrations were observed in the monitoring stations (MS1)-(MS10) of Fig. 1. For our data analytics, we selected the MS5 station because it had high levels of pollution in the period of critical events of air quality (April 1 to August 31) in Santiago (Marchant et al. 2013). We use data of PM2.5 and PM10 concentrations from the MS5 station and denote them as "PM2015MS5." We employ the Chilean guidelines values as targets in this case study. First, we carry out a correlation analysis to detect if PM2.5 and PM10 concentrations of PM2015MS5 data are statistically associated.

4.2 Data Exploratory Analysis for PM2.5 and PM10

Figure 2 shows the scatterplot for PM2.5 and PM10 concentrations. From this figure, we detect that there is a high positive association between these concentrations being corroborated by a Pearson coefficient of correlation equal to 0.85 in MS5 station. Therefore, in order to monitor urban environmental pollution in Santiago, following the guideline of the Chilean Ministry of Health, which indicates that both PM2.5 and PM10 must be considered, we propose to use a methodology based on np and bivariate statistical control charts. This methodology allows us, on the one hand, to determine the number of times that the Chilean guidelines for PM2.5 and PM10 are exceeded each hour of the day and, on the other hand, to monitor PM10 and

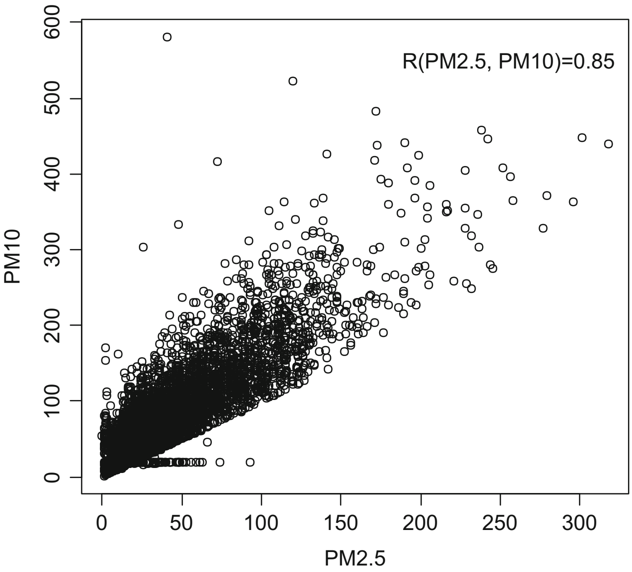


Fig. 2 Scatterplot and correlation between PM2.5 and PM10 concentrations with PM2015MS5 data

Table 1 Summary statistics for data sets in study

	Phase I		Phase II	
Statistic	PM2.5	PM10	PM2.5	PM10
n	1416	1416	744	744
Minimun	3	10	1	3
Mean	19.08	54.75	34.77	60.62
Median	18	51.5	29	47
Maximun	76	214	216	350
SD	8.68	24.13	26.33	50.15
CV	45.49%	44.06%	75.73%	82.73%
CS	1.78	1.304	2.04	1.9
CK	5.55	3.61	7.83	4.62

PM2.5 concentrations simultaneously, predicting critical periods of contamination adequately.

We use the methodology proposed in Sect. 3 to monitor PM pollution in Santiago, Chile. This methodology was implemented by the authors in a computational routine in R, a noncommercial and open-source software for statistical computing and graphs, which may be secured at no cost from http://www.r-project.org. The R software is currently very popular in the international scientific community and is one of the more used around of world. We carry out an exploratory data analysis for PM2015MS5. Table 1 provides descriptive statistics for each variable, including minimum and maximum concentrations, central tendency statistics, standard deviation (SD), and coefficients of variation (CV), skewness (CS), and kurtosis (CK). This table shows empirical distributions with positive skewness, different degrees of kurtosis, and a considerable amount of concentrations that exceed the Chilean guidelines for PM2.5 and PM10, that is, 50 μg/Nm^3 and 150 μg/Nm^3, respectively. Note that the exploratory analysis for each variable indicates marginal Birnbaum-Saunders or Birnbaum-Saunders-t distributions that seem to be good candidates for describing PM2015MS5 data.

4.3 *Univariate and Bivariate Control Charts*

To calculate the control limits in Phase I, we utilize data for the months of January and February of 2019 with $k = 59$, $n = 24$, $N = 1416$, B = 10,000 (bootstrap replications) and FAR $\eta = 0.0027$. We use these months since their air quality is stable (i.e., assumed as an in-control process), because the meteorological and topographical conditions favor no saturation of PM concentrations. We consider the degrees of freedom parameter $v = 4$ for the Birnbaum-Saunders-t distribution according to the robustness aspects mentioned in Marchant et al. (2016a). Note that this parameter v allows us accommodate outliers suitably.

Figure 3a, b displays the theoretical probability versus empirical probability (PP) plots with acceptance bands for a significance level of 1% in MS5 station

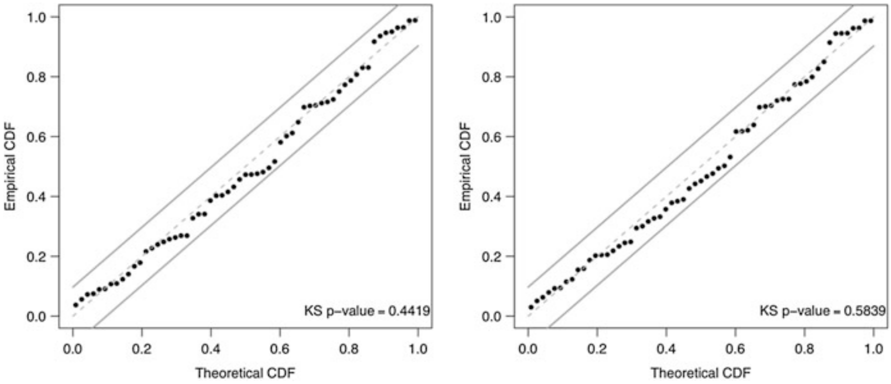


Fig. 3 PP plots in Phase I for bivariate Birnbaum-Saunders (left) and Birnbaum-Saunders-t (right) distributions with PM2015MS5 data

based on bivariate Birnbaum-Saunders and bivariate Birnbaum-Saunders-t distributions, respectively. From this figure, we confirm the good fit of the bivariate Birnbaum-Saunders and bivariate Birnbaum-Saunders-t distributions to the data in Phase I, which is supported by the p-values 0.4419 and 0.5839, respectively, of the Kolmogorov-Smirnov (KS) test associated with these PP plots (Marchant et al. 2016a). To monitor air quality of August 2015 in Phase II, we employ bivariate Birnbaum-Saunders and np univariate Birnbaum-Saunders charts. For bivariate Birnbaum-Saunders-t charts, we use the LCL and UCL obtained in Phase I summarized in Algorithm 5. For the control chart of this month, the number of subgroups and the subgroup size are $r = 31$ days and $n = 24$ h, respectively, giving a total of 744 observations. Furthermore, we use the transformed MD with the Wilson-Hilferty approximation to obtain a normal distribution and then to assess the fit of the most appropriate distribution to these data. For details about the Wilson-Hilferty approximation, see Marchant et al. (2016a, b).

Figure 4a, b displays the PP plots with acceptance bands for a significance level of 1% in MS5 station based on bivariate Birnbaum-Saunders and Birnbaum-Saunders-t distributions, respectively. From this figure, the Birnbaum-Saunders-t distribution has a better fit than the Birnbaum-Saunders distribution to the data in Phase II, which is supported by the p-values 0.609 and 0.3091, respectively, of the KS test associated with these PP plots (Marchant et al. 2016a). Due to such a situation, we continue this study only with the Birnbaum-Saunders-t distribution because of its robust estimation of parameters and the good fit to these data.

Figure 5 shows the bivariate Birnbaum-Saunders-t control chart for PM2015MS5 data. From this figure, it is possible to observe that there are no out-of-control episodes during this month, when considering the joint behavior of PM2.5 and PM10 concentrations. This type of chart is appropriate when there is a high correlation between the concentrations of PM2.5 and PM10 such as in our case; see Fig. 2. In addition, to monitor the number of times that the Chilean guidelines for PM2.5 and PM10 are exceeded each hour of the day of August-2015 in Phase II, we employ

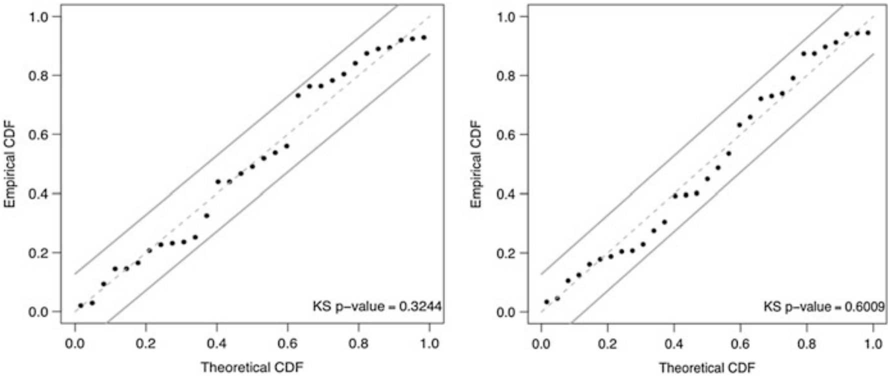
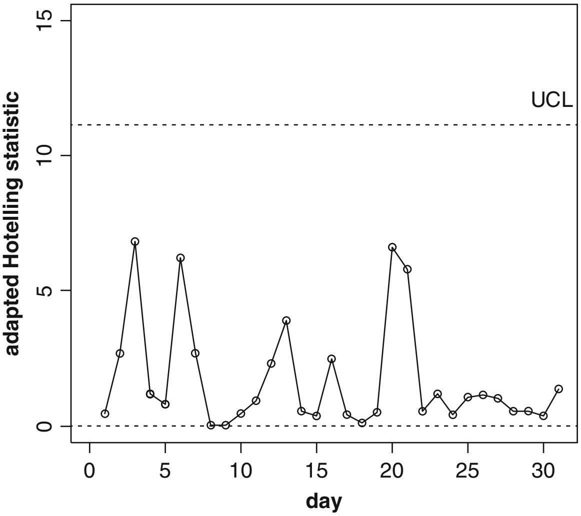


Fig. 4 PP plots in Phase II for bivariate Birnbaum-Saunders (left) and Birnbaum-Saunders-t (right) distributions with PM2015MS5 data

Fig. 5 Bivariate Birnbaum-Saunders-t chart for August 2015 with PM2015MS5 data



the univariate Birnbaum-Saunders np-chart. For the univariate chart of this month, the number of subgroups and the subgroup size are the same as for the bivariate chart.

Figure 6a, b shows the np Birnbaum-Saunders control charts for PM2.5 and PM10 concentrations, respectively. From this figure, it is possible to observe that the concentrations of PM2.5 exceed the Chilean guidelines much more than those of PM10. This occurs specifically in the first days of the month of August, where the Chilean guidelines are exceeded more than 15 times during a day, considering a maximum of 24 observations each day. Such a situation is highly detrimental to health as consequence of breathing air with high concentrations of PM, especially PM2.5, as mentioned in Sects. 1 and 2.

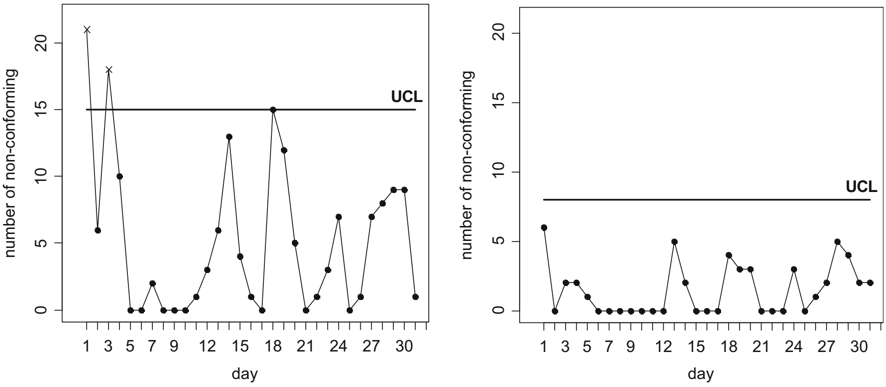


Fig. 6 np Birnbaum-Saunders chart for August 2015 for PM2.5 (left) and PM10 (right) concentrations with PM2015MS5 data

4.4 Big Data, Analytics Results, and Its Connection to Data-Driven Decision-Making

Current technologies, such as computer-based transactions, digital instruments, and sensors, allow us to generate large-scale data from different processes. These data may be collected efficiently, rapidly, and automatically and are frequently available online for decision-makers and analysts access. This is known as big data, a term often employed to describe large, diverse, and complex (structured and non-structured) data sets, which have high volume, variety, and velocity in their generation, otherwise known as the 3Vs (Baesen 2014; Dietrich 2015). Such a situation results in enormous opportunities for data-based knowledge discovery, and it is expected that the importance of data science will continue to increase in the future, becoming relevant for researchers in diverse areas who will be ready to exploit new opportunities for data-driven decision-making. In this new big data era, many methodologies need to be updated, as, for example, control charts (Aykroyd et al. 2019), where big data sources are providing new avenues for such charts because of continuous monitoring in diverse fields.

Control charts have primarily been used to monitor industry processes (Montgomery 2009), but recently, these methodologies are also being used to monitor service processes, such as banking and finance, distribution of electrical energy, public transportation, and retail (Aykroyd et al. 2019). Furthermore, control charts have also been used in education, government policies, healthcare, and marketing. The use of control charts in environmental monitoring processes is currently limited, but we expect it may become a popular alternative in the big data era.

The data-driven methodology proposed in this paper, based on tools of control charts for environmental monitoring, shows a good performance when assessing air quality, particularly when two correlated statistically variables are considered. The analytics results obtained with our methodology are consistent with the official information of the Chilean Ministry of the Environment for PM10 (https://bit.ly/2W2jb1V). Specifically, there is an agreement between the critical episodes empirically detected with our methodology based on the robust bivariate Birnbaum-Saunders control chart and those verified by the Chilean Health Authority, that is, if our methodology were used, the same environmental decision made by the authority would be established. Note that joint analysis of PM10 and PM2.5 concentrations permits us to monitor air quality using one model, instead of employing two models as currently applied to perform this monitoring. With the current model, the interaction and/or dependence of the PM10 and PM2.5 is not considered. In addition, this data science tool helps to prevent and/or adequately alert the population about possible critical episodes of air contamination, providing support to regulatory decision-making when appropriate mitigation measures are needed, such as the prohibition of outdoor physical activities or domestic coal or firewood burning or restrictions on the use of internal combustion vehicles.

5 Summary

Airborne particulate matter pollution is a serious environmental problem. We propose that monitoring of air quality may be achieved by employing data analytics to generate information within the context of data-driven decision making to prevent and/or adequately alert the population about possible critical episodes of air contamination. In this paper, we propose a methodology for monitoring particulate matter pollution in Santiago of Chile, based on bivariate quality control charts and an asymmetric distribution. A case study with real particulate matter pollution from Santiago is provided, which shows that the methodology is suitable to alert early episodes of extreme air pollution. The results are in agreement with the critical episodes reported with the current model used by the Chilean health authority.

6 Conclusions

In this work, we have proposed and implemented a methodology based on bivariate control charts with heavy-tailed asymmetric distributions. These distributions have a theoretical support and can be applied to atmospheric environmental data. This methodology is useful for monitoring environmental risk when the particulate matter concentrations follows bivariate Birnbaum-Saunders or Birnbaum-Saunders-Student-t distributions. We have illustrated the proposed methodology with a case study of real-world data of air quality in Santiago, Chile. This case study has shown that the new methodology is useful for alerting episodes of extreme urban environmental pollution, allowing us to prevent adverse effects on human health for the population of Santiago. We have empirically demonstrated an agreement between our methodology and real-world situations, as when the Chilean health authority detected environmental critical episodes and dictated environmental alert, pre-emergency, and emergency in Santiago, Chile.

The random variables to be modeled, related to PM2.5 and PM10 concentrations, correspond to an aggregation of a great amount of compounds, which are adsorbed on a solid or liquid surface in the atmosphere. Depending on the diverse composition of these particles, they can show different reactivity and balance between their degradation and production processes. Sometimes these particles show seasonal time dependence, or if the sources vary, their concentration may also vary, such as when drastic measures are taken to reduce their emissions. Therefore, a limitation of this study is not considering time series components in the modeling, which is an open problem to be conducted in future research (Decanini and Volta 2003; Querol et al. 2004; Kessler et al. 2010). Regarding this, we must mention that PM2.5 and PM10 levels are considered simple dilutions and concentrations in the air masses, without taking into account factors such as composition, chemical reactivity, production-degradation equilibrium, and evolution over time of these quantities. In particular, the chemical reactivity of these compounds obeys to different kinetic processes of formation and degradation, described in detail by Sander et al. (2006). Thus, this last aspect is also an open issue to be considered in a future study.

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Statement of Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

Adams K, Greenbaum DS, Shaikh R, van Erp AM, Russell AG (2015) Particulate matter components, sources, and health: systematic approaches to testing effects. J Air Waste Manag Assoc 65:544–558

Aitchison J, Brown JAC (1973) The lognormal distribution. Cambridge University Press, London

Athayde E, Azevedo A, Barros M, Leiva V (2019) Failure rate of Birnbaum-Saunders distributions: shape, change-point, estimation and robustness. Braz J Probab Stat 33:301–328

Aykroyd RG, Leiva V, Ruggeri F (2019) Recent developments of control charts, identification of big data sources and future trends of current research. Technol Forecast Soc Change 144:221–232

Baesen B (2014) Analytics in a big data world: the essential guide to data science and its applications. Wiley, New York

Ben-Gal I (2005) Outlier detection. In: Maimon O, Rockach L (eds) Data mining and knowledge discovery handbook. Springer, Boston, pp 321–352

Cakmak S, Dales RE, Gultekin T, Vidal CB, Farnendaz M, Rubio MA, Oyola P (2009) Components of particulate air pollution and emergency department visits in Chile. Arch Environ Occup Health 64:148–155

Cifuentes LA, Vega J, Köpfer K, Lave LB (2000) Effect of the fine fraction of particulate matter versus the coarse mass and other pollutants on daily mortality in Santiago, Chile. J Air Waste Manag Assoc 50:1287–1298

CONAMA (1998) Establishment of primary quality guideline for PM10 that regulates environmental alerts. Technical Report Decree 59, Ministry of Environment (CONAMA) of the Chilean Government, Santiago, Chile

Decanini E, Volta M (2003) Application to Northern Italy of a new modelling system for air quality planning: a comparison between different chemical mechanisms. Int J Environ Pollut 20:85–95

Díaz-García JA, Leiva V (2005) A new family of life distributions based on elliptically contoured distributions. J Stat Plan Inference 128:445–457

Dietrich D (2015) Data science and big data analytics: discovering, analyzing, visualizing and presenting data. Wiley, New York

Falcon-Rodriguez CI, Osornio-Vargas AR, Sada-Ovalle I, Segura-Medina P (2016) Aeroparticles, composition, and lung diseases. Front Immunol 7:1–9

Ferreira M, Gomes MI, Leiva V (2012) On an extreme value version of the Birnbaum-Saunders distribution. Rev Stat J 10:181–210

Franck U, Leitte AM, Suppan P (2014) Multiple exposures to airborne pollutants and hospital admissions due to diseases of the circulatory system in Santiago de Chile. Sci Total Environ 15:746–756

Franck U, Leitte AM, Suppan P (2015) Multifactorial airborne exposures and respiratory hospital admissions – the example of Santiago de Chile. Sci Total Environ 502:114–121

Hall P (2013) The bootstrap and edge worth expansion. Springer, New York

Henríquez G, Urrea C (2017) Association between air pollution and emergency consultations for respiratory diseases. Rev Med Chil 145:1371–1377

Hime NJ, Marks GB, Cowie CT (2018) A comparison of the health effects of ambient particulate matter air pollution from five emission sources. Int J Environ Res Public Health 15:1206

Ilabaca M, Olaeta I, Campos E, Villaire J, Tellez-Rojo M, Romieu I (1999) Association between levels of fine particulate and emergency visits for pneumonia and other respiratory illnesses among children in Santiago, Chile. J Air Waste Manag Assoc 49:154–163

International Agency on Cancer Research (2016) Outdoor air pollution. IARC monographs on the evaluation of carcinogenic risks to humans, vol 109, Lyon, France

Jackson J (1985) Multivariate quality control. Comm Stat Theor Meth 14:2657–2688

Kessler SH, Smith JD, Che DL, Worsnop DR, Wilson KR, Kroll JH (2010) Chemical sinks of organic aerosol: kinetics and products of the heterogeneous oxidation of erythritol and levoglucosan. Environ Sci Technol 44:7005–7010

Kim KH, Kabir E, Kabir S (2015) A review on the human health impact of airborne particulate matter. Environ Int 74:136–143

Kinney PL (2008) Climate change, air quality, and human health. Am J Prev Med 35:459–467

Leiva V (2016) The Birnbaum-Saunders distribution. Academic Press, New York

Leiva V, Barros M, Paula GA, Sanhueza A (2008) Generalized Birnbaum-Saunders distribution applied to air pollutant concentration. Environmetrics 19:235–249

Leiva V, Marchant C, Ruggeri F, Saulo H (2015) A criterion for environmental assessment using Birnbaum-Saunders attribute control charts. Environmetrics 26:463–476

Logan WP (1953) Mortality in the London fog incident, 1952. Lancet 1:336–338

Lowry CA, Montgomery DC (1995) A review of multivariate control charts. IEE Trans 27:800–806

Marchant C, Leiva V, Cavieres M, Sanhueza A (2013) Air contaminant statistical distributions with application to PM10 in Santiago, Chile. Rev Environ Contam Toxicol 223:1–31

Marchant C, Leiva V, Cysneiros FJA (2016a) A multivariate log-linear model for Birnbaum-Saunders distributions. IEEE Trans Reliab 65:816–827

Marchant C, Leiva V, Cysneiros FJA, Vivanco JF (2016b) Diagnostics in multivariate generalized Birnbaum-Saunders regression models. J Appl Stat 43:2829–2849

Marchant C, Leiva V, Cysneiros FJA, Liu S (2018) Robust multivariate control charts based on Birnbaum-Saunders distributions. J Stat Comput Sim 88:182–202

Marchant C, Leiva V, Christakos G, Cavieres MF (2019) Monitoring urban environmental pollution by bivariate control charts: New methodology and case study in Santiago, Chile. Environmetrics 30:e2551

Matus CP, Oyarzún GM (2019) Impact of particulate matter (PM 2.5) and children's hospitalizations for respiratory diseases. A case cross-over study. Rev Chil Pediatr 90:166–174

Mendoza Y, Loyola R, Aguilar A, Escalante R (2019) Valuation of air quality in Chile: the life satisfaction approach. Soc Indic Res:1–21

MMA (2011) Establishment of primary quality guideline for inhalable fine particulate matter PM2.5. Technical Report Decree 12, Ministry of Environment (MMA) of the Chilean Government, Santiago, Chile

Montgomery DC (2009) Introduction to statistical quality control. Wiley, New York

Morales RGE, Llanos A, Merino M, Gonzalez-Rojas CH (2012) A semi-empirical method of PM10 atmospheric pollution forecast at Santiago de Chile city. NEPT 11:181–186

Ostro BD (2003) Air pollution and its impacts on health in Santiago, Chile. In: McGranahan G, Murray F (eds) Air pollution and health in rapidly developing countries, vol 189. Earthscan, London

Ott WR (1990) A physical explanation of the lognormality of pollution concentrations. J Air Waste Manag Assoc 40:1378–1383

Perez-Padilla R, Menezes AMB (2019) Chronic obstructive pulmonary disease in Latin America. Ann Glob Health 85:7

Préndez M, Alvarado G, Serey I (2011) Some guidelines to improve the air quality management of Santiago, Chile. In: Air quality monitoring, assessment and management. IntechOpen, London

Querol X, Alastuey A, Viana MM, Rodriguez S, Artiñano B, Salvador P, Garcia do Santos S, Fernandez Patier R, Ruiz CR, de la Rosae J, Sanchez de la Campa A, Menendez M, Gil JI (2004) Speciation and origin of PM10 and PM2. 5 in Spain. J Aerosol Sci 35:1151–1172

Requia WJ, Adams MD, Arain A, Papatheodorou S, Koutrakis P, Mahmoud M (2018) Global association of air pollution and cardiorespiratory diseases: a systematic review, meta-analysis, and investigation of modifier variables. Am J Public Health 108:S123–S130

Romieu I, Gouveia N, Cifuentes LA, de Leon AP, Junger W, Vera J, Strappa V, Hurtado-Díaz M, Miranda-Soberanis V, Rojas-Bracho L, Carbajal-Arroyo L, Tzintzun-Cervantes G, HEI Health Review Committee (2012) Multicity study of air pollution and mortality in Latin America (the ESCALA study). Res Rep Health Eff 171:5–86

Sander SP, Golden DM, Kurylo MJ et al (2006) Chemical kinetics and photochemical data for use in atmospheric studies evaluation number 15. Technical Report JPL Publication 06-2, Jet Propulsion Laboratory, NASA, Pasadena, CA

Santos-Neto M, Cysneiros FJA, Leiva V, Barros M (2014) On a reparameterized Birnbaum-Saunders distribution and its moments, estimation and applications. REVSTAT Stat J 12:247–272

Thompson JE (2018) Airborne particulate matter: human exposure and health effects. Int J Occup Environ Med 60:392–423

Toro R, Kvakić M, Klaić ZV, Koračin D, Morales RG, Leiva MA (2019) Exploring atmospheric stagnation during a severe particulate matter air pollution episode over complex terrain in Santiago, Chile. Environ Pollut 244:705–714

Vilca F, Sanhueza A, Leiva V, Christakos G (2010) An extended Birnbaum-Saunders model and its application in the study of environmental quality in Santiago, Chile. Stoch Environ Res Risk Assess 24:771–782

Villalobos AM, Barraza F, Jorquera H, Schauer JJ (2015) Chemical speciation and source apportionment of fine particulate matter in Santiago, Chile, 2013. Sci Total Environ 512:133–142

WHO (2000) Air quality guidelines for Europe. Chapter 7.3 Particulate matter. World Health Organization, Regional Office for Europe, Copenhagen

WHO (2013) Health effects of particulate matter. Technical report, World Health Organization, Regional Office for Europe, Copenhagen

Wu W, Jin Y, Carlsten C (2018) Inflammatory health effects of indoor and outdoor particulate matter. J Allergy Clin Immunol 14:833–844

Sulfur or Pollen? Chemical, Biological, and Toxicological Basis for the Correct Risk Communication of Urban Yellow Dust Deposition

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1 Introduction

Atmospheric pollution is the lasting presence in the air of chemical substances at concentrations above their natural levels, which could potentially lead to adverse effects. One of its sources is anthropogenic activities, including industrial generation of volatile compounds that are emitted into the air. The World Health Organization (WHO) has labelled air pollution as the "silent killer" as it estimates that 4.2 million deaths every year are a result of poor air quality (https://www.who.int/airpollution/en/). People are very aware of risks imposed to their health by breathing polluted air, especially those that live in or around industrial areas. In many parts of the world, lack of updated air quality guidelines and/or poor industry compliance with existing guidelines may lead to peak concentrations of contaminants in air, inducing acute events of respiratory and cardiovascular diseases in exposed populations (Logan 1953; Franck et al. 2014, 2015; Pothirat et al. 2019), further enhancing risk perception of toxicity linked to contaminated air exposure.

During the flowering seasons of various wind-pollinated species (e.g., various tree species in spring time, grasses in summer, and Cedrus even in autumn), people may notice yellow dust deposited on streets, roofs, and other surfaces. Very often, the yellow deposits appear as fine dust easily blown over by wind, or, if enough humidity is present, such as mist or rain, the deposits may acquire an oily, water-insoluble, paste-like fluid appearance (Fig. 1), even forming a film on the surface of

Fig. 1 Appearance of the yellow dust deposition in water bodies around the city of Valparaíso, Chile. It is actually *Acacia dealbata* pollen which is seen in full bloom in both pictures. Images taken by Rodrigo Silva-Haun on August, 2019

water flows such as creeks, rivers, or lakes. If this phenomenon happens in areas with industrial activity, people may think the yellow dust is sulfur. However, sulfur compounds produced during combustion of fossil fuels are usually emitted into the air as sulfides or oxides, and it is chemically impossible for these compounds to become solid sulfur under environmental conditions. In reality, the yellow dust is pollen.

Over 100 years ago, scientists communicated this misunderstanding in nature, after events occurring simultaneously in England, Scotland, and the United States (Carpenter 1879; Wilson 1879), and an even earlier letter was published in 1847 about events in Canada and other parts of the world (Croft 1847–1848). Recently, we had such an event in Central Chile, which, due to lack of scientifically correct communication, led to intense debate in communities, media, and even authorities. Based on simple observations, it is virtually impossible to differentiate sulfur from pollen, so we suggest risk communicators have to be aware of their chemical, biological, and toxicological differences. No recent reviews about the distinctions of sulfur and pollen are found in the literature, so here we review chemical, biological, and toxicological aspects of sulfur and pollen in order to provide a scientific basis for risk communication.

2 Sulfur

2.1 Sulfur Properties

Elemental sulfur (Fig. 2) is a relatively nontoxic and chemically inert substance, insoluble in water and most other liquids, but soluble in carbon disulfide and other nonpolar organic solvents, such as benzene and toluene. Is a crystalline solid at room temperature and reacts with all elements except for gold, platinum, iridium, nitrogen, tellurium, iodine, and the noble gases (Wiberg and Wiberg 2001). It forms cyclic octatomic molecules, which usually occurs in the form of eight-membered rings and is denominated with the chemical formula S_8 (Mokhatab et al. 2018). Octasulfur is a soft, bright-yellow solid with only a faint odor, similar to that of matches. Sulfur forms over 30 solid allotropes, more than any other element (Steudel and Eckert 2003). Several other rings are known; however, S_8 is the most stable (Steudel 1982). For example, removing one atom from the crown of the S_8 structure produces a compound with chemical formula S_7, which is more deeply yellow than S_8. In this context, an analysis by high-pressure liquid chromatography (HPLC) of elemental sulfur reveals an equilibrium mixture of mainly structure type S_8 with small amounts of structures type S_7 and S_6 (Tebbe et al. 1982).

The main crystalline types are rhombic and monocyclic, and these two forms differ in the way in which the rings are stacked (Greenwood and Earnshaw 1997). Rhombic sulfur is the most stable form of the element at room temperature, but if heated to about 95°C, it changes into monocyclic crystals. During this slow transition, the solid shrinks and cracks, making it rather friable (Greenwood and Earnshaw

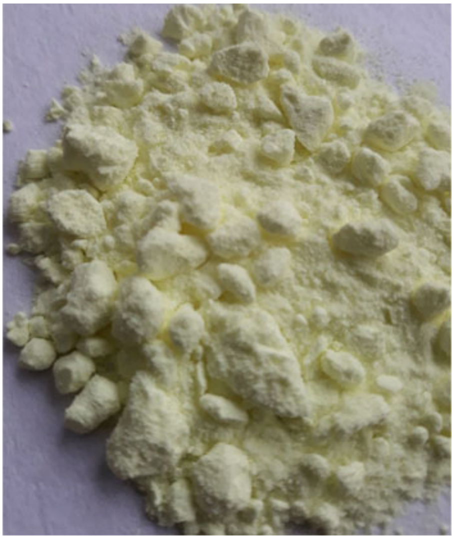

Fig. 2 Elemental sulfur

1997). Elemental sulfur occurs naturally as the element (native sulfur) but most commonly occurs in combined forms as sulfide and sulfate minerals, which can be found near hot springs and volcanic regions in many parts of the world, especially along the Pacific Ring of Fire (Rickwood 1981; Klein and Hurlbut 1985).

At any given time, most of the sulfur is found in the lithosphere, although the atmosphere, hydrosphere, and biosphere are the systems where most transfer of sulfur takes place (Charlson and Anderson 1992). In the lithosphere, sulfur occurs abundantly throughout the earth's crust at an average concentration of about 0.1% (Brown 1982) mainly in volcanic sites, salt domes, petroleum, natural gas, and fossil products.

2.2 *Sulfur Cycle*

The sulfur cycle transfers enormous amounts of this biologically important element through the atmosphere every year. Biogeochemical and geochemical processes occurring in soils, sediments, and water play a vital role in the natural circulation of sulfur between the oceans and landmasses, via the atmosphere and in rivers (Brown 1982). These processes control the rate at which the element is locked up in insoluble forms such as pyrite and organic sulfur or mobilized as soluble sulfate or volatile hydrogen sulfide (H_2S) or organic sulfides.

In general, the sulfur cycle begins with the erosion of sulfate (evaporites) and sulfide containing rocks and minerals (Aneja and Cooper 1989; Moreno et al. 2009; Brimblecombe 2013). This is a process that releases stored sulfur into the air where it becomes sulfate (SO_4^{-2}) which is taken up by plants and microorganisms that convert it into organosulfur compounds. Plants and animals consume the organic sulfur moving this element up through the food chain. As plants and organisms die, some of the sulfur is released back into the environment as sulfate. On the other hand, the breakdown of vegetation in swamps and tidal flats releases hydrogen sulfide (H_2S) gas into the environment, which later converts back to sulfate in aqueous environments (Luo 2018). The other major natural contributors to the sulfur budget in the environment are volcanoes. Their fumarolic activity introduces SO_x (SO_2, SO_3) and hydrogen sulfide gases to the atmosphere, which eventually convert to sulfate ions in water and precipitate as alkali sulfate salts.

The amount of sulfur in the atmosphere at any given time is small, even though the fluxes are large, because the lifetime of most sulfur compounds in air is relatively short (e.g., days). Sulfur in the ocean is cycled much more slowly, and the primary interactions in that cycle are with the solid earth. However, because of the presence of sulfur in fossil fuels and in metal sulfide deposits, environmental contamination by sulfur compounds has increased with the use by man of these raw materials.

2.3 *Main Sulfur Oxidation States*

Sulfur has an atomic number of 16, an atomic mass of 32, 4 oxidation states (−2, +2, +4 and +6), and 4 naturally occurring isotopes ($_{32}S$, $_{33}S$, $_{34}S$ and $_{36}S$), of which $_{32}S$ is most abundant at 95% of the mass (Canfield 2001). Sulfur primarily occurs in four oxidation states in geological environments: S^{-2} (sulfides, sulfosalts, natural gas), S^0 (elemental sulfur), S^{+4} (SO_2 in volcanic gas), and S^{+6} (SO_3 in volcanic gas) (Schippers 2004).

2.3.1 Sulfides and Hydrogen Sulfide

Sulfides

Sulfides include three classes of compounds, inorganic sulfides, organic sulfides (sometimes called thioethers), and phosphine sulfides. Among them, the inorganic sulfides are ionic compounds containing the negatively charged sulfide ion, S^{-2}, which may be regarded as salts of the very weak acid hydrogen sulfide (H_2S). Organic sulfides are compounds in which a sulfur atom is covalently bonded to two organic groups, and the phosphine sulfides are formed from the reaction of organic phosphines with sulfur, in which the sulfur atom is linked to the phosphorus by a bond that has both covalent and ionic properties (Luther et al. 1986).

Sulfides are characterized by a very unpleasant odor, and they constitute a serious threat to the equilibrium of the entire ecosystem, mostly due to their acidic properties. Thus, sulfides cause surface water acidification, negatively affecting the fauna and flora. They are also responsible for the corrosion of metal and concrete elements and the substantial depletion of water oxygenation, causing irreversible environmental damages (Gagol et al. 2019).

Sulfides minerals are very important as they concentrate a wide range of metals as mineable deposits. Several hundred sulfides minerals are known, but only few are sufficiently abundant to have been categorized as rock forming (Bowles et al. 2011) which includes pyrite (iron sulfide), pyrrhotite (iron sulfide), galena (lead sulfide), sphalerite (zinc sulfide), and chalcopyrite (cupper and iron sulfide). The industry of these minerals is responsible for the concentration of a wide range of metals, which are also potential sources of pollution of air, surface waters, or soils.

Water contamination can arise from several sources of the sulfide mining industry, for example, the removal of earth and vegetation at the mining site causes erosion and sedimentation (US Environmental Protection Agency 2004). The erosion or blowing of tailings can also be a source of toxic sedimentation or even other waste materials such as leaching chemicals (which are toxic) or other processing chemicals of this industry (Ochieng et al. 2010; Ninga et al. 2011; Gyamfia et al. 2019).

The acid mine drainage process may cause soils near mine site or within the mine pit to become acidic (Bohan et al. 2005). Additionally, sediments downstream of mine sites often contain high levels of heavy metals. In the case of air pollution resulting from sulfide mining, these can include dust emissions from mine pits, dried tailings, haul roads, and in some cases the sulfur dioxide emissions from stacks at smelters (Aboka et al. 2018).

Hydrogen Sulfide

Hydrogen sulfide is a pollutant that is commonly regarded as toxic and to low concentrations is easily recognizable by its characteristic foul odor much like rotten eggs (Bhomick and Rao 2014). Approximately 90% of hydrogen sulfide present in air comes from decomposition of dead plants and animals, especially when this occurs in wet conditions with limited oxygen, such as swamps (US Environmental Protection Agency 1993). Hot springs, volcanoes, and other geothermal sources also emit H_2S. The hydrogen sulfide remains in the atmosphere for approximately 1 day in the summer and 42 days in winter and is then converted to sulfur dioxide and sulfuric acid in a hydroxyl radical catalyzed reaction (Bottenheim and Strausz 1980).

On the other hand, anthropogenic releases of H_2S into the air result from industrial processes, primarily from the extraction and refining of oil and natural gas, geothermal power plants, coke ovens, food processing facilities, tanneries, and pulp or paper. While H_2S is primarily released in the gaseous form, it can also be found in liquid waste related to industrialization (Maebashi 2011). Petroleum oil and natural gas are the products of thermal conversion of decayed organic matter (called kerogen) that is trapped in sedimentary rocks. High-sulfur kerogens release hydrogen sulfide during decomposition, and this H_2S stays trapped in the oil and gas deposits. On this matter, between 15% and 25% of natural gas in the United States

$$H_2S_{(g)} + \frac{1}{2}O_{2(g)} \Rightarrow SO_{2(g)} + H_2O_{(g)} \text{ Thermal Stage } [1223 - 1623\ \mathrm{K}]$$

$$SO_{2(g)} + 2H_2S_{(g)} \Leftrightarrow 3S_{(g)} + H_2O_{(g)} \text{ Thermal and Catalytic Stage } [473 - 573\ \mathrm{K}]$$

Fig. 3 The Claus process which uses the reaction between hydrogen sulfide and sulfur dioxide to yield elemental sulfur and water vapor

may contain hydrogen sulfide, while worldwide, the figure could be as high as 30% (Dalrymple et al. 1991).

For commercial purposes, H_2S is used to produce sulfur through the Claus process (Fig. 3), using the reaction between hydrogen sulfide and sulfur dioxide (produced in the Claus process furnace from the combustion of H_2S with oxygen or air/oxygen) yielding elemental sulfur and water vapor (Sassi and Gupta 2008; Zarei 2018) and, subsequently, sulfuric acid (H_2SO_4) by the contact process (King et al. 2013).

2.4 *Sulfates*

Sulfur enters the atmosphere principally as sulfur dioxide (SO_2), an air pollutant with a lifetime of about 1–2 days, before it is normally deposited or oxidized into sulfate (SO^{-4}). After oxidation, lifetime increases to 3 or more days, depending on the state of the atmosphere and the injection height. Because of its longer lifetime, sulfate can be spread over greater distances (Giannoni et al. 2014).

Sulfate is especially a problem where acidic soils and mine tailings are periodically affected by drought and rain and in places where sulfuric acid is used to process the ore and mineral concentrates. Sulfate may enter to the surface and groundwater through industrial sources as the discharge or disposal of sulfate-containing tailings or seepage from acidic tailings ponds (Bussière et al. 2004; Geurts et al. 2009). In this context, the irrigation water containing high concentrations of sulfate could generate white nontoxic stains on the leaves and fruits of trees (Little et al. 2000).

2.5 *Sulfur Oxides*

Around 75% of the sulfur emitted into the atmosphere is related to the use of fossil fuels and activities of the metallurgical industry. It has been estimated that during combustion processes, approximately 90% of the sulfur contained in petroleum and its derivatives is emitted into the atmosphere in the form of sulfur dioxide (SO_2) (Monticello 2000). These fuels are mainly used in motor vehicles and thermoelectric plants, and the annual release into the atmosphere of SO_2 has been estimated to be approximately 2 tons (Doney et al. 2007).

SO_2 produced from the combustion of oil is transformed into SO_3 by the action of sunlight, and in the presence of air, humidity generates sulfuric acid (H_2SO_4) (Huang et al. 2019). This compound generates a rain of acidic pH which enters the “water cycle,” depresses the pH of the lakes with low buffer capacity, and endangers the marine life (US Environmental Protection Agency 2004). It can be transferred to soil, damage the foliage, and affect flora and fauna. As air streams transport SO_2, it can be produced in one area and show its adverse impacts in another remote place thousands of kilometers away from where it was produced. SO_2 also causes corrosion of building materials, pipes, and circuits, but the greatest deterioration is that which occurs in historical monuments (Xie et al. 2004), mainly those made of limestone and marble. This bears not only a high economic cost to society but also a huge loss in cultural heritage (Soleimani et al. 2007).

3 Pollen

Pollen grains represent the highly reduced haploid male gametophyte generation in flowering plants, consisting of just two or three cells inside individual pollen grains when released from the anthers (Borg et al. 2009).

3.1 Biology of Pollen

Pollen grain consists of two cells: the vegetative and the generative cell. Ultimately the generative cell forms two sperm cells or male gametes (Fig. 4). The mature pollen wall of gymnosperms and angiosperms consists in principle of two fundamentally different layers, the complex, thick, sporopolleninous exine and the homogeneous, thin, single-layered pectocellulosic intine (Pacini and Hesse 2012). The size and morphology of the pollen grains vary according to species, genus, or family. In most species, the length of the polar axis, the equatorial axis, and tetrad diameter

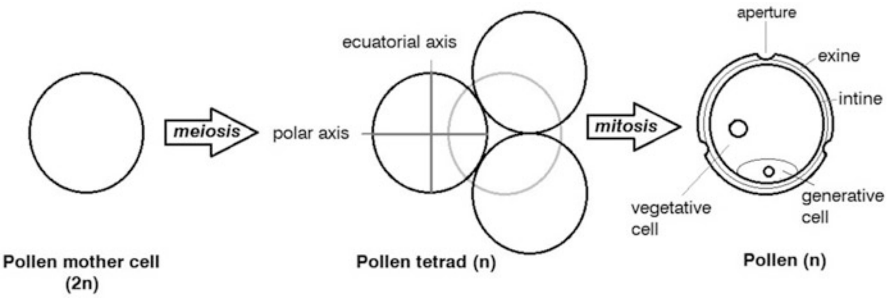

Fig. 4 Pollen development and nomenclature

vary according to species (Fig. 4). In most species the pollen wall is interrupted by apertures, which are areas generally characterized by a thinning of the exine and a thickening of the intine (Albert et al. 2010) (Fig. 4). Mature pollen is shed in dispersal units. When the postmeiotic products become separated, the dispersal unit is a single pollen grain, a monad, which can also become partly separated or remain permanently united, resulting in dyads, tetrads, or polyads (Halbritter et al. 2018).

3.2 Pollen Release

Pollination describes the process of transferring pollen grains from the male anther of one flower to the female stigma of a different flower. Once in contact, pollen develops a pollen tube that acts as a passageway for the sperm into the ovary. Thus, the ovule is fertilized as the first step for seed production (Pacini 2008).

For pollination to occur, pollen needs to be released from the anthers and then dispersed by rain, air currents, and insects. For many tree species, such as pine trees, this process results in the liberation of thousands of pollen cells at a time, creating a mist or cloud that can easily be seen with the naked eye (Fig. 5). Plants have developed strategies for their pollen to successfully reach female flowers. For instance, pollen from certain pine trees has an air sac, which renders pollen very light and easy to be carried by the wind (Jones and Harrison 2004). Wind pollination is very unpredictable, and there is a clear tendency for wind-pollinated species to produce much more pollen than species relying on insect pollination (Moore et al. 1991). Therefore yellow dust often will consist of pollen produced by wind-pollinated species.

Fig. 5 Pollen release from a pine tree. Photograph by Jon Houseman, distributed under a CC-AS 4.0 license

Meteorological factors affect both pollen release and dispersal and pollination. Those factors that modulate release and dispersal may also be determining the amount of pollen that reaches urban surfaces. For instance, high temperature damages flowers and pollen, while low temperature may slow pollen release; rain and mist purge pollen from air, especially at low temperature; air currents and wind disperse pollen and facilitate flower opening and anther dehydration which is necessary for pollen release; and atmospheric pressure facilitating ascending air currents favors long distance dispersal, while descending air currents facilitate pollen fallout (Jones and Harrison 2004; Pacini 2008).

3.3 Pollen Identification

There is no simple manner to correctly identify and differentiate pollen from sulfur. To the naked eye, they are both yellow and have a similar fine powder appearance. They both float on top of water, and both are water-insoluble. Sulfur has a distinct match-like odor which could help in guiding their differentiation. However, this odor could be difficult to perceive in urban settings, especially when the yellow powder mixes with soil or water.

Pollen identification and characterization can only be performed by observing a sample under the microscope. Even for people who are not trained in microscopy – the organic particles with a uniform morphology (most of them are rounded to ellipsoidal) that are responsible for the yellow dust deposition would be recognizable as pollen grains. However, an exact identification of pollen grains could require the participation of a trained palynologist. In Fig. 6 we show the habitus and pollen of *Acacia dealbata* collected on September 11, 2011 in El Olivar, Viña del Mar (−33.032°, −71.496°, Chile). Under the light microscope, we found polyads characteristic of this species which blooms profusely and releases a lot of pollen during late winter and early spring.

Fig. 6 Habitus and pollen of *Acacia dealbata*. Bar = 20 μm

4 Toxicology

4.1 Sulfur and Sulfur Compounds

Most acute health effects of airborne sulfur compounds – especially sulfur dioxide and hydrogen sulfide – are related to their irritant capacity of ocular and respiratory tract mucosa. At low doses, the manifestations include cough, sneezing, conjunctivitis, and lacrimation, while at higher exposure, symptoms worsen and may include bronchospasms, difficulty in breathing, and pulmonary edema (Komarnisky et al. 2003; Borron and Bebarta 2015; Guidotti 2015). In addition, hydrogen sulfide acts as a potent neurotoxicant and may render a person unconscious in a matter of few minutes (Guidotti 2015).

SO_2 has been shown to be the cause of sulfate aerosol formation with an average diameter of 2.5 μm which can be transported into the lungs and cause respiratory illnesses. Chronic effects of sulfur dioxide may provoke symptoms such as corneal inflammation (keratitis), difficulty in breathing, airway irritation, eye irritation due to the formation of sulfuric acid on mucous membranes, psychic disturbances, pulmonary edema, cardiac arrest, and circulatory collapse (World Bank Group 1999; Liu et al. 2009). It has also been linked to asthma and chronic bronchitis, increasing morbidity and mortality in older adults and children (Gong et al. 2001). In fact, SO_2 was an important risk factor for the thousands of deaths resulting from the December 1952 air pollution London disaster (Logan 1953).

Since the yellow dust we describe in this article is pollen and not sulfur, none of these effects are relevant in case of exposure.

4.2 Pollen

Pollen allergens are one of the main causes of type I allergies affecting up to 30% of the population in industrialized countries (Pablos et al. 2016). Susceptibility of people to pollen allergens vary according to plant species. However grass pollen (family Poaceae) is one of the main causes of allergy in the world, followed by tree species including birch (Betula), olive (Olea), cypress (Cupressus), oriental plane (Platanus), and weeds (D'Amato et al. 2007; Xie et al. 2019).

Pollen grains store allergenic proteins and glycoproteins in their cytoplasm. These proteins probably serve biological and physiological functions in pollen cells such as profillins which control actin polymerization in cells (Garcia-Mozo 2017). Upon pollen rehydration, these proteins are readily expelled through the apertures (Fig. 4) and remain on the surface of pollen grains (Grote et al. 2001; Akio et al. 2006). If pollen is breathed in, these water-soluble proteins are capable of fastly evoking an allergic reaction mediated by IgE, the clinical manifestations of which include ocular pruritus, coryza, sneezing, nasal or pharyngeal-palatal pruritus, and nasal obstruction. Bronchial hyper-reactivity with associated asthma may be present in 15–20% of patients (Akio et al. 2006).

Global climate change in combination with air pollution may lead to a change in concentration and distribution of pollen, as plants are subjected to higher environmental stress which in turn may lead to higher pollen production (Garcia-Mozo 2017). This is a matter that should be considered by allergy-prone people.

5 Suggestions for Risk Communication

Risk communication about air pollution is a matter of high importance. It also includes the correct differentiation of sulfur from pollen in events of yellow dust deposition on urban surfaces. A quick search in Internet using keywords such as "sulfur shower," "sulfur rain," "pollen storm," or "pollen floats" can lead to educational sites which correctly explain the process of pollen release and dispersal. We further summarize the distinction between sulfur and pollen in the following brief sentences:

1. Sulfur is released into the air by natural processes as well as anthropogenic industrial activities. In this last case, sulfur compounds are mainly produced by combustion of fossil fuels and mining of mineral deposits.
2. Sulfur is released into air under the form of sulfur dioxide and hydrogen sulfide. In the presence of sunlight and air humidity, these compounds can be further oxidized to generate sulfuric acid.
3. The production of solid yellow sulfur from volatile sulfur dioxide, hydrogen sulfide, or sulfuric acid is impossible at environmental conditions.
4. Sulfur toxicity from exposure to these volatile compounds results from their oxidant capacity. They are strong irritants to biological tissues such as the eye and respiratory mucosa.
5. Since the yellow dust is pollen and not sulfur, no irritation should be expected if exposed.
6. Pollen is an evolutionary means for plant reproduction. It is released from male flowers so that insects may carry it to female flowers. Some species – especially those that are wind-pollinated, such as birch (Betula), pine (Pinus), and alder (Alnus) – may release high quantities of pollen into the air.
7. The main toxicity risk from pollen deposition is the induction of allergies. Susceptible people should be aware of pollen concentrations in their cities as a precautionary measure.

6 Conclusion

The occurrence of yellow dust deposition on urban surfaces may induce a false perception of risk exposure to sulfur, when in fact the phenomenon is due to pollen release from trees. Based on simple observation without using a microscope, it is virtually impossible to differentiate sulfur from pollen, so risk communication should consider the chemical, biological, and toxicological aspects of these agents. In this review, we suggest messages that risk communicators may use when explaining the phenomenon to their communities.

7 Summary

Urban yellow dust deposition is a common phenomenon in many parts of the world, which is sometimes called “sulfur shower,” “sulfur rain,” or “pollen storm.” Some people may believe the “yellow powder” is a serious threat to their health. Based on simple observations, it is virtually impossible to differentiate sulfur from pollen, so risk communication should consider the chemical, biological, and toxicological aspects of these agents. In this review, we clarify that the yellow dust is actually pollen, and we explain that it is chemically impossible for gaseous sulfur to become solid yellow sulfur under normal environmental conditions.

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Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

Aboka YE, Cobbina SJ, Doke AD (2018) Review of environmental and health impacts of mining in Ghana. J Health Pollut Mar 8:43–52

Akio E, Camargo M, Ferreira P, Machado F (2006) Pollen allergic disease: pollens and its major allergens. Rev Bras Otorrinolaringol 72:562–567

Albert B, Nadot S, Dreyer L, Ressayre A (2010) The influence of tetrad shape and intersporal callose wall formation on pollen apertura pattern ontogeny in two eudicots species. Ann Bot 106:557–564

Aneja VP, Cooper WJ (1989) Biogenic sulfur emissions. In: American Chemical Society (ed) Biogenic sulfur in the environment, vol 393. pp 2–13

Bhomick PC, Rao KS (2014) Sources and effects of hydrogen sulphide. J Appl Chem 3(3):914–918

Bohan L, Guo Z, Probst A, Probst J (2005) Soil heavy metal contamination and acid deposition: experimental approach on two forest soils in Hunan, Southern China. Geoderma 127:91–103

Borg M, Brownfield L, Twell C (2009) Male gametophyte development: a molecular perspective. J Exp Bot 60:1465–1478

Borron SW, Bebarta VS (2015) Asphyxiants. Emerg Med Clin N Am 33:89–115

Bottenheim JW, Strausz OP (1980) Gas-phase chemistry of clean air at 55 degree. N latitude. Environ Sci Technol 14:709–718

Bowles JFW, Howie RA, Vaughan DJ, Zussman J (2011) Rock-forming minerals vol. 5A non-silicates: oxides, hydroxides, and sulphides. The Geological Society, London, p 920

Brimblecombe P (2013) The global sulfur cycle treatise on geochemistry, vol 10, 2nd edn. University of East Anglia, Norwich, pp 559–591

Brown KA (1982) Sulphur in the environment: a review. Environ Pollut B 3:47–80

Bussière B, Benzaazoua M, Aubertin M, Mbonimpa M (2004) A laboratory study of covers made of low-sulphide tailings to prevent acid mine drainage. Environ Geol 45:609–622

Canfield DE (2001) Biogeochemistry of sulfur isotopes. Rev Mineral Geochem 43:607–636

Carpenter PH (1879) Pine pollen mistaken for flowers of Sulphur. Nature 20:195–196

Charlson RJ, Anderson TL (1992) The sulfur cycle. In: International geophysics, vol 50. Academic Press, London, pp 285–300

Croft H (1847–1848) Sulphur rains. Br Am J Med Phys Sci 3:171

D'Amato G, Cecchi L, Bonini S, Nunes C, Annesi-Maesano I, Behrendt H, Liccardi G, Popov T, van Cauwenberge P (2007) Allergenic pollen and pollen allergy in Europe. Allergy 62:976–990

Dalrymple DA, Skinner FD, Meserole NP (1991) Investigation of U.S. natural gas reserve demographics and gas treatment processes. Topical Report, GRI-91/0019, pp 3-1–3-13

Doney S, Mahowald N, Lima I, Feely RA, Mackenzie FT, Lamarque JF, Rasch PJ (2007) Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system. Proc Natl Acad Sci U S A 104:14580–14585

Franck U, Leitte AM, Suppanb P (2014) Multiple exposures to airborne pollutants and hospital admissions due to diseases of the circulatory system in Santiago de Chile. Sci Total Environ 468–469:746–756

Franck U, Leitte AM, Suppanb P (2015) Multifactorial airborne exposures and respiratory hospital admissions - The example of Santiago de Chile. Sci Total Environ 502:114–121

Gagol M, Soltani RDC, Przyjazny A, Boczkaj G (2019) Effective degradation of sulfide ions and organic sulfides in cavitation-based advanced oxidation processes (AOPs). Ultrason Sonochem 58:104610

Garcia-Mozo H (2017) Poaceae pollen as the leading aeroallergen worldwide: a review. Allergy 72:1849–1858

Geurts JJM, Sarneel JM, Willers BJ, Roelofs J, Verhoeven JT, Lamers LP (2009) Interacting effects of sulphate pollution, sulphide toxicity and eutrophication on vegetation development in fens: a mesocosm experiment. Environ Pollut 157:2072–2081

Giannoni SM, Rollenbeck R, Trachte K, Bendix J (2014) Natural or anthropogenic? On the origin of atmospheric sulfate deposition in the Andes of southeastern Ecuador. Atmos Chem Phys 14:11297–11312

Gong H, Linn SW, Terrell S (2001) Anti-inflammatory and lung function effects of montelukast in asthmatic volunteer exposed to sulfur dioxide. Ann Intern Med 119:402–408

Greenwood N, Earnshaw NA (1997) Chemistry of the elements, 2nd edn. Butterworth-Heinemann, Oxford, pp 645–665

Grote M, Vrtala S, Niederberger V, Wiermann R, Valenta R, Reichelt R (2001) Release of allergen-bearing cytoplasm from hydrated pollen: a mechanism common to a variety of grass (Poacea) species revealed by electron microscopy. J Allergy Clin Immunol 108:109–115

Guidotti TL (2015) Hydrogen sulfide intoxication. In: Lotti M, Bleecker ML (eds) Handbook of clinical neurology, Occupational neurology, vol 131, 3rd edn, pp 111–133

Gyamfia E, Appiah-Adjeia EK, Adjeia KA (2019) Potential heavy metal pollution of soil and water resources from artisanal T mining in Kokoteasua, Ghana. Groundw Sustain Dev 8:450–456

Halbritter H, Ulrich S, Grímsson F, Weber M, Zetter R, Hesse M, Buchner R, Svojtka M, Frosch-Radivo A (2018) Illustrated pollen terminology. Springer, Cham. https://doi.org/10.1007/978-3-319-71365-6

Huang T, Fan Y, Long Y, Pang Z (2019) Quantitative calculation for the contribution of acid rain to carbonate weathering. J Hydrol 568:360–371

Jones AM, Harrison RM (2004) The effects of meteorological factors on atmospheric bioaerosol concentrations – a review. Sci Tot Environ 326:151–180

King M, Moats M, Davenport WG (2013) Sulfuric acid manufacture: analysis, control and optimization. Elsevier, Burlington

Klein C, Hurlbut C (1985) Manual of mineralogy, 20th edn. Wiley, New York, pp 265–266

Komarnisky LA, Christophersn RJ, Basu TK (2003) Sulfur: its clinical and toxicologic aspects. Nutrition 19:54–61

Little BJ, Ray RI, Pope RK (2000) Relationship between corrosion and the biological Sulphur cycle: a review. Corrosion 56:433–443

Liu L, Poon R, Chen L, Frescura AM, Montuschi P, Ciabattoni G, Wheeler A, Dales R (2009) Acute effects of air pollution on pulmonary function, airway inflammation, and oxidative stress in asthmatic children. Environ Health Perspect 117:668–677

Logan WP (1953) Mortality in the London fog incident, 1952. Lancet 1:336–338

Luo Y (2018) Geochemical cycle and environmental effects of sulfur in lakes. In: IOP conference series: materials science and engineering, vol 394. IOP Publishing, p 52039

Luther GW, Church TM, Scudlark JR, Cosman M (1986) Inorganic and organic sulfur cycling in salt-marsh pore waters. Science 232:746–749

Maebashi K (2011) Toxicological analysis of 17 autopsy cases of hydrogen sulfide poisoning resulting from the inhalation of intentionally generated hydrogen sulfide gas. Forensic Sci Int 207:91–95

Mokhatab S, Poe W, Mak J (2018) Handbook of natural gas transmission and processing principles and practices book, USA

Monticello D (2000) Biodesulfurization and the upgrading of petroleum distillates. Curr Opin Chem Biol 11:540–546

Moore PD, Webb JA, Collinson ME (1991) Pollen analysis. Blackwell, Oxford

Moreno P, Aral H, Vecchio A (2009). Environmental impact and toxicology of sulphate. In: Conference paper, enviromine 2009, Santiago, Chile

Ninga L, Liyuana Y, Jiruib D, Xugui P (2011) Heavy metal pollution in surface water of linglong gold mining area, China. Procedia Environ Sci 10:914–917

Ochieng GM, Seanego ES, Nkwonta OI (2010) Impacts of mining on water resources in South Africa: a review. Sci Res Essays 5:3351–3357

Pablos I, Wildner S, Asam C, Wallner M, Gadermaier G (2016) Pollen allergens for molecular diagnosis. Curr Allergy Asthma Rep 16:31. https://doi.org/10.1007/s11882-016-0603-z

Pacini E (2008) Pollination. Encyclopedia of Ecology:2857–2861. https://doi.org/10.1016/b978-008045405-4.00859-4

Pacini E, Hesse M (2012) Uncommon pollen walls: reasons and consequences. Verh Zool Bot Ges Österreich 148/149:291–306

Pothirat C, Chaiwong W, Liwsrisakun C, Bumroongkit C, Deesomchok A, Theerakittikul T, Limsukon A, Tajarernmuang P, Phetsuk N (2019) Acute effects of air pollutants on daily mortality and hospitalizations due to cardiovascular and respiratory diseases. J Thorac Dis 11:3070–3083

Rickwood PC (1981) The largest crystals. Amer Miner 66:885–907

Sassi M, Gupta AK (2008) Sulfur recovery from acid gas using the claus process and high temperature air combustion (HiTAC) technology. Am J Environ Sci 4(5):502–511

Schippers A (2004) Biogeochemistry of metal sulphide oxidation in mining environments, sediments and soils. Sulfur biogeochemistry past and present: Boulder, Colorado. Geol Soc Am Spec 379:49–62

Soleimani M, Amarjeet B, Argyrios M (2007) Biodesulfurization of refractory organic sulfur compounds in fossil fuels. Biotechnol Adv 25:570–596

Steudel R (1982) Homocyclic sulfur molecules. In: Inorganic ring systems. Topics in current chemistry, vol 102. Springer, Berlin, pp 149–176

Steudel R, Eckert B (2003) Solid sulfur allotropes. In: Steudel R (ed) Elemental sulfur and sulfur-rich compounds I. Topics in current chemistry, vol 230. Springer, Berlin, pp 1–80

Tebbe FN, Wasserman E, Peet WG, Vatvars A, Hayman AC (1982) Composition of elemental sulfur in solution: equilibrium of S_6, S_7, and S_8 at ambient temperatures. J Am Chem Soc 104:4971–4972

US Environmental Protection Agency (1993) Report to congress on hydrogen sulfide air emissions associated with the extraction of oil and natural gas. EPA-453/R-93-045. p 4

US Environmental Protection Agency (2004) Technical resource document extraction and beneficiation of ore and minerals, volume 4: copper. Office of Solid Waste, Washington

Wiberg E, Wiberg N (2001) Inorganic chemistry. 1st English, New York, p 513

Wilson A (1879) Pine pollen and sulphur. Nature 20:266–267

World Bank Group (1999) Pollution prevention and abatement handbook 1998: towards cleaner production. World Bank Group Publishers, Washington

Xie S, Qi L, Zhou D (2004) Investigation of the effects of acid rain on the deterioration of cement concrete using accelerated tests established in laboratory. Atmos Environ 38:4457–4466

Xie Z-J, Guan K, Yin J (2019) Advance in the clinical and mechanism research of pollen induced seasonal allergic asthma. Am J Exp Immunol 8:1–8

Zarei S (2018) A modified kinetic reaction scheme for Claus reaction furnaces in oil refineries. Innov Ener Res 7:2–9

Natural Purification Through Soils: Risks and Opportunities of Sewage Effluent Reuse in Sub-surface Irrigation

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https://doi.org/10.1007/398_2020_49

Abbreviations

CoEC(s)	Contaminant(s) of emerging concern
EC	European Commission
EU	European Union
FAO	The Food and Agriculture Organization of the United Nations
HQ	Hazard quotient
IARC	International Agency for Research and Cancer
ISO	International Organization for Standardization
IWA	International Water Association
OECD	Organization for Economic Cooperation and Development
PEC	Predicted environmental concentration
PNEC	Predicted no-effect concentration
PTMB	Persistent, toxic, mobile, or bio-accumulative
RQ	Risk quotient
SOM	Soil organic matter
SSI	Sub-surface irrigation
STP	Sewage treatment plant
TTC	Threshold of toxicological concern
UN-Water	United Nations Water
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

1 Introduction

Worldwide freshwater resources are under increasing stress, with a mismatch between demand and availability of water resources across both temporal and geographical scales (IWA 2018; UN-Water 2018). The main causes of freshwater resources being under stress are interlinked and include changes in water availability due to climate change, increases in water withdrawal for food security, and other economic activities. This was also analyzed with different socio-economic pathways indicating an increased global water withdrawal between 12 and 29% for 2050 compared to 2010 (Bijl et al. 2018), which will enhance prolonged dry periods (Chen et al. 2018). Increase in agricultural irrigation is currently one of the main global threats accounting for 69% of freshwater withdrawal (FAO 2016). This is not only an issue for arid regions with low rainfall and high population density that are prone to increasing water stress; also temperate areas with intense agriculture suffer from frequent non-potable freshwater shortages (Massoud et al. 2018; Voulvoulis 2018). Therefore, alternative water resources are explored in order to meet the current and future water demand.

Sewage treatment plant (STP) effluent may provide such an alternative freshwater source. Agricultural STP effluent reuse can compensate water shortages caused by seasonality or by irregular availability of other water sources for crop irrigation throughout the year. Furthermore, STP effluent contains many nutrients such as nitrogen, phosphorus, and potassium that can be used as fertilizer and save the cost of crop production (Jaramillo and Restrepo 2017). Irrigation with STP effluent is already used widespread, particularly in regions such as the Middle East, South and North Africa, and other Mediterranean countries, where the availability of freshwater is limited (Faour-Klingbeil and Todd 2018; FAO 2016; Khalid et al. 2018). Moreover, STP effluent is currently discharged in large volumes to surface water, including its contaminants of emerging concern (CoECs), such as pharmaceuticals, metabolites, antimicrobial-resistant bacteria, and resistance genes (Council of the European Communities 2000). The load of these contaminants to surface water may however be reduced, due to soil passage and related sorption and (bio)transformation processes (Ghattas et al. 2017).

Controlled drainage systems allow to both prevent waterlogging and retain groundwater within agricultural parcels; groundwater levels and soil moisture conditions can be actively controlled (Ayars et al. 2006). Adding water to such a system turns it into an infiltration system, which is called sub-surface irrigation (SSI). The goal of SSI is to raise the groundwater level and improve the soil moisture conditions for plant growth through capillary rise. SSI systems can supply STP effluent to crops while the soil is used as a filter and buffer zone. Two major advantages that SSI via a controlled drainage system may have compared to sprinkling irrigation are that (1) there is no direct contact between fieldworkers and STP effluent lowering human health risks and (2) SSI could make optimal use of soil processes that minimize environmental occurrence and dispersion of CoECs (Hamann et al. 2016; Nham et al. 2015; van der Waals et al. 2018). Nevertheless, there are uncertainties concerning the environmental and public health implications which are associated with the reuse of STP effluent for SSI in agriculture. These are knowledge gaps pertaining (1) the fate of a broad range of CoECs during soil passage under field conditions including their transformation products (Li et al. 2014; Petrie et al. 2018), (2) the extent to which the dispersion of the mixture of CoECs is diminished and/or retained during SSI in agricultural fields (Christou et al. 2017a; Greskowiak et al. 2017), and (3) the adequate adaptation of current risk assessment tools for assessing both the possible opportunities and limitations of STP effluent water reuse (Baken et al. 2018; Christou et al. 2017b; Kase et al. 2018). The aim of this review paper is to collate recent knowledge on the risk and opportunities associated with the reuse STP effluent for sub-surface irrigation in agriculture. The knowledge gaps listed above will be discussed and highlighted. Additionally the policies and guidelines concerning non-potable water reuse on a global and

European level will be presented. Finally, the review is enriched with concluding remarks and future perspectives of understanding the fate of CoECs in SSI with special emphasis on contaminants removal.

2 Policies and Guidelines Concerning Non-potable Water Reuse

2.1 Worldwide

At global level there are several guidelines, i.e., non-mandatory recommendations, available concerning water reuse (Table 1). In 2006 the World Health Organization (WHO) published guidelines on the safe use of wastewater, intended as a tool for decision-makers and regulators to provide a consistent level of health protection in different settings. The guidelines can be adapted for implementation under specific environmental, sociocultural, and economic conditions at a national level (WHO 2006). The United States Environmental Protection Agency issued the last version of the "Guidelines for Water Reuse" (USEPA 2012). These guidelines include a wide range of reuse applications (e.g., agricultural irrigation and aquifer recharge) and apply similar approaches as described by the WHO (2006) and the Australian Government Initiative (2006) for controlling health and environmental risks. The most recent global guidelines for STP effluent reuse in agricultural irrigation were published in 2015 by the International Organization for Standardization (ISO 2015). These ISO guidelines include water quality requirements for CoECs.

Remarkably, the State of California overtakes these global guidelines with specific regulations for CoECs (California Water Boards 2019). Consequently, these California water reuse regulations are being used as a global benchmark for the development of water reuse regulations worldwide. Noteworthy, California recently signed the Senate Bill No. 996 (Legislative Counsel Bureau 2018), which encourages communities to reuse STP effluent on-site.

2.2 Europe

At European level the need to address management of water resources to prevent scarcity and droughts was acknowledged in the EU's Blueprint to safeguard Europe's water resources (Table 1). In this Blueprint the need to use STP effluent as an alternative water resource for irrigation purposes is re-emphasized (European Commission 2012). Six EU Member States (Cyprus, Greece, Spain, France, Italy, and Portugal), all with (semi) Mediterranean climate, have requirements on water reuse in place in national legislation or in non-regulatory standards (Joint Research Centre 2017). Aquifer recharge (by surface spreading or direct injection) is only

Table 1 Directives, policies, and guidelines related to water reuse

	Standards	
	Chemicals[a]	Pathogens[b]
Worldwide		
Guidelines for the safe use of waste water, excreta and greywater. Vol. II Waste water use in agriculture (WHO 2006)	-	×
Guidelines for Water Reuse (USEPA 2012)	×	×
Guidelines for treated wastewater reuse (ISO 16075 2015)	×[c]	×[c]
Regulations Related to Recycled Water. Title 22, CDPH (2018) (California). Draft amendment to the recycled water policy	×[c]	×[c]
Europe		
Directive Nitrates (1991/676/EC) (Council of the European Communities 1991)	×	-
Directive Urban Waste Water Treatment (1991/271/EC) (EEC Council 1991)	×	-
Directive Water Framework (2000/60/EC) (Council of the European Communities 2000)	?	?
Regulation on the hygiene of foodstuffs (2004/852/EC) (European Commission 2004)	-	×
Regulation on laying down requirements for feed hygiene (2005/183/EC) (European Parliament and the Council of the European Union 2005)	×	×
Regulation on microbiological criteria for foodstuffs (2005/2073/EC) (European Commission 2005)	-	×
Regulation on maximum residue levels of pesticides in or on food and feed of crop and animal origin (2005/396/EC) (European Parliament and the Council 2005)	×	-
Regulation setting maximum levels for certain contaminants in foodstuffs (2006/1881/EC) (European Commission 2006)	×	-
Directive on environmental quality standards in the field of water policy in order to meet the environmental quality standards for priority substances and certain other pollutants (2008/105/EC) (European Commission 2008)	×	-
Regulation Animal by-products and derived products (2011/142/EC) (European Commission 2011)	-	×
Directive Groundwater (2014/80/EC) (European Commission 2014)	×	-

x yes
- no
? inconclusive

[a] The heading “Chemicals” of the column in this table refers to standard measured indicator parameters such as biological oxygen demand (BOD), total suspended solids (TSS), and turbidity

[b] The heading “Pathogens” of the column in this table refers to standard measured indicator parameters such as *E. coli*, *Legionella* spp., and intestinal nematodes

[c] Includes chemical contaminants of emerging concern or antimicrobial resistance

considered as a permitted use in Cyprus, Greece, and Spain (Drewes et al. 2017). Many of the standards developed at Member State level have been informed by the 2006 WHO Water Reuse Guidelines (WHO 2006), the ISO guidelines on safe use of STP effluent for irrigation use (ISO 2015), and regulatory approaches in other countries (e.g., California, Australia, and Israel) but also by specific national considerations such as environmental, sociocultural, and economic conditions.

In the Water Framework Directive (2000/60/EC) and the Urban Waste Water Treatment Directive (91/271/ECC), treatment of STP effluent is encouraged whenever appropriate to remove nutrients and organic material. One of the main barriers that the Blueprint recognizes for STP effluent reuse in the EU is a lack of common standards. Existing EU instruments for water reuse are listed in Table 1, which do not specify conditions for reuse. As the crops produced by SSI can be consumed by both animals and humans, instruments related to food quality and animal feed are also included in this table.

To overcome the abovementioned barrier, the Joint Research Centre (2017) selected a risk management framework to establish minimum quality requirements for water reuse in agricultural irrigation and aquifer recharge. The European Commission recently proposed a European regulation on minimum requirements for water reuse for irrigation (European Commission 2018). However, the proposed regulation is generic and provides a few minimum requirements, focused on general quality and public microbial health, but lacks minimum requirements for CoECs (Rizzo et al. 2018).

3 STP Effluent Reuse in Agriculture

It is useful to differentiate between *de facto* or unintentional reuse and intentional reuse. Both types of reuse can have significant socio-economic benefits but also institutional challenges and risks which require different management approaches (Rice et al. 2016).

3.1 De Facto *or Unintentional Reuse*

STP effluent is commonly indirectly reused in agriculture by irrigating with surface water in which STP effluent was discharged (Drewes et al. 2017). Conventional STPs are not optimized for the removal of CoECs, and their discharge will affect the receiving surface water quality (Blum et al. 2018; Grill et al. 2016; Jaime et al. 2018; Reemtsma et al. 2016; Sousa et al. 2017; Tran et al. 2018; van Wezel et al. 2018; Yang et al. 2017). During times of normal flow, this impact is less significant, but during low flow conditions with usually high irrigation demand, surface water can consist primarily out of effluent (Drewes et al. 2017; Fekadu et al. 2019; Munz et al. 2016; Roberts et al. 2016; Yadav et al. 2017). High flow conditions may also favor high impact of STP effluent, as during heavy rain sewer overflows will contribute to surface water contamination (Ccanccapa et al. 2016; Roberts et al. 2016). Water from these streams is in many cases directly applied to crops by sprinkler irrigation, resulting in potential exposure to human pathogens and organic micropollutants (Beard et al. 2019; Dulio et al. 2018; Munz et al. 2016; Schmitt et al. 2017; Thebo et al. 2017). For example, within the Llobregat river district (Spain), STP effluents were estimated to contribute between 8 and 82% to the total river flow (Drewes et al. 2017).

The risk associated with *de facto* STP effluent reuse might not be properly managed (Faour-Klingbeil and Todd 2018; Hong et al. 2018; Ncube et al. 2018; Nguyen et al. 2018). Where stream flows vary and the use of irrigation water is occurring only seasonally, the need to execute a comprehensive monitoring program of irrigation water with high frequency for CoECs monitoring parameters might not be obvious, feasible, or affordable. Therefore, to ensure the protection of human and the environment adequately, guidelines and minimum quality requirements for STP effluent are needed (Bieber et al. 2018; EurEau 2018; Rizzo et al. 2018; Sousa et al. 2017).

3.2 Intentional Reuse

Intentional reuse offers better control and management possibilities than *de facto* reuse. Planned non-potable water reuse requires that the treated effluent water quality is safe for crops and workers, and does not compromise local groundwater, surface water, or soil quality.

Many non-potable reuse applications (e.g., agricultural irrigation; cooling water) exhibit high seasonal dependencies, requiring either storage options or alternative reuse practices during off-season (Chen et al. 2018). While significant attention has been paid to more arid regions of the world, temperate climates also experience seasonal irrigation water shortages (Beneduce et al. 2017; Faour-Klingbeil and Todd 2018; Gude 2017; Voulvoulis 2018). Multiple planned reuse applications around the world demonstrated that the use of STP effluent for crop growth can be a safe practice (García-Santiago et al. 2017; Jaramillo and Restrepo 2017; Tal 2016). Intentional reuse has therefore become the norm in large parts of southern France, Spain, Portugal, Italy, Greece, and Cyprus (Drewes et al. 2017). According to Voulvoulis (2018), in 2006 2.4% of the total available treated effluent in the EU was reused for non-potable applications. Spain accounted for about a third of this (347 Mm^3/year), and Italy used approximately 223 Mm^3/year. As minimum stream flow conditions are required for ecosystem functioning (Poff 2018), in some basins not all STP effluent can be reused for irrigational purposes (Drewes et al. 2017).

3.3 Public Perception

To promote intentional non-potable STP effluent reuse, possible public rejection to consume food irrigated with STP effluent needs to be understood (Massoud et al. 2018; Voulvoulis 2018). Public's distrust in authorities who are responsible for managing STP effluent is the result of fear in regard to (1) the level of human contact with the STP effluent; (2) the perceived dirtiness or filthiness; (3) increasing incidences of disease outbreaks (the “yuck factor”); (4) the lack of skilled labor and efficient management; (5) the cost of treatment, distribution, and the system; and (6) the amount of available freshwater for non-potable reuse (Massoud et al. 2018; Ricart et al. 2019; Smith et al. 2018).

Providing two-sided messages that present advantages and refute criticisms in order to justify the logic for the positive aspects of STP effluent reuse may aid in public acceptance. Better yet, providing information about the low risks of STP effluent reuse is more critical than communicating about the benefits of the water source (Price et al. 2015; Šteflová et al. 2018). One of the key challenges here is that trust, and efforts to build trust through public engagement, may ultimately be shaped by pre-cognitive reactions, i.e., the “yuck factor” (Garcia-Cuerva et al. 2016). Similarly, recent research has shown that awareness of existing unplanned (de facto) reuse practices has the potential to improve acceptance (Rice et al. 2016). This suggests that, rather than awareness of the need for STP effluent reuse as a solution to water supply issues, awareness of STP effluent reuse as an existing normal part of the water resource context, even in potable applications, may be a significant driver of acceptance (Smith et al. 2018). Thus, well-planned and well-executed water reuse programs and applying consistent risk-based standards for agricultural irrigation may have the potential to reduce the overall perceived risk while offering an alternative and sustainable water supply (Drewes et al. 2017; Gonzales-Gustavson et al. 2019).

3.4 *Irrigation Systems*

The environmental fate processes of the CoECs present in STP effluent and the exposure pathways to humans and the environment differ between various irrigation systems which are being used. Here we compare sprinkler irrigation, drip irrigation, and SSI (Table 2).

Table 2 Fate processes of CoECs in irrigation systems

	Irrigation systems			
		Drip		
	Sprinkler	Surface	Sub-surface	Sub-surface
Sorption	×	××		×××
Photolysis	×××	×××	××	*Insignificant*
(Bio)transformation	×	×	××	×××
Run-off	×××	*Insignificant*		*Insignificant*
Volatilization	×××	×××	××	*Insignificant*
Crop uptake	×××	×××		××

Christou et al. (2019a), Gupta and Madramootoo (2017), Kibuye et al. (2019), Pepper and Gerba (2018)

××× Means process is prevailing compared to the other systems

×× Means process is present in system, but not prevailing in comparison to the other systems

× Means process may be present in system

In sprinkler irrigation STP effluent is supplied under pressure and segregated into particles or droplets of variable size and comes in direct contact with the above-ground parts of crops. The size of droplets determines the distance that the droplets will be transported through the air. As predicted by Stokes' Law, the smaller the droplet size, the further the droplets will be transported (Christou et al. 2019a; Gupta and Madramootoo 2017; Kibuye et al. 2019; Pepper and Gerba 2018). Sprinkler irrigation systems can be classified into two major types: (1) rotating head or revolving sprinkler system and (2) perforated pipe system, also referred to as "spray irrigation." The rotating head type consists of small-size nozzles on riser pipes fixed at uniform intervals along the length of the lateral pipe that are usually laid on the ground surface. The perforated pipe system is comprised of drilled holes or nozzles along the length through which water is sprayed under pressure (Mukherjee and Adhikary 2019).

Drip irrigation, which slowly applies STP effluent to individual points, can overcome the drawbacks of sprinkler irrigation by way of low energy requirements, not being affected by wind and preventing crop interception storage and evaporation losses (Gunarathna et al. 2017; Martínez and Reca 2014; Zapata et al. 2018). However, drip irrigation may perform poorly due to clogging of emitters (Gunarathna et al. 2017).

The application of STP effluent by means of SSI is less-time-variable then for sprinkler or drip irrigation. SSI has perforated or porous pipes buried in the soil and can sustain crops with high water requirements, as soil moisture content and groundwater are kept at desired levels (Siyal and Skaggs 2009). STP effluent seeps from the pipes into shallow groundwater by gravity and recharges it; thereupon soil capillarity provides the irrigation water to the crops (Fig. 1). Thus, in SSI as opposed to sprinkler and drip irrigation, CoECs are expected to primarily be removed via sorption and anaerobic transformation processes. Anaerobic transformation of CoECs is generally less energetically favorable than transformation under aerobic conditions. However, some aerobically recalcitrant CoECs can be

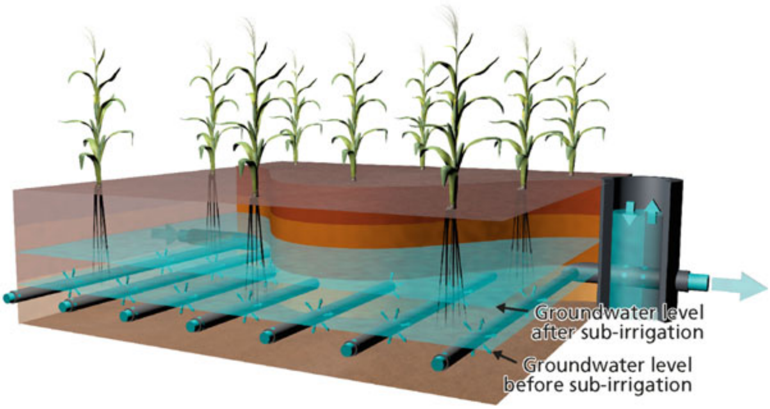

Fig. 1 Schematic overview of a sub-surface irrigation system

bio-transformed under strictly anaerobic conditions, and little is known about the organisms and enzymatic processes involved in their transformation (Ghattas et al. 2017; Reemtsma et al. 2016).

In addition, SSI provides a soil barrier surpassing drip and sprinkler irrigation where the STP effluent comes in direct contact with the crops (Ghattas et al. 2017; Hamann et al. 2016; Nham et al. 2015; van der Waals et al. 2018). Furthermore, using SSI as a method of supply can decrease CoECs owing to filtration and buffer functions of soil. These functions are the result of fate processes, i.e., sorption- and (bio)transformation-related processes, which CoECs endure during soil passage in SSI systems. The efficiency of SSI may be affected by the hydrological boundary conditions and soil type which determine the extent of deep percolation water losses, the water application rate, and design parameters such as the size, depth, and spacing of pipes (Ayars et al. 2015; Martínez and Reca 2014; Bonaiti and Borin 2010). Ergo, the fate of CoECs present in STP effluent is highly dependent on the method of supply (Ricart et al. 2019).

Be that as it may, not all soils are suitable for SSI, i.e., to retain irrigated water in the rhizosphere. Suitable soils typically consist of a permeable top soil to allow water to infiltrate and a resistant layer below the drainage/infiltration tubes to prevent quick losses due to deep percolation (Benard et al. 2016; Shakir et al. 2017).

Independent of the irrigation method, using STP effluent for irrigation on soils with a high clay content may deteriorate the soil quality (Rengasamy 2018).

4 Fate Processes of CoECs During SSI

Environmental fate of CoECs during soil passage in SSI will be affected by sorption and (bio)transformation processes and crop uptake (Gillefalk et al. 2018; Nham et al. 2015). These fate processes are affected by the intrinsic properties of CoECs, such as hydrophobicity, charge, ionization state, structure and molecular weight, as well as the extrinsic parameters of the system, such as residence times, cation exchange capacity, pH, temperature, and the structure of microbial communities (Arp et al. 2017; Ren et al. 2018; Schulze et al. 2018, 2019). Furthermore, the abovementioned fate processes will determine the bioavailability of the CoECs. For most CoECs, the freely dissolved concentration is closely related to the risk of the contaminants, because only this concentration equilibrates with the internal tissue concentration that initiates a toxic effect (Cipullo et al. 2018).

The environmental fate processes, which in SSI systems will occur to a large extent under anaerobic conditions, can also be observed in other systems such as vertical flow constructed wetlands, river bank filtration, and managed aquifer recharge (Gorito et al. 2017; Hamann et al. 2016; Nham et al. 2015; Petrie et al. 2018). Horizontal flow constructed wetlands also offer insight into these primarily anaerobic processes; however here the transport medium is water instead of soil (Wagner et al. 2018). As experimental data on CoECs fate processes for SSI are largely lacking, we will review the soil processes in the other aforementioned constructed wetland, river bank filtration, and managed aquifer recharge systems. In the following sections, studies concerning these main environmental fate processes which will occur during SSI are reviewed.

4.1 Sorption and (Bio)transformation

In water treatment applications, soil passage has proven to have the ability to filter CoECs from STP effluent as a result of sorption and (bio)transformation processes (Bertelkamp et al. 2014; Hamann et al. 2016; Nham et al. 2015). Sorption is typically quantified by an equilibrium organic carbon–water partition coefficient (K_{oc}), defined as the ratio of the concentration in soil or sediment organic carbon (mg/kg) vs. the concentration in surrounding water (mg/L) at equilibrium (Arp et al. 2017). The terms transformation or degradation refer to structural modification of an organic chemical (primary transformation) or its complete breakdown to CO_2 and water (ultimate transformation) (Poursat et al. 2019). The degree to which an organic CoEC will react to its environment is dependent on its intrinsic and extrinsic characteristics (Schulze et al. 2019). These will be discussed in the below-mentioned paragraphs and are summarized in Table 3.

4.1.1 Intrinsic Properties of Organic CoECs

The intrinsic properties of CoECs greatly affect their occurrence and behavior in the environment. Their complexity, i.e., long structures, ionic strength, and the presence of functional groups, determines the rate at which they are transformed and subsequently mineralized (Ghattas et al. 2017). These intrinsic characteristics, including

Table 3 Factors that influence sorption and (bio)-transformation of CoECs during soil passage

Intrinsic	Hydrophobicity
	Functional groups
	Charge
	Ion-strength
	Structure length
Extrinsic	Time and continuity of irrigation
	Volume of effluent versus volume of soil
	STP effluent matrix
	Organic matter
	Residence times
	Microbes
	pH
	Redox conditions
	Seasonal temperature variations
	Concentration of competing ions

standard test protocols, are well described for target and suspect compounds in Sjerps et al. (2016), PubChem, ChemSpider, Stoffident, and Toxnet (NORMAN 2019). New treatment processes, such as reverse osmosis coupled with advanced oxidation, achieve high removal efficiency toward pharmaceutical products and other CoECs (Albergamo et al. 2019; Luo et al. 2014; Magdeburg et al. 2014; Pan et al. 2019). Their implementation is however strongly impeded by high operation and maintenance cost, and they may not be feasible to treat large volumes of STP effluent at low CoECs concentrations (Pan et al. 2019). Accordingly, significant interest continues to grow in the most efficient, feasible, and environmentally friendly approaches for the transformation of CoECs (Bilal et al. 2019). This includes the induction of microbial adaptation (Poursat et al. 2019), which will be discussed in the next section.

4.1.2 Extrinsic Properties of Organic CoECs

Besides microbial adaptation, redox conditions, organic matter, residence times, and seasonal temperature variations make up the aforementioned environmental conditions of the SSI system that influence the fate of organic CoECs in SSI systems.

Redox Conditions

The oxygen demand exerted by the incoming STP effluent exceeds the amount of oxygen available within the SSI system. Therefore, anaerobic pathways will become an important mechanism for removal of CoECs (Arden and Ma 2018; Kahl et al. 2017; Petrie et al. 2018). Under anaerobic conditions, extracellular respiration bacteria oxidize electron donors (organic matter) and transport electrons to exogenous electron acceptor, by which the microorganisms can grow (Peng et al. 2016; Ren et al. 2018). The transformation of CoECs is based on the presence of microorganisms with specific catalytic activities targeting certain functional moieties in the compound. Thus, organic CoECs have the potential to serve as substrates or electron acceptors for anaerobic microorganisms in SSI (Ghattas et al. 2017). For example, compounds with ether moieties (especially methyl-aryl-ethers) and iodinated aromatic compounds (e.g., iodinated X-ray contrast media as well as their aerobic transformation products) were reported by Ghattas et al. (2017) to be prone to anaerobic transformation.

Organic Matter

The sorption potential of soils is positively correlated to the amount of organic matter. However, soils with the same organic matter content may have different sorption potentials for CoECs, depending on the soil organic matter (SOM) structure (aromaticity and aliphaticity) at nanoscale, such as polarity, spatial arrangement, and physical conformation (Mao et al. 2019; Ren et al. 2018). In SSI, sorption is expected to have a larger effect compared to other irrigation systems, as the STP effluent is introduced into the saturated soil. Highly specific surface areas in the saturated soil enable colloids to effectively sorb hydrophobic contaminants (Quesada et al. 2019; Ren et al. 2018). In addition, electrical characteristics of SOM can induce electrical attraction with positively charged chemical compounds (Park et al. 2018), decreasing their bioavailability. Soil pH determines the surface charge of SOM and minerals, and the existing forms of CoECs, which have significant impact on charge-dependent adsorption process (Arp et al. 2017). Consensus is lacking on which domain of SOM dominates sorption, probably caused by different types of SOM used in different experiments (Jin et al. 2015; Quesada et al. 2019; Ricart et al. 2019; Tran et al. 2017). Furthermore, dissolved organic matter may contribute to the movement of microbes (Ren et al. 2018).

Residence Times

Prolonged exposure of soils to STP effluent can also cause CoECs to form strong bonds to soil, i.e., aging, consequently causing a decline in bioavailability (Brunsch et al. 2018; Ren et al. 2018). For ionizable substances, sorption is quantified with the pH-dependent organic carbon–water distribution coefficient (D_{oc}, dependent on the dissociation constant or pKa of the specific chemical), accounting for the total sum of neutral and charged species sorbed and dissolved (Arp et al. 2017). For positively charged ionic and ionizable molecules, there are other interactions that can decrease mobility in the environment that are not accounted for with D_{oc} or the solubility in water (S_{water}) alone, such as cationic or anionic exchange interactions to minerals and other surfaces or precipitation with counter-ions. Thus, in the absence of accounting for such additional interactions, basing mobility on pH dependent D_{oc} or S_{water} represents a maximum assumption for mobility (Schulze et al. 2018). Accordingly, prolonged sorption may lead to microbial responses such as the formation of biofilms (Adrion et al. 2016; Bezza and Chirwa 2017; Singleton et al. 2016). Biofilms can reach thicknesses of multiple centimeters. This results in limited oxygen diffusion to the inner parts, which consequently leads to an oxygen gradient within the biofilm; in other words both aerobic and anaerobic transformation processes are made possible (Wagner et al. 2018). In constructed wetlands the presence of biofilms is identified as a key removal mechanism (Gorito et al. 2017; Kahl et al. 2017; Petrie et al. 2018). It can be expected that the prolonged exposure of croplands to STP effluent during SSI will also induce the formation of biofilms. This may limit the infiltration capacity of the SSI system. However, when groundwater is not fed by STP effluent, it has the potential to decrease below desired levels, leading to deterioration of the formed biofilms.

Seasonal Temperature Variations

Most adsorption reactions in soil are spontaneous and exothermic processes, resulting in a decrease in the adsorption extent with higher temperatures (Lamichhane et al. 2016). Kahl et al. (2017) studied the effect of design and operational conditions on the performance of subsurface flow treatment wetlands, with CoECs as indicators. Six pilot-scale subsurface flow treatment wetlands loaded with primary STP effluent were monitored over one year. The results from this study suggested that in horizontal flow constructed wetlands, biotransformation is the major removal process during high temperature seasons, while sorption in the rhizosphere and crop uptake might be more prevalent during cold-low temperature seasons (Gorito et al. 2017; Kahl et al. 2017; Petrie et al. 2018). Notwithstanding, this is highly dependent on the intrinsic characteristics of the CoECs (Arp et al. 2017). Thereupon, it can be inferred that in SSI systems, biotransformation may also be the major removal process of organic CoECs during the growing season, while sorption may take on a more significant role during cold temperature seasons.

Microbial Adaptation

Besides the formation of biofilms, long-term exposure of microorganisms to CoECs can alter the microbial community structure and result in a higher resistance to CoECs and an improved potential for biotransformation.

Microbial Resistance to CoECs

Direct evidence indicating the impact of CoECs on the microbial resistance in the agricultural environment as a result of STP effluent SSI irrigation is scarce and controversial. One (Cycoń et al. 2019) refers to the fact that soil contains a high abundance of bacteria that compete to survive, which means that even if STP effluent-derived bacteria accumulate in the soil, it may take several decades to produce noticeable effects, while another states that the continuous release of antimicrobial-resistant bacteria and genes could create a potential reservoir for antimicrobial resistance (Christou et al. 2017a; Larsson et al. 2018; Manaia 2017).

Enhanced Biotransformation

Biotransformation of CoECs can be enhanced through induction of microbial adaptation. Microbial community adaptation is controlled by three mechanisms: (1) microbial interactions within the community and governed by microbial ecology concepts, (2) the genetic information that controls the functional potential of the whole community, and (3) the interplay between the microbial community and the environment. At the level of the individual cell, adaptation can refer either to phenotypic or genetic adaption (Poursat et al. 2019). Several studies have described the adaptation of microorganisms to chemical stressors, which they then use as energy sources, i.e., growth-linked transformation, or acquire the ability to co-metabolize (Campa et al. 2018; Poursat et al. 2019; Wagner et al. 2018; Winkler et al. 2019). In addition, microbes can make a series of adjustments to environmental changes (limited bioavailability of chemicals), involving morphological, physiological, and behavioral adaptation. Behavioral adaptation can positively influence the transformation rate of CoECs; however, it may also lead to an increase in microbial resistance (Bertelkamp et al. 2016; Christou et al. 2017a; Otto et al. 2016; Poursat et al. 2019; Ren et al. 2018). The greatest uncertainty concerning the complex process of microbial adaptation is estimating the time required for adaptation to a new molecule on the one hand and the parameters that promote the adaptation process on the other hand (Poursat et al. 2019). However the review by Poursat et al. (2019) showed that adaptation can be induced under certain laboratory conditions, even with persistent or inherently biodegradable compounds. Among all techniques used to trigger adaptation events, pre-exposure of microorganisms present in the soil of croplands to STP effluent before cultivating crops seems to be the best candidate to optimize the biotransformation in SSI (Poursat et al. 2019; Reid et al. 2020; Wang et al. 2020).

4.2 Crop Uptake and Bioaccumulation

Numerous studies, mainly conducted under controlled conditions, highlighted that crops exposed to known concentrations of individual or cocktails of CoECs through irrigation with STP effluent uptake and accumulate these contaminants in their tissues, in the range of low μg/kg to low mg/kg (Christou et al. 2019b). In SSI systems, the uptake of CoECs by crops is largely dependent on their bioavailability in soil pore water near the rhizosphere, driven by their intrinsic and extrinsic properties (Christou et al. 2017a; Goldstein et al. 2014). This paragraph will focus on these intrinsic and extrinsic properties.

4.2.1 Intrinsic Properties of Organic CoECs

Root uptake of most organic CoECs is passive. The mechanisms of CoECs uptake by crops are driven by the transpiration derived mass flow and largely dependent among others on the intrinsic properties of the compounds, especially their hydrophobicity, chemical structure, and charge (Christou et al. 2017b; Goldstein et al. 2014; Miller et al. 2016). For neutral compounds hydrophobicity is one of the key transport factors, whereas for ionizable CoECs the movement and distribution also depend on the dissociation constant (p*K*a), charge of the chemical, and pH of the various crop compartments. Thus, the electrical attraction or repulsion of ionizable CoECs to the negatively charged root surface and ion trap effects may affect their accumulation in roots (Christou et al. 2019b). The ionic trapped CoECs are expected to be translocated preferentially in the phloem rather than in the xylem and as opposed to the nonionic CoECs, be accumulated in the fruit rather than in the leaves (Goldstein et al. 2014). During transport within the crop, organic CoECs can be metabolized and sequestered within various crop tissues. Crops contain enzymatic systems such as cytochrome P-450s and their (bio)transformation capacity may be compound as well as crop specific. Non-ionizable, polar, highly water-soluble organic compounds are most likely to be taken up by crops and translocated to shoot tissue (Doucette et al. 2018).

4.2.2 Extrinsic Properties of Organic CoECs

The extrinsic properties of CoECs which determine their bioavailability in SSI systems are environmental conditions such as the amount of oxygen, pH, and temperature that crops are exposed to.

Growing on well-aerated soils, contrary to partially or non-aerated ones, such as waterlogged soils, may facilitate the uptake of CoECs by crops (Christou et al. 2019b). CoECs in their ionic form, which is predominant in soils with pH higher than the p*K*a of the compound, have a lower potential for crop uptake, due to repulsion forces exerted by the negatively charged root epidermis. Similarly, soils with acidic pH values (e.g., soil pH<compound p*K*a) may result in the presence of contaminants in their neutral form (high fraction of neutral molecules (*fn*) values), thus facilitating their uptake (Goldstein et al. 2014; Miller et al. 2016). Remarkably, the pH in different crop organelles (vacuole, xylem, phloem, and cytosol) may differ from each other and from the pH in the irrigation water. Therefore, compounds taken up easily do not necessarily distribute well within crops. Compounds that are neutral within a wide range of pH such as carbamazepine and caffeine have been proven to cross membranes easily (Riemenschneider et al. 2016).

Drought stress, implying dry climatic conditions and limited water availability, also affects the uptake of CoECs by crops, independent of the method of supply. Crops such as bananas, citrus, fruit trees, walnut (fruit trees), cucumber, eggplant, green beans, melons, pepper, tomatoes (vegetable crops), peanuts, and alfalfa (arable crops) have a higher potential for CoECs uptake when grown in hot and dry conditions (thus irrigated in short intervals). Seasonal crops that are growing during the summer period (i.e., vegetables) and crops grown in greenhouses irrigated with STP effluent, as well as perennial crops for which STP effluent irrigation is practiced all year round for a prolonged period (i.e., fruit trees), may also be categorized as crops with high potential for CoECs uptake. On the contrary, crops grown during the autumn and winter period, where irrigation with STP effluent is irregularly practiced because of the precipitation events, as well as succulent crops (i.e., agave, aloe vera), may be categorized as crops with the lowest potential for CoECs uptake (Zhang et al. 2016). Noteworthy, leafy vegetables (i.e., lettuce, spinach, cabbage, broccoli, celery, etc.), often cultivated intensively all year round (thus irrigated), may accumulate greater concentrations of CoECs in their edible tissues (Christou et al. 2019b). With SSI a combination of the abovementioned extrinsic factors that influence crop uptake is at play.

Independent of the method of supply, other environmental factors, like ambient temperature, wind speed, and air humidity, may also affect crop uptake of CoECs by shaping their evapotranspiration rate, and therefore their water uptake (Christou et al. 2019b). Accordingly, it can be expected that SSI compared to other irrigation systems, where the total amount of irrigated STP effluent comes in direct contact with either the above or below ground parts of crops, minimizes crop uptake by reducing the amount of effluent that comes in direct contact with the roots through capillary rise. In SSI this is achieved as a result of STP effluent seeping from the pipes into shallow groundwater and subsequently lowering CoECs their bioavailability due to sorption and anaerobic (bio)transformation processes. Yet, aerobic conditions which are present in the rhizosphere may also affect the bioavailability of CoECs to crops. These are issues poorly understood, but the current knowledge cannot exclude the possibility of CoECs uptake by crops in SSI systems.

Only few studies followed an experimental setup where real STP effluent was applied for irrigation of crops in field, representing actual farming practices. Moreover, even fewer studies have reported concentrations of the studied CoECs in both the growing medium (i.e., soil) and the edible tissues of the crops, thus allowing for the estimation of the bioconcentration factor (Christou et al. 2017b, 2019a, b; Franklin et al. 2015; Goldstein et al. 2014; Pan et al. 2014; Picó et al. 2019; Riemenschneider et al. 2016). For example, Goldstein et al. (2014) reported that the concentration of CoECs in cucumber and tomato leaves of crops grown in three different soils in pots was of similar order, whereas their concentration in the tomato fruit was much lower compared to that in the cucumber fruit. This was attributed to differences in fruit physiology and specifically to the fact that cucumber fruits exert physiological responses and functions similar to those of leaves, as the chlorophyll content of the exocarp and the efficiency of photosystem II of fruits are similar to that of leaves (cucumber fruits transpire water while also facilitating the direct fixation of atmospheric CO_2 and recapturing of respired CO_2, contributing to fruit growth). Riemenschneider et al. (2016) observed that the concentration of CoECs in fruits increased with the increasing duration of STP effluent irrigation, reaching the highest concentration values during the last harvest of the third year of the study. The overall concentration showed the following decrease of order: roots > leaf > shoot > fruit, which may have been due to the limited distribution of ionic compounds in aerial crop organs. It is worth noting that generally the sum concentration of micropollutants decreased in the order of leaf > root > fruit-bearing vegetables (Christou et al. 2017b; Riemenschneider et al. 2016).

5 Risk Assessment of SSI with STP Effluent

A variety of CoECs are present in STP effluent, and their mixtures vary intra- and inter-daily, seasonally, and inter-annually (Petrie et al. 2015; van Wezel et al. 2018). Reuse of STP effluent may result in exposure of croplands to a large group of compounds that are not commonly monitored, for which there is scarce information on possible effects, and for which no regulatory criteria or quality standards exist while they potentially might pose risks (Halden 2015; Rizzo et al. 2018).

Any concern about health or environmental risks of SSI based on STP effluent reuse might hinder its acceptance (Rice et al. 2016). Therefore a better understanding is needed on environmental fate processes of the CoECs and their exposure pathways to humans and the environment during SSI for an adequate risk assessment.

5.1 Exposure Assessment

Within the risk assessment process of STP effluent reuse in SSI, a critical step is the identification of the exposure pathways, including their magnitude, frequency, and duration (Klaassen 2008). There are various ways in which contaminants can move from the source through media to points of exposure in a sub-surface irrigation system (Fig. 2). Although the vast majority of CoECs present in STP effluent are in

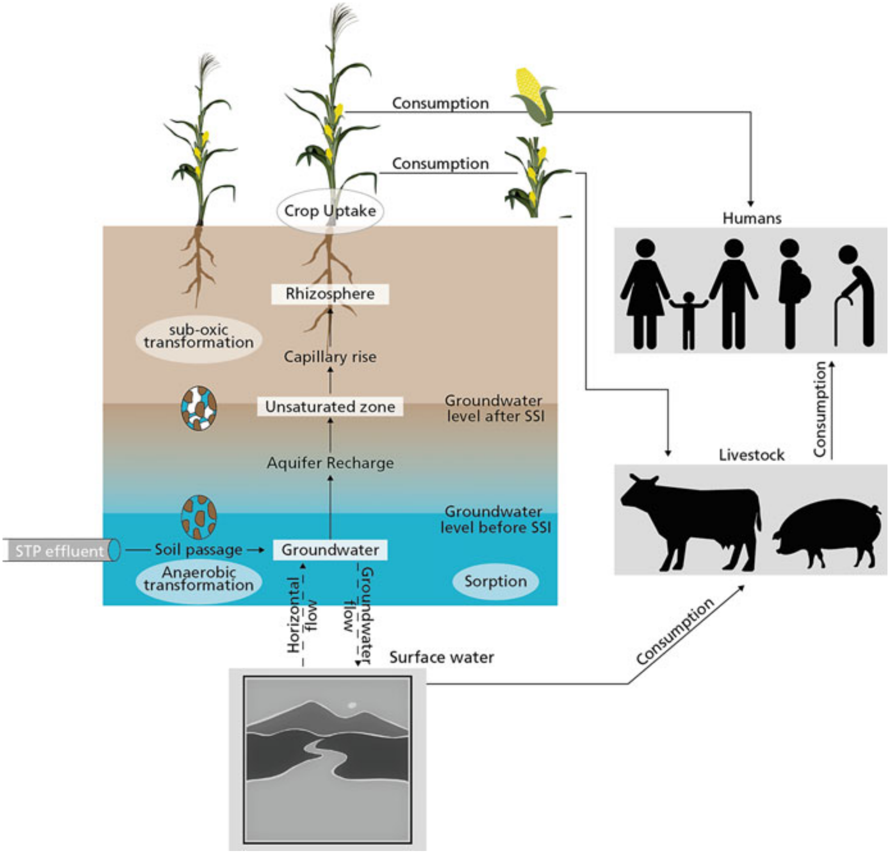

Fig. 2 The exposure routes of STP effluent in a SSI system. The dashed lines represent additional pathways to the primary route (bold lines)

the low ng per liter range, many of these compounds can raise environmental and human health issues (Nohmi 2018; Reemtsma et al. 2016).

Few studies have assessed the long-term opportunities and limitations of the most environmentally relevant compounds. These are compounds that are used and produced in significant quantities and are persistent, toxic, mobile, or bio-accumulative (PTMB) (ECHA 2017; Reemtsma et al. 2016). One essential difficulty in conducting risk assessments for highly mobile substances is that techniques to measure these substances are sparse and new methods are emerging (Albergamo et al. 2019; Gago-Ferrero et al. 2018; Sjerps et al. 2016). Transformation product monitoring of PTMB compounds remains challenging as most of them are so-called unknown unknowns, that is, compounds of which the structure is unknown and which are not present in chemical databases. Indeed, liquid chromatography-mass spectrometry technology has been one of the most competitive areas over the last two decades in terms of instrumental development, with advances in the speed and the sensitivity of analysis. State-of-the-art instruments now allow ultra-trace multiresidue analysis with hundreds of chemicals being measured in a single run, even after a simple direct injection of an aqueous sample (Brunner et al. 2019; Hollender et al. 2017; Reemtsma et al. 2016). Another important development is the popularization of high resolution MS (HRMS) analyzers, which has been a huge step for the identification of transformation products of organic CoECs as well as for the screening of unknown substances (Brunner et al. 2018, 2019). Therefore, many of these CoECs may already be in the environment, going unnoticed (Arp et al. 2017; Gago-Ferrero et al. 2018; Kase et al. 2018; Schulze et al. 2019). Apart from occurrence in effluent samples, prioritized compounds should fill all of the PTB cut-off values from Table 4.

For this purpose five CoECs that are known to be present in STP effluent are assessed: carbamazepine, paracetamol, perfluorooctanoic acid, sulfamethoxazole, and triclosan (Delli Compagni et al. 2020; Fraz et al. 2019; García-Santiago et al. 2017). These CoECs cover a broad range of physicochemical properties in terms of air/water partitioning coefficient (K_{aw}), normalized organic carbon partitioning

Table 4 PTB cut-off hazard classification criteria according to Annex XIII, REACH

Property	PBT-criteria	
Persistence	Fresh- or estuarine water: Marine water: Marine sediment: Fresh- or estuarine sediment: In soil:	$t^{1}/_{2}$ (half-life) > 40 days $t^{1}/_{2} > 60$ days $t^{1}/_{2} > 180$ days $t^{1}/_{2} > 120$ days $t^{1}/_{2} > 120$ days
Toxicity	• A ratio of predicted environmental concentration to predicted no-effect concentration (PEC/PNEC) ≥ 0.01 • Classified as carcinogenic, germ cell mutagenic, or toxic for reproduction • There is other evidence of chronic toxicity, as identified by the classifications: Specific Target Organ Toxicant (STOT)	
Bioaccumulation	Bioconcentration factor (BCF) > 2,000	

Arp et al. (2017), ECHA (2017)

Table 5 Physiochemical properties of selected CoECs

CoEC	Chemical classification	p*K*a (p*K*b)[a]	Log *D* (pH = 7)[a]	Property category[b]
Carbamazepine	Anti-epileptic drug	16	2.8	I
Paracetamol	Nonsteroidal Anti-inflammatory drug	0.4	1.2	II
Perfluorooctanoic acid	Surfactant	−4.2	1.6	III
Sulfamethoxazole	Antibiotic	6.2	0.2	III
Triclosan	Antibiotic	7.7	4.9	I

[a] p*K*a, p*K*b, and Log *D* calculated with Chemaxon (http://www.chemicalize.com)

[b] Properties Category I: neutral and moderate hydrophobic MPs (log*D*(pH 7) > 2); Category II: neutral hydrophilic MPs (logD (pH 7) < 2); Category III: anionic MPs

coefficient (K_{oc}), and ionization state at the environmental pH. In addition, they belong to different CoECs classes (Table 5).

CoECs with a property category I have the capability of passing through lipid bilayers of crop membranes due to their moderate hydrophobicity. Yet, they are still slightly water soluble and capable of traveling into cell fluids (Shenker et al. 2011). Property category III CoECs are characterized by weak interactions and sorption in soil. For example, the majority of sulfamethoxazole would be in the anionic species given a soil pH of 7, with a smaller proportion remaining neutral. The anionic species would repel from soil particles and reside in the soil solution, whereas the neutral species would preferentially interact with organic carbon (Franklin et al. 2015).

5.2 *Risk Assessment*

There is only a risk if exposure occurs above an acceptable level. In the proposed regulation (European Commission 2018), a risk is defined as "the likelihood of identified hazards causing harm in a specified timeframe, including the severity of the consequences." In this chapter risks associated with SSI of STP effluent in regard to the ecosystem and humans are emphasized. Understanding these risks is crucial in allocating trade-offs in water supply, STP effluent reuse, and CoECs emission reduction.

A mixture made up of the organic compounds among the five highest reported concentrations in STP effluent represents a high risk quotient (RQ) of 120.70 (Table 6). RQs were calculated for each CoEC as predicted environmental concentration (PEC)/predicted no-effect concentration (PNEC). The PEC is based on a realistic worst-case scenario, with maximum reported concentrations in STP effluent (*C*max). Except for carbamazepine and perfluorooctanoic acid, all of the chemicals have RQs higher than 1, indicating a risk, paracetamol showing the highest RQ. Sulfamethoxazole is classified by the International Agency for Research and

Table 6 Risk quotients of selected CoECs

	*C*max in STP effluent (ng/l)	PNEC (ng/l)	RQ=PEC/PNEC
Carbamazepine	4,000[a]	9,000[b]	0.5
Paracetamol	32,000[c]	367[d]	87
Perfluorooctanoic acid	66[e]	1.07[e]+06[f]	0.00006
Sulfamethoxazole	25,700[g]	890[h]	28.9
Triclosan	11.3[i]	2.6[f]	4.3
Total			120.70

Maximum concentration found in STP effluent (*C*max = PEC) retrieved from [g]Franklin et al. (2015), [a]Christou et al. (2019a), [c]Pereira et al. (2016), [i]Zheng et al. (2020), [e]Man et al. (2018). PNEC values obtained from [b]Zhao et al. (2017), [d]Riva et al. (2019), [f]Gredelj et al. (2018), [h]Huang et al. (2018)

Cancer (IARC) as possibly carcinogenic to humans (category 2B) (IARC 2016). The other compounds are not classified as to their carcinogenicity.

It should be noted that the RQ calculation does not take into account the filtration and purification function of the soil during SSI. Therefore, this RQ calculation may give an overestimation of the potential risks.

Typically, humans are exposed to a mixture of CoECs, which can give rise to mixture effects, i.e., they can elicit similar effects or exhibit the same mode of action. For mixtures of independently acting chemicals, the effects can be estimated directly from the probability of responses to the individual components (response addition) or the sum of biological responses (effects addition). Both concepts (independent action and dose/concentration addition) are based on the assumption that chemicals in a mixture do not influence each other's toxicity, i.e., they do not interact with each other at the biological target site (Blum et al. 2018; SCHER 2011). However, dose/concentration addition can produce reliable estimates of combined effects, if the components share either a strictly identical molecular mechanism of action or belong to the group of so-called baseline toxicants (Boberg et al. 2019; SCHER 2011; Thomaidi et al. 2016). Yet, interactions may vary according to the relative dose levels, the routes, timing, and duration of exposure. Boberg et al. (2019) suggest a pragmatic step-by- step procedure for mixture risk assessment and propose tools for grouping of chemicals, whereby CoECs should be grouped for mixture risk assessment based on integrated in vivo and in vitro data, read-across as well as computational methods such as QSAR models or integrative systems biology.

Often the Threshold of Toxicological Concern (TTC) concept is used to provide an abbreviated risk assessment for the thousands of low molecular weight contaminants and other chemicals in food, provided that there is a sound intake estimate while specific toxicological data is lacking (Baken et al. 2018; Hollender et al. 2018; Riemenschneider et al. 2016). TTC is defined by examining the distribution of threshold values of the 5th percentile of non-observable effect level and the safety factor which is usually 100 (=10 × 10), reflecting species difference between rodents and humans (10-fold) and individual variations in humans (10-fold). The concept underlying this risk management approach is exactly the principle established by Paracelsus: any poison can be non-toxic if the dose is below the appropriate threshold and by WHO in numerous publications and all regulatory schemes of risk assessment in e.g. OECD countries. This principle cannot be applied to the regulation of genotoxic chemicals. Owing to their DNA interaction properties, genotoxic chemicals are not considered to have a safe threshold or dose (Baken et al. 2018; Bieber et al. 2018; Nohmi 2018).

6 Conclusion

Intentional reuse of sewage treatment plant (STP) effluent with sub-surface irrigation (SSI) can partly solve water scarcity issues. Consequently, an increased demand for STP effluent as freshwater source, rather than discharging it to the surface water, may lead to the installation and optimization of treatment facilities to produce effluent of a desired quality for irrigation purposes. Worldwide, guidelines related to contaminants of emerging concern (CoECs) and water reuse have only been adopted by a few states in the United states. California produced specific national mandatory regulations related to CoECs. At European level, the current proposed regulation for STP effluent reuse lacks minimum requirements for CoECs. Enhancing the water policy framework with STP effluent reuse may promote well-planned water reuse programs, which will require consistent risk-based standards for different types of agricultural irrigation systems.

The quality of the irrigation water that reaches the crop and the risk associated with STP effluent is highly dependent on the method of supply. SSI provides a (saturated) soil barrier, surpassing drip and sprinkler irrigation where the STP effluent comes in direct contact with the crops. On the contrary, SSI directly introduces STP effluent into groundwater which may lead to deep groundwater seepage.

Not many studies are available with regard to the fate and risks for a broad list of CoECs in SSI systems. Indeed, studies done in river bank filtration, managed aquifer recharge, and constructed wetlands have proven that the soil may have the ability to act as a filter and buffer zone. These systems are similar in terms of their anaerobic medium; it can therefore be expected that biotransformation processes which are key removal processes in these systems will also be dominant in SSI. On the other hand, these systems were constructed for purification functions, while SSI also serves as an irrigation system which may have shorter residence times with regard to crop uptake and longer residence times for groundwater seepage. This objective of SSI is the basis for the difference in design and operational conditions compared to the other systems. Therefore, the mechanisms of biotransformation processes for a broad list of CoECs are still unknown. In addition the interplay between aerobic and anaerobic conditions of SSI remains not yet fully understood. Furthermore, the balance between irrigation supply with STP effluent and the minimum stream flow needed for ecosystem functioning should be conserved. As a consequence, to explore the full potential, i.e., risk and opportunities, of STP effluent reuse in SSI, the following topics should be addressed in profound studies:

- Identification of a broad list of CoECs and their transformation products in groundwater, soil, and crops of SSI systems for several years before, during, and after the growing season. The conditions of SSI system will primarily be anaerobic, but sub-oxic conditions are not excluded. These fate studies may additionally pinpoint how and to what degree SSI with STP effluent can contribute to reduced CoECs emission to surface water compared with current direct discharge.
- Anaerobic biotransformation mechanism in SSI and the interplay with aerobic conditions in the rhizosphere. From the constructed wetlands and river bank filtration studies assessed in this review, it can be expected that biotransformation may be the most dominant removal process present in SSI. Especially the residence time distribution during the year can highly influence the effect of biotransformation due to among others microbiological adaptation.
- Adequate risk assessment which results in classifying trade-offs in water supply, STP effluent reuse, and CoECs emission reduction. These trade-offs determine critical factors in upscaling SSI to larger scales.

7 Summary

Worldwide, fresh water scarcity is often caused by a high demand from the agricultural sector that globally accounts for 69% of fresh water withdrawal. This is not only an issue for arid regions with low rainfall and high population density that are prone to increasing water stress; temperate areas with intense agriculture also suffer from frequent non-potable water shortages. The intentional reuse of sewage treatment plant (STP) effluent in sub-surface irrigation (SSI), which is currently discharged in large volumes to surface water, may provide an alternative freshwater source. Additionally, the load of contaminants of emerging concern (CoECs) to surface water may be reduced due to soil passage and related (bio)transformation processes. In this review, the policies and guidelines concerning non-potable water reuse are highlighted. We discuss the processes that affect the fate of CoECs in SSI, and the expectations with regard to exposure and risks. Furthermore, knowledge gaps as well as challenges and opportunities of intentional STP effluent reuse via SSI are addressed with the aim of stimulating future research toward an enhanced understanding of the fate and risks of CoECs in SSI.

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References

Adrion AC, Nakamura J, Shea D, Aitken MD (2016) Screening nonionic surfactants for enhanced biodegradation of polycyclic aromatic hydrocarbons remaining in soil after conventional biological treatment. Environ Sci Technol 50:3838–3845. https://doi.org/10.1021/acs.est.5b05243

Albergamo V, Blankert B, Cornelissen ER, Hofs B, Knibbe WJ, van der Meer W, de Voogt P (2019) Removal of polar organic micropollutants by pilot-scale reverse osmosis drinking water treatment. Water Res 148:535–545. https://doi.org/10.1016/j.watres.2018.09.029

Arden S, Ma X (2018) Constructed wetlands for greywater recycle and reuse: a review. Sci Total Environ 630:587–599. https://doi.org/10.1016/j.scitotenv.2018.02.218

Arp HPH, Brown TN, Berger U, Hale SE (2017) Ranking REACH registered neutral, ionizable and ionic organic chemicals based on their aquatic persistency and mobility. Environ Sci Process Impacts 19:939–955. https://doi.org/10.1039/c7em00158d

Australian Government Initiative (2006) Australian guidelines for water recycling [WWW Document]. http://www.waterquality.gov.au/guidelines/recycled-water. Accessed 26 Apr 2019

Ayars JE, Christen EW, Hornbuckle JW (2006) Controlled drainage for improved water management in arid regions irrigated agriculture. Agric Water Manag 86:128–139. https://doi.org/10.1016/j.agwat.2006.07.004

Ayars JE, Fulton A, Taylor B (2015) Subsurface drip irrigation in California-here to stay? Agric Water Manag 157:39–47. https://doi.org/10.1016/j.agwat.2015.01.001

Baken KA, Sjerps RMA, Schriks M, van Wezel AP (2018) Toxicological risk assessment and prioritization of drinking water relevant contaminants of emerging concern. Environ Int 118:293–303. https://doi.org/10.1016/j.envint.2018.05.006

Beard JE, Bierkens MFP, Bartholomeus RP (2019) Following the water: characterising de facto wastewater reuse in agriculture in the Netherlands. Sustain 11:1–20. https://doi.org/10.3390/su11215936

Benard P, Kroener E, Vontobel P, Kaestner A, Carminati A (2016) Advances in water resources water percolation through the root-soil interface. Adv Water Resour 95:190–198. https://doi.org/10.1016/j.advwatres.2015.09.014

Beneduce L, Gatta G, Bevilacqua A, Libutti A, Tarantino E, Bellucci M, Troiano E, Spano G (2017) Impact of the reusing of food manufacturing wastewater for irrigation in a closed system on the microbiological quality of the food crops. Int J Food Microbiol 260:51–58. https://doi.org/10.1016/j.ijfoodmicro.2017.08.009

Bertelkamp C, Reungoat J, Cornelissen ER, Singhal N, Reynisson J, Cabo AJ, van der Hoek JP, Verliefde ARD (2014) Sorption and biodegradation of organic micropollutants during river bank filtration: a laboratory column study. Water Res 52:231–241. https://doi.org/10.1016/j.watres.2013.10.068

Bertelkamp C, Verliefde ARD, Schoutteten K, Vanhaecke L, Vanden Bussche J, Singhal N, van der Hoek JP (2016) The effect of redox conditions and adaptation time on organic micropollutant removal during river bank filtration: a laboratory-scale column study. Sci Total Environ 544:309–318. https://doi.org/10.1016/j.scitotenv.2015.11.035

Bezza FA, Chirwa EMN (2017) The role of lipopeptide biosurfactant on microbial remediation of aged polycyclic aromatic hydrocarbons (PAHs)-contaminated soil. Chem Eng J 309:563–576. https://doi.org/10.1016/j.cej.2016.10.055

Bieber S, Snyder SA, Dagnino S, Rauch-Williams T, Drewes JE (2018) Management strategies for trace organic chemicals in water – a review of international approaches. Chemosphere 195:410–426. https://doi.org/10.1016/j.chemosphere.2017.12.100

Bijl DL, Biemans H, Bogaart PW, Dekker SC, Doelman JC, Stehfest E, van Vuuren DP (2018) A global analysis of future water deficit based on different allocation mechanisms. Water Resour Res 54:5803–5824. https://doi.org/10.1029/2017WR021688

Bilal M, Adeel M, Rasheed T, Zhao Y, Iqbal HMN (2019) Emerging contaminants of high concern and their enzyme-assisted biodegradation – a review. Environ Int 124:336–353. https://doi.org/10.1016/j.envint.2019.01.011

Blum KM, Andersson PL, Ahrens L, Wiberg K, Haglund P (2018) Persistence, mobility and bioavailability of emerging organic contaminants discharged from sewage treatment plants. Sci Total Environ 612:1532–1542. https://doi.org/10.1016/j.scitotenv.2017.09.006

Boberg J, Dybdahl M, Petersen A, Hass U, Svingen T, Vinggaard AM (2019) A pragmatic approach for human risk assessment of chemical mixtures. Curr Opin Toxicol 15:1–7. https://doi.org/10.1016/j.cotox.2018.11.004

Bonaiti G, Borin M (2010) Efficiency of controlled drainage and subirrigation in reducing nitrogen losses from agricultural fields. Agric Water Manag 98:343–352. https://doi.org/10.1016/j.agwat.2010.09.008

Brunner A, Kolkman A, Hofman-Caris R, Bertelkamp C, Siegers W, Vughs D, ter Laak T (2018) BTO report transformation products in the water (BTO 2018.017 | February 2018)

Brunner AM, Vughs D, Siegers W, Bertelkamp C, Hofman-Caris R, Kolkman A, ter Laak T (2019) Monitoring transformation product formation in the drinking water treatments rapid sand filtration and ozonation. Chemosphere 214:801–811. https://doi.org/10.1016/j.chemosphere.2018.09.140

Brunsch AF, ter Laak TL, Christoffels E, Rijnaarts HHM, Langenhoff AAM (2018) Retention soil filter as post-treatment step to remove micropollutants from sewage treatment plant effluent. Sci Total Environ 637–638:1098–1107. https://doi.org/10.1016/j.scitotenv.2018.05.063

California Department of Public Health (CDPH) (2018) Regulations related to recycled water. Title 22 code of regulations. Californa Waterboards. Draft amendment to the recycled water policy

California Water Boards (2019) Laws and regulations [WWW Document]. https://www.waterboards.ca.gov/laws_regulations/. Accessed 1 Apr 2019

Campa MF, Techtmann SM, Gibson CM, Zhu X, Patterson M, Garcia De Matos Amaral A, Ulrich N, Campagna SR, Grant CJ, Lamendella R, Hazen TC (2018) Impacts of glutaraldehyde on microbial community structure and degradation potential in streams impacted by hydraulic fracturing. Environ Sci Technol 52:5989–5999. https://doi.org/10.1021/acs.est.8b00239

Ccanccapa A, Masiá A, Andreu V, Picó Y (2016) Spatio-temporal patterns of pesticide residues in the Turia and Júcar Rivers (Spain). Sci Total Environ 540:200–210. https://doi.org/10.1016/j.scitotenv.2015.06.063

Chen B, Han MY, Peng K, Zhou SL, Shao L, Wu XF, Wei WD, Liu SY, Li Z, Li JS, Chen GQ (2018) Global land-water nexus: agricultural land and freshwater use embodied in worldwide supply chains. Sci Total Environ 613–614:931–943. https://doi.org/10.1016/j.scitotenv.2017.09.138

Christou A, Agüera A, Bayona JM, Cytryn E, Fotopoulos V, Lambropoulou D, Manaia CM, Michael C, Revitt M, Schröder P, Fatta-Kassinos D (2017a) The potential implications of reclaimed wastewater reuse for irrigation on the agricultural environment: the knowns and unknowns of the fate of antibiotics and antibiotic resistant bacteria and resistance genes – a review. Water Res 123:448–467. https://doi.org/10.1016/j.watres.2017.07.004

Christou A, Karaolia P, Hapeshi E, Michael C, Fatta-Kassinos D (2017b) Corrigendum to: "Long-term wastewater irrigation of vegetables in real agricultural systems: Concentration of pharmaceuticals in soil, uptake and bioaccumulation in tomato fruits and human health risk assessment." [Water Res. 109 (2017) 24–34] (S004313541). Water Res. 119:312. https://doi.org/10.1016/j.watres.2017.04.065

Christou A, Kyriacou MC, Georgiadou EC, Papamarkou R, Hapeshi E, Karaolia P, Michael C, Fotopoulos V, Fatta-Kassinos D (2019a) Uptake and bioaccumulation of three widely prescribed pharmaceutically active compounds in tomato fruits and mediated effects on fruit quality attributes. Sci Total Environ 647:1169–1178. https://doi.org/10.1016/j.scitotenv.2018.08.053

Christou A, Papadavid G, Dalias P, Fotopoulos V, Michael C, Bayona JM, Piña B, Fatta-Kassinos D (2019b) Ranking of crop plants according to their potential to uptake and accumulate contaminants of emerging concern. Environ Res 170:422–432. https://doi.org/10.1016/j.envres.2018.12.048

Cipullo S, Prpich G, Campo P, Coulon F (2018) Assessing bioavailability of complex chemical mixtures in contaminated soils: progress made and research needs. Sci Total Environ 615:708–723. https://doi.org/10.1016/j.scitotenv.2017.09.321

Council of the European Communities (1991) Directive concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC). Off J Eur Communities

Council of the European Communities (2000) Water Framework Directive (2000/60/EC). Off J Eur Communities 1. https://doi.org/10.1039/ap9842100196

Cycoń M, Mrozik A, Piotrowska-Seget Z (2019) Antibiotics in the soil environment – degradation and their impact on microbial activity and diversity. Front Microbiol 10. https://doi.org/10.3389/fmicb.2019.00338

Delli Compagni R, Gabrielli M, Polesel F, Turolla A, Trapp S, Vezzaro L, Antonelli M (2020) Risk assessment of contaminants of emerging concern in the context of wastewater reuse for irrigation: an integrated modelling approach. Chemosphere 242:125185. https://doi.org/10.1016/j.chemosphere.2019.125185

Doucette WJ, Shunthirasingham C, Dettenmaier EM, Zaleski RT, Fantke P, Arnot JA (2018) A review of measured bioaccumulation data on terrestrial plants for organic chemicals: metrics, variability, and the need for standardized measurement protocols. Environ Toxicol Chem 37:21–33. https://doi.org/10.1002/etc.3992

Drewes JE, Uwe H, Zhitenev Veronikaa SK (2017) Characterization of unplanned water reuse in the EU final report:64. https://doi.org/10.2779/597701

Dulio V, van Bavel B, Brorström-Lundén E, Harmsen J, Hollender J, Schlabach M, Slobodnik J, Thomas K, Koschorreck J (2018) Emerging pollutants in the EU: 10 years of NORMAN in support of environmental policies and regulations. Environ Sci Eur 30. https://doi.org/10.1186/s12302-018-0135-3

ECHA (2017) Guidance on information requirements and chemical safety assessment – part E: risk characterisation. Eur Chem Agency:1–58. https://doi.org/10.2823/139408

EEC Council (1991) 91/271/EEC of 21 May 1991 concerning urban waste-water treatment. EEC Counc Dir 10. https://doi.org/http://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX:31991L0271

EurEau (2018) EurEau position on the regulation on minimum requirements for water reuse. 32:1–7

European Comission (2008) Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy. Off J Eur Union:L348/84–L348/97. https://doi.org/http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:32008L0105

European Commission (2004) Regulation (EC) No 852/2004 of the European Parliament and of the Council of 29 April 2004 on the hygiene of foodstuffs. Off J Eur Communities 2002:1–54. https://doi.org/http://eur-lex.europa.eu/pri/en/oj/dat/2003/l_285/l_28520031101en00330037.pdf

European Commission (2005) Regulation (EC) No. 2073/2005 of The European Parliament and of The Council of 15 November 2005 on microbiological criteria for foodstuffs. Off J Eur Union

European Commission (2006) Commission regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs. Off J Eur Union 2006:5–24

European Commission (2011) Commission Regulation (EU) No 142/2011 of 25 February 2011 implementing Regulation (EC) No 1069/2009 of the European Parliament and of the Council laying down health rules as regards animal by-products and derived products not intended for human consumption. Off J Eur Union

European Commission (2014) Directive of 20 June 2014 amending Annex II to Directive 2006/118/EC of the European Parliament and of the Council on the protection of groundwater against pollution and deterioration (2014/80/EU) 2014, 4

European Commission (2018) Proposal for a REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on minimum requirements for water reuse

European Parliament and the Council of the European Union (2005) Regulation (EC) No 183/2005 of the European Parliament and of the Council of 12 January 2005 laying down requirements for feed hygiene. Off J Eur Union 2004

European Parliament and the Council (2005) Regulation (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC. Off J Eur Union

Europian Commission (2012) Blueprint to Safeguard Europe's Water Resources.

Faour-Klingbeil D, Todd ECD (2018) The impact of climate change on raw and untreated wastewater use for agriculture, especially in arid regions: a review. Foodborne Pathog Dis 15:61–72. https://doi.org/10.1089/fpd.2017.2389

Fekadu S, Alemayehu E, Dewil R, Van der Bruggen B (2019) Pharmaceuticals in freshwater aquatic environments: a comparison of the African and European challenge. Sci Total Environ 654:324–337. https://doi.org/10.1016/j.scitotenv.2018.11.072

Food and Agriculture Organization of the United Nations (2016) Theme: water uses [WWW Document]. http://www.fao.org/nr/water/aquastat/water_use/index.stm. Accessed 14 Apr 2018

Franklin AM, Williams CF, Andrews DM, Woodward EE, Watson JE (2015) Uptake of three antibiotics and an antiepileptic drug by wheat crops spray irrigated with wastewater treatment plant effluent. J Environ Qual 45:546. https://doi.org/10.2134/jeq2015.05.0257

Fraz S, Lee AH, Pollard S, Srinivasan K, Vermani A, Wilson JY (2019) Parental gemfibrozil exposure impacts zebrafish F1 offspring, but not subsequent generations. Aquat Toxicol 212:194–204. https://doi.org/10.1016/j.aquatox.2019.04.020

Gago-Ferrero P, Krettek A, Fischer S, Wiberg K, Ahrens L (2018) Suspect screening and regulatory databases: a powerful combination to identify emerging micropollutants. Environ Sci Technol 52:6881–6894. https://doi.org/10.1021/acs.est.7b06598

Garcia-Cuerva L, Berglund EZ, Binder AR (2016) Public perceptions of water shortages, conservation behaviors, and support for water reuse in the U.S. Resour Conserv Recycl 113:106–115. https://doi.org/10.1016/j.resconrec.2016.06.006

García-Santiago X, Garrido JM, Lema JM, Franco-Uría A (2017) Fate of pharmaceuticals in soil after application of STPs products: influence of physicochemical properties and modelling approach. Chemosphere 182:406–415. https://doi.org/10.1016/j.chemosphere.2017.05.049

Ghattas AK, Fischer F, Wick A, Ternes TA (2017) Anaerobic biodegradation of (emerging) organic contaminants in the aquatic environment. Water Res 116:268–295. https://doi.org/10.1016/j.watres.2017.02.001

Gillefalk M, Massmann G, Nützmann G, Hilt S (2018) Potential impacts of induced bank filtration on surface water quality: a conceptual framework for future research. Water (Switzerland):10. https://doi.org/10.3390/w10091240

Goldstein M, Shenker M, Chefetz B (2014) Insights into the uptake processes of wastewater-borne pharmaceuticals by vegetables. Environ Sci Technol 48:5593–5600. https://doi.org/10.1021/es5008615

Gonzales-Gustavson E, Rusiñol M, Medema G, Calvo M, Girones R (2019) Quantitative risk assessment of norovirus and adenovirus for the use of reclaimed water to irrigate lettuce in Catalonia. Water Res 153:91–99. https://doi.org/10.1016/j.watres.2018.12.070

Gorito AM, Ribeiro AR, Almeida CMR, Silva AMT (2017) A review on the application of constructed wetlands for the removal of priority substances and contaminants of emerging concern listed in recently launched EU legislation. Environ Pollut 227:428–443. https://doi.org/10.1016/j.envpol.2017.04.060

Gredelj A, Barausse A, Grechi L, Palmeri L (2018) Deriving predicted no-effect concentrations (PNECs) for emerging contaminants in the river Po, Italy, using three approaches: assessment factor, species sensitivity distribution and AQUATOX ecosystem modelling. Environ Int 119:66–78. https://doi.org/10.1016/j.envint.2018.06.017

Greskowiak J, Hamann E, Burke V, Massmann G (2017) The uncertainty of biodegradation rate constants of emerging organic compounds in soil and groundwater – a compilation of literature values for 82 substances. Water Res 126:122–133. https://doi.org/10.1016/j.watres.2017.09.017

Grill G, Khan U, Lehner B, Nicell J, Ariwi J (2016) Risk assessment of down-the-drain chemicals at large spatial scales: model development and application to contaminants originating from urban areas in the Saint Lawrence River Basin. Sci Total Environ 541:825–838. https://doi.org/10.1016/j.scitotenv.2015.09.100

Gude VG (2017) Desalination and water reuse to address global water scarcity. Rev Environ Sci Biotechnol 16:591–609. https://doi.org/10.1007/s11157-017-9449-7

Gunarathna MHJP, Sakai K, Nakandakari T, Kazuro M, Onodera T, Kaneshiro H, Uehara H, Wakasugi K (2017) Optimized subsurface irrigation system (OPSIS): beyond traditional subsurface irrigation. Water (Switzerland) 9. https://doi.org/10.3390/w9080599

Gupta D, Madramootoo CA (2017) Fate and transport of Escherichia coli in tomato production. Expo Heal 9:13–25. https://doi.org/10.1007/s12403-016-0217-7

Halden RU (2015) Epistemology of contaminants of emerging concern and literature meta-analysis. J Hazard Mater 282:2–9. https://doi.org/10.1016/j.jhazmat.2014.08.074

Hamann E, Stuyfzand PJ, Greskowiak J, Timmer H, Massmann G (2016) The fate of organic micropollutants during long-term/long-distance river bank filtration. Sci Total Environ 545–546:629–640. https://doi.org/10.1016/j.scitotenv.2015.12.057

Hollender J, Schymanski EL, Singer H, Ferguson PL (2017) Non-target screening with high resolution mass spectrometry in the environment: ready to go? Environ Sci Technol. https://doi.org/10.1021/acs.est.7b02184

Hollender J, Rothardt J, Radny D, Loos M, Epting J, Huggenberger P, Borer P, Singer H (2018) Comprehensive micropollutant screening using LC-HRMS/MS at three riverbank filtration sites to assess natural attenuation and potential implications for human health. Water Res X 1:100007. https://doi.org/10.1016/j.wroa.2018.100007

Hong PY, Julian TR, Pype ML, Jiang SC, Nelson KL, Graham D, Pruden A, Manaia CM (2018) Reusing treated wastewater: consideration of the safety aspects associated with antibiotic-resistant bacteria and antibiotic resistance genes. Water (Switzerland):10. https://doi.org/10.3390/w10030244

Huang Q, Bu Q, Zhong W, Shi K, Cao Z, Yu G (2018) Derivation of aquatic predicted no-effect concentration (PNEC) for ibuprofen and sulfamethoxazole based on various toxicity endpoints and the associated risks. Chemosphere 193:223–229. https://doi.org/10.1016/j.chemosphere.2017.11.029

International Agency for Research and Cancer (2016) Some chemicals used as solvents and in polymer manufacture, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans

International Organization for Standardization (2015) Guidelines for treated wastewater use for irrigation projects [WWW Document]. ISO 16075. https://www.iso.org/standard/62756.html

IWA (2018) The reuse opportunity. Atmos Chem Phys Discuss 1–26. https://doi.org/10.5194/acp-2016-176

Jaime N, Peta N, Tobias H, Stefanie K, Maria K, Roland M, Thorsten R, Rita S, Beate E (2018) Application of cell-based bioassays to evaluate treatment efficacy of conventional and intensified treatment wetlands. Environ Sci Water Res Technol 4(2):206–217. https://doi.org/10.1016/j.watres.2017.09.004

Jaramillo MF, Restrepo I (2017) Wastewater reuse in agriculture: a review about its limitations and benefits. Sustain 9. https://doi.org/10.3390/su9101734

Jin J, Sun K, Wang Z, Han L, Pan Z, Wu F, Liu X, Zhao Y, Xing B (2015) Characterization and phthalate esters sorption of organic matter fractions isolated from soils and sediments. Environ Pollut 206:24–31. https://doi.org/10.1016/j.envpol.2015.06.031

Joint Research Centre (2017) Minimum quality requirements for water reuse in agricultural irrigation and aquifer recharge – towards a water reuse regulatory instrument at EU level. https://doi.org/10.2760/887727

Kahl S, Nivala J, van Afferden M, Müller RA, Reemtsma T (2017) Effect of design and operational conditions on the performance of subsurface flow treatment wetlands: emerging organic contaminants as indicators. Water Res 125:490–500. https://doi.org/10.1016/j.watres.2017.09.004

Kase R, Javurkova B, Simon E, Swart K, Buchinger S, Könemann S, Escher BI, Carere M, Dulio V, Ait-Aissa S, Hollert H, Valsecchi S, Polesello S, Behnisch P, di Paolo C, Olbrich D, Sychrova E, Gundlach M, Schlichting R, Leborgne L, Clara M, Scheffknecht C, Marneffe Y, Chalon C, Tusil P, Soldan P, von Danwitz B, Schwaiger J, Morán A, Bersani F, Perceval O, Kienle C, Vermeirssen E, Hilscherova K, Reifferscheid G, Werner I (2018) Screening and risk management solutions for steroidal estrogens in surface and wastewater. Trends Anal Chem 102:343–358. https://doi.org/10.1016/j.trac.2018.02.013

Khalid S, Shahid M, Natasha IB, Sarwar T, Shah AH, Niazi NK (2018) A review of environmental contamination and health risk assessment of wastewater use for crop irrigation with a focus on low and high-income countries. Int J Environ Res Public Health 15:1–36. https://doi.org/10.3390/ijerph15050895

Kibuye FA, Gall HE, Elkin KR, Ayers B, Veith TL, Miller M, Jacob S, Hayden KR, Watson JE, Elliott HA (2019) Fate of pharmaceuticals in a spray-irrigation system: from wastewater to groundwater. Sci Total Environ 654:197–208. https://doi.org/10.1016/j.scitotenv.2018.10.442

Klaassen C (2008) Toxicology: the basic science of poison. McGraw-Hill, New York. ISBN 978-1-259-86374-5

Lamichhane S, Bal Krishna KC, Sarukkalige R (2016) Polycyclic aromatic hydrocarbons (PAHs) removal by sorption: a review. Chemosphere 148:336–353. https://doi.org/10.1016/j.chemosphere.2016.01.036

Larsson DGJ, Andremont A, Bengtsson-Palme J, Brandt KK, de Roda Husman AM, Fagerstedt P, Fick J, Flach C-F, Gaze WH, Kuroda M, Kvint K, Laxminarayan R, Manaia CM, Nielsen KM, Plant L, Ploy M-C, Segovia C, Simonet P, Smalla K, Snape J, Topp E, van Hengel AJ, Verner-Jeffreys DW, Virta MPJ, Wellington EM, Wernersson A-S (2018) Critical knowledge gaps and research needs related to the environmental dimensions of antibiotic resistance. Environ Int 117:132–138. https://doi.org/10.1016/j.envint.2018.04.041

Legislative Counsel Bureau (2018) Senate Bill No. 966 1–4

Li Y, Zhu G, Ng WJ, Tan SK (2014) A review on removing pharmaceutical contaminants from wastewater by constructed wetlands: design, performance and mechanism. Sci Total Environ 468–469:908–932. https://doi.org/10.1016/j.scitotenv.2013.09.018

Luo Y, Guo W, Hao H, Duc L, Ibney F, Zhang J, Liang S, Wang XC (2014) Science of the total environment a review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Sci Total Environ 473–474:619–641. https://doi.org/10.1016/j.scitotenv.2013.12.065

Magdeburg A, Stalter D, Schlu M, Ternes T (2014) ScienceDirect evaluating the efficiency of advanced wastewater treatment: target analysis of organic contaminants and (geno-) toxicity assessment tell a different 0. https://doi.org/10.1016/j.watres.2013.11.041

Man YB, Chow KL, Tsang YF, Lau FTK, Fung WC, Wong MH (2018) Fate of bisphenol A, perfluorooctanoic acid and perfluorooctanesulfonate in two different types of sewage treatment works in Hong Kong. Chemosphere 190:358–367. https://doi.org/10.1016/j.chemosphere.2017.10.001

Manaia CM (2017) Assessing the risk of antibiotic resistance transmission from the environment to humans: non-direct proportionality between abundance and risk. Trends Microbiol 25:173–181. https://doi.org/10.1016/j.tim.2016.11.014

Mao J, Nierop KGJ, Dekker SC, Dekker LW, Chen B (2019) Understanding the mechanisms of soil water repellency from nanoscale to ecosystem scale: a review. J Soil Sediment 19:171–185. https://doi.org/10.1007/s11368-018-2195-9

Martínez J, Reca J (2014) Water use efficiency of surface drip irrigation versus an alternative subsurface drip irrigation method. J Irrig Drain Eng 140:04014030. https://doi.org/10.1061/(asce)ir.1943-4774.0000745

Massoud MA, Kazarian A, Alameddine I, Al-Hindi M (2018) Factors influencing the reuse of reclaimed water as a management option to augment water supplies. Environ Monit Assess 190. https://doi.org/10.1007/s10661-018-6905-y

Miller EL, Nason SL, Karthikeyan KG, Pedersen JA (2016) Root uptake of pharmaceuticals and personal care product ingredients. Environ Sci Technol 50:525–541. https://doi.org/10.1021/acs.est.5b01546

Mukherjee B, Adhikary S (2019) Chapter-3 water efficient rice cultivation: technological interventions, Water efficient rice cultivation: technological interventions. https://doi.org/10.22271/ed.book.386

Munz NA, Burdon FJ, de Zwart D, Junghans M, Melo L, Reyes M, Schönenberger U, Singer HP, Spycher B, Hollender J, Stamm C (2016) Pesticides drive risk of micropollutants in wastewater-impacted streams during low flow conditions. Water Res 110:366–377. https://doi.org/10.1016/j.watres.2016.11.001

Ncube S, Madikizela LM, Chimuka L, Nindi MM (2018) Environmental fate and ecotoxicological effects of antiretrovirals: a current global status and future perspectives. Water Res 145:231–247. https://doi.org/10.1016/j.watres.2018.08.017

Nguyen T, Westerhoff P, Furlong E, Kolpin DW, Batt AL, Mash HE, Schenck KM, Scott Boone J, Jacelyn R, Glassmeyer ST (2018) Peer reviewed modeled de facto reuse and contaminants of emerging concern in drinking water source. J Am Water Works Assoc 110(4):E2–E18. https://doi.org/10.1002/awwa.1052

Nham HTT, Greskowiak J, Nödler K, Rahman MA, Spachos T, Rusteberg B, Massmann G, Sauter M, Licha T (2015) Modeling the transport behavior of 16 emerging organic contaminants during soil aquifer treatment. Sci Total Environ 514:450–458. https://doi.org/10.1016/j.scitotenv.2015.01.096

Nohmi T (2018) Thresholds of genotoxic and non-genotoxic carcinogens. Toxicol Res 34:281–290. https://doi.org/10.5487/TR.2018.34.4.281

NORMAN (2019) NORMAN Suspect List Exchange [WWW Document]. https://www.norman-network.com/?q=suspect-list-exchange

Otto S, Banitz T, Thullner M, Harms H, Wick LY (2016) Effects of facilitated bacterial dispersal on the degradation and emission of a desorbing contaminant. Environ Sci Technol 50:6320–6326. https://doi.org/10.1021/acs.est.6b00567

Pan M, Wong CKC, Chu LM (2014) Distribution of antibiotics in wastewater-irrigated soils and their accumulation in vegetable crops in the Pearl River Delta, Southern China. J Agric Food Chem 62:11062–11069. https://doi.org/10.1021/jf503850v

Pan Z, Song C, Li L, Wang H, Pan Y, Wang C, Li J, Wang T, Feng X (2019) Membrane technology coupled with electrochemical advanced oxidation processes for organic wastewater treatment: recent advances and future prospects. Chem Eng J 1–19. https://doi.org/10.1016/j.cej.2019.01.188

Park J, Cho KH, Lee E, Lee S, Cho J (2018) Sorption of pharmaceuticals to soil organic matter in a constructed wetland by electrostatic interaction. Sci Total Environ 635:1345–1350. https://doi.org/10.1016/j.scitotenv.2018.04.212

Peng L, Zhang XT, Yin J, Xu SY, Zhang Y, Xie DT, Li ZL (2016) Geobacter sulfurreducens adapts to low electrode potential for extracellular electron transfer. Electrochim Acta 191:743–749. https://doi.org/10.1016/j.electacta.2016.01.033

Pepper IL, Gerba CP (2018) Risk of infection from Legionella associated with spray irrigation of reclaimed water. Water Res 139:101–107. https://doi.org/10.1016/j.watres.2018.04.001

Pereira AMPT, Silva LJG, Lino CM, Meisel LM, Pena A (2016) Assessing environmental risk of pharmaceuticals in Portugal: an approach for the selection of the Portuguese monitoring stations in line with Directive 2013/39/EU. Chemosphere 144:2507–2515. https://doi.org/10.1016/j.chemosphere.2015.10.100

Petrie B, Barden R, Kasprzyk-Hordern B (2015) A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. Water Res 72:3–27. https://doi.org/10.1016/j.watres.2014.08.053

Petrie B, Rood S, Smith BD, Proctor K, Youdan J, Barden R, Kasprzyk-Hordern B (2018) Biotic phase micropollutant distribution in horizontal sub-surface flow constructed wetlands. Sci Total Environ 630:648–657. https://doi.org/10.1016/j.scitotenv.2018.02.242

Picó Y, Alvarez-Ruiz R, Alfarhan AH, El-Sheikh MA, Alobaid SM, Barceló D (2019) Uptake and accumulation of emerging contaminants in soil and plant treated with wastewater under real-world environmental conditions in the Al Hayer area (Saudi Arabia). Sci Total Environ 652:562–572. https://doi.org/10.1016/j.scitotenv.2018.10.224

Poff NLR (2018) Beyond the natural flow regime? Broadening the hydro-ecological foundation to meet environmental flows challenges in a non-stationary world. Freshw Biol 63:1011–1021. https://doi.org/10.1111/fwb.13038

Poursat BAJ, Van Spanning RJM, de Voogt P, Parsons J (2019) Implications of microbial adaptation for the assessment of environmental persistence of chemicals. Crit Rev Environ Sci Technol. https://doi.org/10.1080/10643389.2019.1607687

Price J, Fielding KS, Gardner J, Leviston Z, Green M (2015) Developing effective messages about potable recycled water: the importance of message structure and content. Water Resour Res 51:2174–2187. https://doi.org/10.1002/2014WR016514

Quesada HB, Baptista ATA, Cusioli LF, Seibert D, de Oliveira Bezerra C, Bergamasco R (2019) Surface water pollution by pharmaceuticals and an alternative of removal by low-cost adsorbents: a review. Chemosphere 222:766–780. https://doi.org/10.1016/j.chemosphere.2019.02.009

Reemtsma T, Berger U, Arp HPH, Gallard H, Knepper TP, Neumann M, Quintana JB, De Voogt P (2016) Mind the gap: persistent and mobile organic compounds – water contaminants that slip through. Environ Sci Technol 50:10308–10315. https://doi.org/10.1021/acs.est.6b03338

Reid T, Droppo IG, Weisener CG (2020) Tracking functional bacterial biomarkers in response to a gradient of contaminant exposure within a river continuum. Water Res 168:115167. https://doi.org/10.1016/j.watres.2019.115167

Ren X, Zeng G, Tang L, Wang J, Wan J, Liu Y, Yu J, Yi H, Ye S, Deng R (2018) Sorption, transport and biodegradation – an insight into bioavailability of persistent organic pollutants in soil. Sci Total Environ 610–611:1154–1163. https://doi.org/10.1016/j.scitotenv.2017.08.089

Rengasamy P (2018) Irrigation water quality and soil structural stability: a perspective with some new insights. Agronomy 8:72. https://doi.org/10.3390/agronomy8050072

Ricart S, Rico AM, Ribas A (2019) Risk-yuck factor nexus in reclaimed wastewater for irrigation: comparing farmers' attitudes and public perception. Water (Switzerland):11. https://doi.org/10.3390/w11020187

Rice J, Wutich A, White DD, Westerhoff P (2016) Comparing actual de facto wastewater reuse and its public acceptability: a three city case study. Sustain Cities Soc 27:467–474. https://doi.org/10.1016/j.scs.2016.06.007

Riemenschneider C, Al-Raggad M, Moeder M, Seiwert B, Salameh E, Reemtsma T (2016) Pharmaceuticals, their metabolites, and other polar pollutants in field-grown vegetables irrigated with treated municipal wastewater. J Agric Food Chem 64:5784–5792. https://doi.org/10.1021/acs.jafc.6b01696

Riva F, Zuccato E, Davoli E, Fattore E, Castiglioni S (2019) Risk assessment of a mixture of emerging contaminants in surface water in a highly urbanized area in Italy. J Hazard Mater 361:103–110. https://doi.org/10.1016/j.jhazmat.2018.07.099

Rizzo L, Krätke R, Linders J, Scott M, Vighi M, de Voogt P (2018) Proposed EU minimum quality requirements for water reuse in agricultural irrigation and aquifer recharge: SCHEER scientific advice. Curr Opin Environ Sci Heal 2:7–11. https://doi.org/10.1016/j.coesh.2017.12.004

Roberts J, Kumar A, Du J, Hepplewhite C, Ellis DJ, Christy AG, Beavis SG (2016) Pharmaceuticals and personal care products (PPCPs) in Australia's largest inland sewage treatment plant, and its contribution to a major Australian river during high and low flow. Sci Total Environ 541:1625–1637. https://doi.org/10.1016/j.scitotenv.2015.03.145

SCHER (2011) Scientific Committee on Health and Environmental Risks SCHER Scientific Committee on Emerging and Newly Identified Health Risks SCENIHR Scientific Committee on Consumer Safety SCCS Toxicity and Assessment of Chemical Mixtures. Eur Commision Toxic Assess Chem Mix 1–50. https://doi.org/10.2772/37863

Schmitt H, Blaak H, Kemper M, van Passel M, Hierink F, van Leuken J, De Roda Husman AM, van der Grinten E, Rutgers M, Schijven R, de Man H, Hoeksma P, Zuidema T (2017) Bronnen va antibioticaresistentie in het milieu en mogelijke maatregelen. 114. https://doi.org/10.21945/RIVM-2017-0058

Schulze S, Sättler D, Neumann M, Arp HPH, Reemtsma T, Berger U (2018) Using REACH registration data to rank the environmental emission potential of persistent and mobile organic chemicals. Sci Total Environ 625:1122–1128. https://doi.org/10.1016/j.scitotenv.2017.12.305

Schulze S, Zahn D, Montes R, Rodil R, Quintana JB, Knepper TP, Reemtsma T, Berger U (2019) Occurrence of emerging persistent and mobile organic contaminants in European water samples. 153:80–90. https://doi.org/10.1016/j.watres.2019.01.008

Shakir E, Zahraw Z, Al-Obaidy AHMJ (2017) Environmental and health risks associated with reuse of wastewater for irrigation. Egypt J Pet 26:95–102. https://doi.org/10.1016/j.ejpe.2016.01.003

Shenker M, Harush D, Ben-Ari J, Chefetz B (2011) Uptake of carbamazepine by cucumber plants – a case study related to irrigation with reclaimed wastewater. Chemosphere 82:905–910. https://doi.org/10.1016/j.chemosphere.2010.10.052

Singleton DR, Adrion AC, Aitken MD (2016) Surfactant-induced bacterial community changes correlated with increased polycyclic aromatic hydrocarbon degradation in contaminated soil. Appl Microbiol Biotechnol 100:10165–10177. https://doi.org/10.1007/s00253-016-7867-z

Siyal AA, Skaggs TH (2009) Measured and simulated soil wetting patterns under porous clay pipe sub-surface irrigation. Agric Water Manag 96:893–904. https://doi.org/10.1016/j.agwat.2008.11.013

Sjerps RMA, Vughs D, van Leerdam JA, ter Laak TL, van Wezel AP (2016) Data-driven prioritization of chemicals for various water types using suspect screening LC-HRMS. Water Res 93:254–264. https://doi.org/10.1016/j.watres.2016.02.034

Smith HM, Brouwer S, Jeffrey P, Frijns J (2018) Public responses to water reuse – understanding the evidence. J Environ Manage 207:43–50. https://doi.org/10.1016/j.jenvman.2017.11.021

Sousa JCG, Ribeiro AR, Barbosa MO, Pereira MFR, Silva AMT (2017) A review on environmental monitoring of water organic pollutants identified by EU guidelines. J Hazard Mater 344:146–162. https://doi.org/10.1016/j.jhazmat.2017.09.058

Šteflová M, Koop S, Elelman R, Vinyoles J, Van Leeuwen CJK (2018) Governing non-potable water-reuse to alleviate water stress: the case of Sabadell, Spain. Water (Switzerland) 10:1–16. https://doi.org/10.3390/w10060739

Tal A (2016) Rethinking the sustainability of Israel's irrigation practices in the Drylands. Water Res 90:387–394. https://doi.org/10.1016/j.watres.2015.12.016

Thebo AL, Drechsel P, Lambin EF, Nelson KL (2017) A global, spatially-explicit assessment of irrigated croplands influenced by urban wastewater flows. Environ Res Lett 12. https://doi.org/10.1088/1748-9326/aa75d1

Thomaidi VS, Stasinakis AS, Borova VL, Thomaidis NS (2016) Assessing the risk associated with the presence of emerging organic contaminants in sludge-amended soil: a country-level analysis. Sci Total Environ 548–549:280–288. https://doi.org/10.1016/j.scitotenv.2016.01.043

Tran HN, You SJ, Hosseini-Bandegharaei A, Chao HP (2017) Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review. Water Res 120:88–116. https://doi.org/10.1016/j.watres.2017.04.014

Tran NH, Reinhard M, Gin KYH (2018) Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions – a review. Water Res 133:182–207. https://doi.org/10.1016/j.watres.2017.12.029

UN-Water (2018) Sustainable development goal 6 synthesis report on water and sanitation 2018, Un. https://doi.org/10.1126/science.278.5339.827

USEPA (2012) Guidelines for water reuse. U.S. Agency Int Dev. 643. https://doi.org/EPA16251R-921004

van der Waals MJ, Pijls C, Sinke AJC, Langenhoff AAM, Smidt H, Gerritse J (2018) Anaerobic degradation of a mixture of MtBE, EtBE, TBA, and benzene under different redox conditions. https://doi.org/10.1007/s00253-018-8853-4

van Wezel AP, van den Hurk F, Sjerps RMA, Meijers EM, Roex EWM, ter Laak TL (2018) Impact of industrial waste water treatment plants on Dutch surface waters and drinking water sources. Sci Total Environ 640–641:1489–1499. https://doi.org/10.1016/j.scitotenv.2018.05.325

Voulvoulis N (2018) Water reuse from a circular economy perspective and potential risks from an unregulated approach. Curr Opin Environ Sci Heal 2:32–45. https://doi.org/10.1016/j.coesh.2018.01.005

Wagner TV, Parsons JR, Rijnaarts HHM, de Voogt P, Langenhoff AAM (2018) A review on the removal of conditioning chemicals from cooling tower water in constructed wetlands. Crit Rev Environ Sci Technol 48:1094–1125. https://doi.org/10.1080/10643389.2018.1512289

Wang L, Hossen EH, Aziz TN, Ducoste JJ, de los Reyes FL (2020) Increased loading stress leads to convergence of microbial communities and high methane yields in adapted anaerobic co-digesters. Water Res 169:115155. https://doi.org/10.1016/j.watres.2019.115155

Winkler P, Kaiser K, Jahn R, Mikutta R, Fiedler S, Cerli C, Kölbl A, Schulz S, Jankowska M, Schloter M, Müller-Niggemann C, Schwark L, Woche SK, Kümmel S, Utami SR, Kalbitz K (2019) Tracing organic carbon and microbial community structure in mineralogically different soils exposed to redox fluctuations. Biogeochemistry 143:31–54. https://doi.org/10.1007/s10533-019-00548-7

World Health Organization (WHO) (2006) Excreta and greywater in agriculture. Guidel. Safe use wastewater, excreta, greywater, vol II Wa, 204. https://doi.org/10.1007/s13398-014-0173-7.2

Yadav MK, Short MD, Aryal R, Gerber C, van den Akker B, Saint CP (2017) Occurrence of illicit drugs in water and wastewater and their removal during wastewater treatment. Water Res 124:713–727. https://doi.org/10.1016/j.watres.2017.07.068

Yang Y, Ok YS, Kim KH, Kwon EE, Tsang YF (2017) Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: a review. Sci Total Environ 596–597:303–320. https://doi.org/10.1016/j.scitotenv.2017.04.102

Zapata N, Robles O, Playán E, Paniagua P, Romano C, Salvador R, Montoya F (2018) Low-pressure sprinkler irrigation in maize: differences in water distribution above and below the crop canopy. Agric Water Manag 203:353–365. https://doi.org/10.1016/j.agwat.2018.03.025

Zhang Y, Sallach JB, Hodges L, Snow DD, Bartelt-Hunt SL, Eskridge KM, Li X (2016) Effects of soil texture and drought stress on the uptake of antibiotics and the internalization of Salmonella in lettuce following wastewater irrigation. Environ Pollut 208:523–531. https://doi.org/10.1016/j.envpol.2015.10.025

Zhao W, Wang B, Wang Y, Deng S, Huang J, Yu G (2017) Deriving acute and chronic predicted no effect concentrations of pharmaceuticals and personal care products based on species sensitivity distributions. Ecotoxicol Environ Saf 144:537–542. https://doi.org/10.1016/j.ecoenv.2017.06.058

Zheng G, Yu B, Wang Y, Ma C, Chen T (2020) Removal of triclosan during wastewater treatment process and sewage sludge composting – a case study in the middle reaches of the Yellow River. Environ Int 134:105300. https://doi.org/10.1016/j.envint.2019.105300

Herbicide Exposure and Toxicity to Aquatic Primary Producers

J. Arie Vonk and Michiel H. S. Kraak

Contents

Abbreviations

AF	Assessment factor
EC50	Median effect concentration
ECx	Calculated concentration at which x% of the tested species are affected

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K_{OC}	Organic carbon-water partitioning coefficient
K_{OW}	Octanol-water partition coefficient
LC50	Median lethal concentration
SSD	Species sensitivity distribution

1 Introduction

Herbicides are the most used pesticides in North America and in Europe, and accordingly, herbicides are the most frequently detected pesticide group in North American and European surface waters (Moschet et al. 2014; Booij et al. 2015; Lopez et al. 2015; Schreiner et al. 2016). Herbicides are often well soluble in water to increase the systemic uptake by plants. This increases the chances of transport and discharges into water, and consequently, a wide variety of herbicides often exceed environmental quality standards (EQS) and regulatory acceptable concentrations (RACs) in European surface waters (Moschet et al. 2014; Schreiner et al. 2016; Casado et al. 2019). Hence, herbicides are expected to have a significant effect on aquatic ecosystem functioning (Moschet et al. 2014; Knauer 2016; Schreiner et al. 2016). Herbicides are often phytotoxic to non-target aquatic organisms such as algae and macrophytes, and these adverse effects on primary producers can cascade up the food web altering community structure (DeLorenzo et al. 2001; Ralph et al. 2007; Wood et al. 2016), since algae and plants provide food and habitat for higher trophic levels (e.g. Whatley et al. 2014; Bakker et al. 2016).

Since herbicides specifically target essential processes in primary producers, all substances with a herbicidal mode of action require regulatory testing on non-target primary producers. For the USA, data on five aquatic plants are required and in Europe data on two algal species and on one to three macrophytes. Higher-tier approaches focus on the most sensitive taxonomic groups identified in tier 1 based on obligatory data requirements from regulatory testing. If macrophytes are an order of magnitude more sensitive than algae, additional tests with macrophytes are required. Still, despite the prevalence and their documented effects on primary producers, herbicides remain relatively understudied compared to pesticides targeting various groups of animals. More toxicity tests focus on fish and macroinvertebrates compared to tests focusing on the effects of herbicides on macrophytes and algae in the environment (Birk et al. 2012). Yet, for both marine and freshwater environments, standardized ecotoxicity tests are available for microalgae (unicellular microorganisms sometimes forming larger colonies), including the prokaryotic Cyanobacteria (blue-green algae) and the eukaryotic Chlorophyta (green algae) and Bacillariophyceae (diatoms) (OECD 2011; USEPA 2012d; Wood et al. 2016). Macrophytes (macroalgae and aquatic plants) are multicellular organisms, the latter consisting of differentiated tissues, with several species included in standardized ecotoxicity tests (Knauer et al. 2006; Feiler et al. 2014; Van Wijngaarden and Arts 2018). While macroalgae grow in the water compartment only, aquatic plants are divided into groups related to their growth form (emergent; free-floating; submerged and sediment-rooting; floating and sediment-rooting) and can extend from the sediment (roots, stolons and rhizomes) through the water into the air (Cronk and Fennesy 2001).

There is strong evidence that anthropogenic compounds threaten the ecological integrity and consequently the biodiversity of almost half of the water bodies in Europe, with herbicides accounting for 96% of the risks to algae (Malaj et al. 2014). The aim of the present review was therefore to give an overview of the current state of science concerning herbicide exposure and toxicity to aquatic primary producers. To this end, we assessed the open literature to address the sources and fate of herbicides in the aquatic environment, their bioavailability and subsequent uptake by algae and plants. Next, the hazard of herbicides to primary producers was assessed, including their modes of action and toxicity to algae and aquatic plants determined in the various available toxicity tests, making an inventory of reported effect concentrations. Retrospective risk assessments were performed to determine whether the presence of herbicides represented an actual risk to aquatic primary producers in various environments, including water and sediment of freshwater and marine/estuarine ecosystems.

2 Exposure of Aquatic Primary Producers to Herbicides

Herbicides originate from different urban and agricultural usages and are transferred to surface waters from point and diffuse sources by several transport pathways (Moser et al. 2018). Exposure of aquatic primary producers to herbicides can occur through water for all algae and aquatic plants, through air for emergent and floating plants and through sediment for rooting plants and benthic algae (Fig. 1). For phytoplankton and free-living submerged aquatic plants, water is the main medium through which they are exposed to dissolved herbicides. Resuspension of sediments contaminated with herbicides can result in the release of herbicides into the water column (Pandey et al. 2019). Resuspension can therefore also expose phytoplankton and free-living aquatic plants indirectly to herbicides accumulated in the sediment. Spraying of herbicides near emergent and floating plants can result in direct exposure to herbicides transported by wind (spray drift), while volatilization of herbicides and subsequent transport by wind (vapour drift) can also result in exposure of these aquatic plant growth forms (EFSA PPR 2015). All growth forms of aquatic plants with roots extending into the sediment are additionally exposed via this environmental compartment. Sediment exposure also occurs in macroalgae with rhizoids extending into the sediment (e.g. Characeae and *Caulerpa* spp.) and in microalgae living on top of the sediment (e.g. benthic autotrophic biofilms including diatoms). In this chapter we will focus on sources, fate and concentrations of herbicides in the aquatic environment leading to exposure and subsequent uptake of herbicides by aquatic primary producers through surface water and pore water.

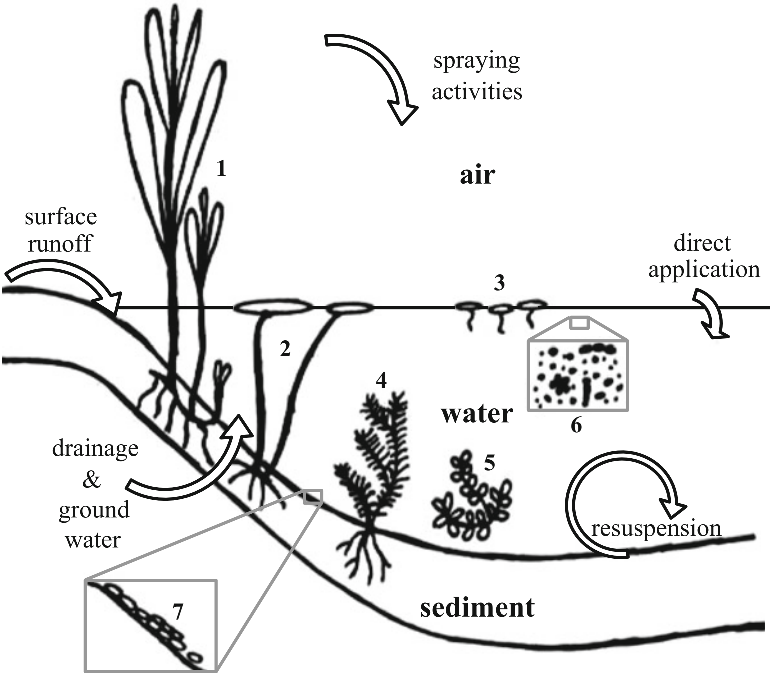

Fig. 1 Potential exposure routes to herbicides for different growth forms of aquatic primary producers through air, water and sediment from indirect sources and direct application. Growth forms depicted are [1] emergent plants, [2] rooting floating plants, [3] free-floating plants, [4] rooting submerged plants and rhizoid macroalgae, [5] free-living submerged plants, [6] phytoplankton and [7] benthic microalgae and biofilms

2.1 Sources of Herbicides in the Aquatic Environment

Herbicides can enter surface waters from several sources through various processes, with the main source being runoff and drainage from agricultural fields (e.g. Knauer 2016). Urban sources of herbicide pollution to surface water are wastewater treatment plants, storm sewers or combined sewer overflows and runoff from urban areas (Wittmer et al. 2010; Ensminger et al. 2013). Herbicides flow into the ditches surrounding the agricultural fields, spread over the surface waters from diffuse and point sources and drain into the groundwater. The mean annual use of herbicides in agriculture, on average 0.69 kg/ha during 2010–2014, is generally higher compared to use of insecticides (0.22 kg/ha) and fungicides and bactericides together (0.32 kg/ha) (Zhang 2018). Compounds ranking at the top of global herbicides use (expressed as tonnes active ingredient in 2014) are amides (38.3k), phenoxy hormone products (23.9k), bipyridyls (17.2k), urea derivatives (9.5k), dinitroanilines (6.5k), carbamate herbicides (4.0k), sulfonylureas (2.7k) and uracil (0.6k) (Zhang 2018).

New compounds are synthesized at high rates (Chemical Abstracts Service, https://www.cas.org/). However, few herbicides make it into a developed and registered product actually entering the market, e.g. in 2019 in Europe only approval for florpyrauxifen-benzyl. The environmental hazard and risk of new compounds have to be investigated and assessed, before any herbicide may enter the market. From a European perspective, the tier 1 data requirement always has to be fulfilled before putting an herbicide on the market. For herbicides, this includes a significant amount of information on effects on non-target plants, which is thus available from regulatory data, but often not yet from the open literature. Herbicides are often marketed as products with two to three different active ingredients. Accordingly, there will be at least some information from regulatory testing on the mixture toxicity of these active ingredients. However, application of a wide variety of herbicides by different users in a river catchment increases the potential of interactions between the active herbicides in the environment. This is especially relevant since there are additional legacies of pesticides in aquatic ecosystems, consisting of herbicides that have already been banned from the regions (e.g. triazine herbicides terbuthylazine and simazine in the EU; Rasmussen et al. 2015).

Herbicides are also directly applied in the aquatic environment to eradicate expansions of invasive aquatic plant species in various parts of the world, especially in North America, Australia and New Zealand (Lake and Minteer 2018). Invasive species targeted by herbicide application include *Phragmites australis* (common reed), *Myriophyllum spicatum* (Eurasian watermilfoil), *Hydrilla verticillata* (water thyme) and *Eichornia crassipes* (water hyacinth) (Hershner and Havens 2008; Kettenring and Adams 2011; Hussner et al. 2017). Various herbicides are used for the control of these invasive species, including glyphosate, 2,4-D, picloram, diquat and triclopyr (Kettenring and Adams 2011; Hussner et al. 2017). Often herbicide applications are combined with other management strategies, including biological controls and plant competition, although herbicide application can influence biological control through direct and indirect effects of the herbicide on other biota (Lake and Minteer 2018). Generally, herbicides need carefully timed and repeated applications, have modest success and induce significant collateral risk (Hershner and Havens 2008). Common problems associated with the application of herbicides include effects on non-target species and novel invasions following control of initial invasive species (Kettenring and Adams 2011). One solution is the application of systemic herbicides to dewatered or drawdown canals to allow herbicides to directly target the plant populations while strongly limiting the transport of the herbicide by the water (Hussner et al. 2017). Hence, the unintentional as well as intentional sources of herbicides in the aquatic environment are numerous, evidently leading to the widespread presence of herbicides, inevitably leading to the exposure of non-target primary producers.

2.2 *Fate of Herbicides in the Aquatic Environment*

The fate of herbicides in the environment is determined by the combination of (1) the chemical properties and the formulation of the pesticides, (2) the local environmental conditions and (3) the timing, rate and method of application (Kookana et al. 1998; Rabodonirina et al. 2015). Together, they govern the fate of herbicides in the aquatic environment by influencing retention processes (e.g. adsorption to particles and uptake by organisms), transformation processes (abiotic and biotic degradation into other (toxic) compounds), and transport processes of the herbicides. Transport of herbicides into aquatic environments is driven by runoff from nearby agricultural or other terrestrial environments, drift of herbicides along the catchment and leaching of herbicides into groundwater sources. Leaching of herbicides into groundwater is a rather negligible source of contamination in Europe, since any compound that might end up in groundwater at a concentration greater than 0.1 μg/L would be prohibited. Instead, in agricultural areas where drainage canals are used, relevant amounts of herbicides may be transported via drainage water into receiving aquatic ecosystems. In this way, local hydrological processes form the main drivers for the mobilization and transport of herbicides into surface water (Klaus et al. 2014). Charged and hydrophilic herbicides generally remain in the water column. However, herbicides with a higher octanol-water partitioning coefficient (K_{OW}) are more hydrophobic and accumulate at higher rates in the sediment through sorption on clay particles and organic matter (Voice and Weber 1983).

Many herbicides interact with the dissolved and particulate organic matter in the water, resulting in the adsorption of active herbicides (Voice and Weber 1983; Chefetz et al. 2004; Pandey et al. 2019). These aggregates may sink to the bottom causing the transport of herbicides from the water column to the sediment. Accumulation of herbicides in the sediment is primarily determined by the organic carbon content of the solid and the clay-size fraction (Chefetz et al. 2004; Clausen et al. 2004) causing sediments to be the main sink for many herbicides. Furthermore, herbicides can be adsorbed or taken up by aquatic primary producers (Crum et al. 1999; Turgut 2005). Especially vascular species, like *Cabomba aquatica*, *Eichhornia crassipes*, *Elodea canadensis*, *Lemna minor*, *Ludwigia peploides*, *Myriophyllum aquaticum* and *Spirodela polyrhiza*, have efficient capacities to take up pesticides from the aquatic environment, leading to accumulation of herbicides at target sites (Turgut 2005; Olette et al. 2008; Anudechakul et al. 2015; Pérez et al. 2017). Reported removal rates of herbicides by phytoplankton species vary considerably, ranging from negligible or a few percent after a couple of days (Weiner et al. 2004; Chalifour et al. 2016) up to 80% removal after 24 h (González-Barreiro et al. 2006), revealing the potential of aquatic primary producers as sink for herbicides.

Environmental conditions such as the pH, redox and light conditions and temperature are important factors determining the degradation of herbicides in the environment. In the absence of light, degradation of herbicides can be one order of magnitude slower (Mercurio et al. 2016). Surface water pH can alter the charge of herbicides and the hydrolysis and degradation rates of herbicides (Schneiders et al. 1993). Degradation of herbicides is often faster at the sediment-water interface compared to the surface water (Rice et al. 2004; Mercurio et al. 2016). Degradation processes of herbicides in the sediment including hydrolysis, volatilization and microbial degradation are related to the pH, redox conditions and temperature of the sediment (Kookana et al. 1998; Graymore et al. 2001). Especially at the interface between water and sediments, microbial activity is higher compared to both surface water and in the sediment. Under anaerobic conditions in aquatic ecosystems, as often present in the sediment, biodegradation is generally limited (Mercurio et al. 2016; Ghattas et al. 2017). Contrary, microbial activity is stimulated by plant exudates, resulting in higher degradation rates or accumulation of herbicides nearby roots in both the water and in the sediment (Anudechakul et al. 2015; Singh and Singh 2016). Overall, microbes are the main vehicle for remediation of herbicides in the environment (Singh and Singh 2016). Half-lives of the herbicides in aquatic ecosystems can be over 100 days, as observed by Mercurio et al. (2016) for diuron, atrazine, hexazinone and tebuthiuron. Only for metolachlor exposed under light conditions and for 2,4-D exposed in dark conditions, these authors measured half-lives of less than 100 days. Metabolites of herbicides are significantly less biologically active than the parent compounds and are generally more polar and more water soluble than the parent compounds. This results in different transport behaviours between the parent herbicides and the metabolites (Boxall et al. 2004). Although, at least in Europe, the hazard and risks of the main metabolites have to be assessed in prospective risk assessments (e.g. EFSA PPR 2013, 2015), the bioavailability and mode of action of metabolites is not always known (Busch et al. 2016).

2.3 *Concentrations of Herbicides in the Aquatic Environment*

Changing and differential use has had a strong impact on the concentrations of herbicides in the aquatic environment. Nevertheless, herbicides are the main contributor to the total amount (expressed in μg/L) of pesticides present in aquatic ecosystems (Casado et al. 2019). The most frequently detected herbicides present in the highest concentrations in source waters in the USA in 1999–2000 had a photosynthesis-inhibiting mode of action (Coupe and Blomquist 2004). In a more recent study, herbicides with an auxin stimulating mode of action (2,4-D, triclopyr and dicamba) were three of the five most frequently detected herbicides (Ensminger et al. 2013). Out of the ten most frequently used herbicides in the USA in 1999–2000 (Coupe and Blomquist 2004), only two, atrazine and simazine, were detected in streams and groundwaters in Europe in 2016 (Schreiner et al. 2016). In a recent analysis of 29 small waterways across 10 countries in the European Union, Casado et al. (2019) analysed in total 103 different pesticides, 45% of them being herbicides. Herbicides were detected in 52% of the samples, and the most frequently detected herbicides were terbuthylazine (100% of the samples) and metolachlor (90%). The same substances are also included in the list of the most frequently detected pesticides in the USA, Germany, France and the Netherlands compiled by Schreiner et al. (2016).

Detection of herbicides is often related to recent application on nearby fields and rain-induced runoff to adjacent aquatic ecosystems. In terms of total amount of pesticides (as ng/L) detected by Casado et al. (2019), 97% corresponded to herbicides, which was mainly due to the outstandingly high concentrations of six herbicides (dimethenamid, MCPA, 2,4-D, ethofumesate, prosulfocarb and terbuthylazine) present in concentrations above 1,000 ng/L at specific sites. These six herbicides were also reported by Moschet et al. (2014) in small Swiss rivers. Concentrations of specific herbicides in surface waters are generally not very high, although a large number of different herbicides can be found. Yet, high peak values with short exposure times occur generally in small streams and ditches related to application in nearby agricultural fields and concurring runoff to these aquatic ecosystems. In larger streams and water bodies lower in the catchment, peak values of specific herbicides are lower due to dilution, while at the same time more different herbicides are present. Monitoring studies on herbicides in the aquatic environment have focused often on the water phase (e.g. Schreiner et al. 2016), while these herbicides have been detected in biota and sediments as well (e.g. Masiá et al. 2013). In fact, herbicides quickly disappear from the surface waters through absorption to the sediment, degradation into other compounds through various processes including hydrolysis and photolysis or accumulation in plants (Kookana et al. 1998; Ramezani et al. 2008; Remucal 2014). The concentrations of herbicides are related to the sediment type (organic matter, sand and clay content) (Kronvang et al. 2003), and sediments have been shown to be a sink for many anthropogenic pollutants including various herbicides. Sediments can also become sources of pesticides. Studying aquatic systems influenced mainly by urban runoff in the USA, Ensminger et al. (2013) observed that concentrations of the most frequently detected pesticides in sediments (bifenthrin and other pyrethroids) increased strongly during storm events in the water. Hence, they concluded that resuspension of sediments was a source of bifenthrin for surface waters.

Comparing herbicides in surface waters and sediments is challenging, since only a few studies present an overview of the most detected herbicides in sediments. Comparing the most frequently detected herbicides in European rivers for sediments (Massei et al. 2018) and surface waters (Schreiner et al. 2016) showed similarities as well as differences between both compartments (Table 1). The five most frequently detected herbicides in the sediment are also in the top ten of the surface waters, albeit in different order, and for terbuthylazine and atrazine, mainly their transformation products were measured in the sediment. The remaining top ten of most frequently detected herbicides were completely different for sediments and surface waters, indicating that the herbicide mixture present in both compartments differs substantially. It is therefore argued that for a complete risk assessment of herbicides, both aquatic environmental compartments, water and sediment, should be taken into consideration.

Although herbicides are also released from treated wastewater discharged from point sources (Munz et al. 2017), diffuse pollution is often the dominant source for herbicides (Moschet et al. 2014). Quantification of herbicides in streams is therefore challenging and especially demanding due to the high spatial-temporal concentration dynamics, which require large sampling and analytical efforts to obtain representative data on the actual water quality (Wittmer et al. 2010). Grab sampling generally provides only a snapshot of the herbicides present in a water body (Jones et al. 2015) and results in underestimations of concentrations, except when sampling occurred

Table 1 The top ten most frequently detected herbicides in the surface waters and sediments of river ecosystems in Europe (rank # in each environmental compartment) based on percentage sites at which the compound was present, analysed by Schreiner et al. (2016; surface water) and by Massei et al. (2018; sediment)

Herbicide			Surface water		Sediment	
Compound	CAS	MoA	Rank #	% Sites detected	Rank #	% Sites detected
Acetochlor	34256821	Inhibition of cell division	-		6	16.7
Atrazine/2-hydroxyatrazine	1912249/ 2163680	Photosynthesis inhibition/?	5	25.9	2	40.0
Bentazon	25057890	Photosynthesis inhibition	8	22.8	-	
Diuron	330541	Photosynthesis inhibition	2	46.2	3	36.7
Flurtamone	96525234	Carotenoid biosynthesis inhibition	-		10	10.0
Irgarol	28159980	Photosynthesis inhibition	-		7	13.3
Isoproturon	34123596	Photosynthesis inhibition	1	51.0	4	26.7
MCPA	94746	Synthetic auxin	3	36.7	-	
Mecoprop	93652	Synthetic auxin	7	22.9	-	
Metazachlor	67129082	Inhibition of cell division	9	22.3	-	
Metolachlor	51218452	Inhibition of cell division	6	25.2	5	23.3
Simazine	122349	Photosynthesis inhibition	10	21.4	-	
Simetryn	1014706	Photosynthesis inhibition	-		9	13.3
Terbuthylazine/terbuthylazine-2-hydroxy	5915413/ 66753079	Photosynthesis inhibition/?	4	29.4	1	70.0
Terbutryn	886500	Photosynthesis inhibition	-		8	13.3

Modes of action (MoA) were obtained from Busch et al. (2016). (rank # '-' means that the herbicide is not in the top ten for that environmental compartment)

during a runoff event (e.g. Casado et al. 2019). Two possible solutions are event-driven sampling and passive sampling. The primary transport routes for pesticides to aquatic ecosystems are surface runoff and tile drainage induced by heavy precipitation events (Leu et al. 2004; Stehle and Schulz 2015). During precipitation events after pesticide application, maximum pesticide concentrations can be a factor of 10–100 higher than during base-flow conditions (e.g. Rasmussen et al. 2015). Therefore, assessing exposure by event-driven sampling following spray application outperforms the widely used automatic water sampling at fixed intervals (Lorenz et al. 2017). Passive sampling can overcome the limitations of grab sampling by exposing a sorbent in the aquatic environment for several weeks to months, accumulating herbicides from the water over time (Vrana et al. 2005). In this way, passive sampling integrates fluctuations in herbicide concentrations in time and simultaneously enriches surface water samples to an extent that (bio)analytical detection limits become very low (De Baat et al. 2019). Passive samplers have been successfully applied to quantify exposure to both lipophilic and more water-soluble compounds (e.g. range log K_{OW} 0.47–4.92; Fernández et al. 2014).

Since hydrological processes are the main drivers for the mobilization and transport of pollutants into surface water (Klaus et al. 2014), key transport mechanisms for herbicides can be derived from insight into concentration and discharge dynamics at the catchment outlet (Wittmer et al. 2010). An alternative method is the event-based hysteresis analysis, regarded as a valuable tool to infer the source areas, transport mechanisms, storage and mobilization capacity of herbicides and biologically active metabolites (Tang et al. 2017). Modelling expected concentrations of herbicides in catchments can provide essential insights into the exposure of aquatic primary producers to herbicides. Moser et al. (2018) showed that key drivers and processes are reasonably well approximated by a simple model that includes land use as a proxy for herbicide use, weather data for the timing of herbicide applications and discharge or precipitation as drivers for transport. They could predict the timing and level of peak concentrations within a factor of 2 to 3 in a spatially distributed manner at the scale of large river basins. Better quantification of episodic pesticide pollution events would result in more comprehensive assessments of variations in herbicide exposure (Munz et al. 2017), and coupled progress in modelling, such as the FOCUS modelling approach, and in measuring herbicide concentrations in the field remain necessary to improve exposure assessments in aquatic ecosystems (Moser et al. 2018).

2.4 Bioavailability of Herbicides to Aquatic Primary Producers

The bioavailable concentration is defined as the concentration that is freely available for uptake, crossing an organism's cellular membrane from the medium the organism inhabits at a given time (Semple et al. 2004). The bioavailability of herbicides depends on the molecular characteristics of the herbicide and on environmental conditions (Landrum et al. 1996; Delle Site 2001), but is also greatly influenced by the test species and their physiology (Gomes and Juneau 2017). Furthermore, after entering the environment, bioavailability of herbicides is altered by the prevailing environmental conditions of the soil, surface waters and sediments (Delle Site 2001; Semple et al. 2013). Only by direct contact to herbicides of aquatic primary producers through nearby spraying activities (direct or wind-driven), the resulting exposure is not altered through processes influencing bioavailability of the herbicide (Lockhart et al. 1989; EFSA PPR 2015).

Environmental conditions affecting the bioavailability of herbicides in the water column are mainly temperature, pH and dissolved organic matter (DOM) concentrations and quality (Landrum et al. 1996). Since herbicides generally have a low hydrophobicity (log $K_{OW} < 3$), the impact of particles on their bioavailability is generally small (Knauer et al. 2017). Water and particle-associated concentrations of herbicides are estimated based on the organic carbon-water partitioning coefficient (K_{OC}). As for neutral organic compounds, the log K_{OC} of herbicides correlates positively with the octanol-water partitioning coefficient (log K_{OW}), but for polar and ionizable herbicides, K_{OW} is a weaker predictor of the K_{OC} (Delle Site 2001). Also, black carbon can sorb herbicides, making them less available to primary producers (Knauer et al. 2006; Semple et al. 2013). Bioavailability of herbicides is high when they are weakly adsorbed or dissolved, in contrast to being part of more complex aggregates or when strongly bound to minerals (Eggleton and Thomas 2004).

The bioavailability of herbicides in sediments depends on a wide range of environmental conditions: sediment particle size distribution, sediment total organic carbon concentration and composition, DOM and colloid concentrations in pore water and sediment redox conditions (Landrum et al. 1996). Sorption and desorption from sediment particles under different conditions make that the exposure and bioavailability of organic contaminants in sediment is difficult to predict. The organic matrix of the sediment is competing with the organism's lipids for the available herbicide molecules (Landrum and Fisher 1998). In sediments, typically between 16 and 50% of the herbicides is bioavailable depending on the compound and characteristics of the sediment (Lamoureux and Brownawell 1999). Bioavailability of herbicides in sediments is determined by adsorption, desorption, non-extractable residue formation and biodegradation, which are all occurring interdependent and in parallel, with the latter also depending on the availability of the herbicide to organisms degrading the compounds (e.g. microorganisms) (Kanissery et al. 2019). Finally, interaction between sediment and surface water can also enhance the bioavailability of herbicides in the water. Sediment resuspension and exchange between surface water and pore water act as important emission sources for both historic-use and current-use herbicides to the water column (Cui et al. 2020).

In regulatory risk assessments, predicted concentrations for herbicides in surface waters are derived using models (e.g. European FOrum for the Co-ordination of pesticide fate models and their USe (FOCUS)), which distinguish between exposure to dissolved and particle-associated compound concentrations, because the dissolved concentration is thought to be the best predictor of bioavailability (Knauer et al. 2017). Assessment of the bioavailability of herbicides in the water column can be achieved by passive sampling, exposing a sorbent in the aquatic environment to accumulate available herbicides from the water over time (Vrana et al. 2005; De Baat et al. 2019). Characterization of the bioavailability of herbicides in the sediment can also be conducted using passive samplers, which have been developed to indirectly measure the freely dissolved concentration of compounds by chemical partitioning (e.g. Wang et al. 2018). Likewise, the ecotoxicological relevant concentration (ERC) in herbicide effect and risk assessment is considered to be the freely dissolved herbicide concentration in pore water and overlying water (ESFA PPR 2015).

2.5 Uptake of Herbicides by Aquatic Primary Producers

Aquatic primary producers take up herbicides from the water and depending on their growth form also from the air (emergent and floating plants) and from the sediment and pore water (all rooting plants, macroalgae with rhizoids and benthic algal communities). Uptake from the air is mainly the result of (intentional) spraying activities nearby aquatic ecosystems and is induced by direct contact of the herbicides dissolved in droplets with the leaves of the plants (Hussner et al. 2017). Aquatic primary producers take up herbicides directly from the surface water and sediment pore water through their cell membranes. Mechanisms for uptake of herbicides by aquatic primary producers are strongly depending on chemical properties of the herbicides. Small and nonpolar ($\log K_{OW} < 1$) herbicides can diffuse into the cell passively by dissolving through the membrane's hydrophobic core, driven by a concentration gradient (Hsu and Kleier 1996), while for large or strongly charged herbicides, active transport via protein transporters is needed (Ge et al. 2014). Dissolved weakly acidic herbicides penetrate the cell membranes primarily in their undissociated lipophilic form and accumulate by an ion trapping mechanism (Fahl et al. 1995). Accumulation inside the cells by ion trapping is based on the relatively low permeability of the membranes to the dissociated species (Devine et al. 1987) and differences in pH between surface water and cell cytoplasm. Uptake of these herbicides by aquatic primary producers is thus strongly influenced by the pH of the environment (Fahl et al. 1995; de Carvalho et al. 2007b).

Reported uptake rates of herbicides vary strongly between compounds and between aquatic primary producer species. For various species of phytoplankton, uptake rates of 1–3% of the total amount of atrazine available in the test vials have been measured over 24 h using ^{14}C-atrazine (Tang et al. 1998; Weiner et al. 2004), while for *Microcystis novacekii*, an uptake rate of around 25% of the total available atrazine over 96 h has been reported (Campos et al. 2013). This large range in uptake rates may be due to differences in phytoplankton cell size and lipid composition (Tang et al. 1998; Tuckey et al. 2002; Weiner et al. 2004). Smaller phytoplankton cells with higher surface area-to-volume ratios will incorporate more herbicides and will be more sensitive to exposure compared to larger phytoplankton cells (Tang et al. 1998; Weiner et al. 2004). Besides cell size, also cell lipid content and composition affect the ability of algae to take up lipophilic compounds, since the presence of sterols influences the fluidity and permeability of cell membranes (Tuckey et al. 2002). In addition to cell characteristics, also environmental conditions influence the uptake of herbicides by aquatic primary producers. Temperature and light conditions alter the uptake of herbicides by phytoplankton species mainly through changes in cell size and photosynthetic activity, although responses to interactions between light, temperature and herbicides are species-specific (Gomes and Juneau 2017). Moreover, the uptake of herbicides by phytoplankton species can occur extremely rapid, with nearly 90% of the total uptake occurring within the first hour of exposure of the algae (Tang et al. 1998), indicating that short pulse exposures occurring after runoff or spill events can rapidly affect phytoplankton communities.

The uptake of herbicides by the roots of aquatic macrophytes occurs also fast, with various phenylureas (range log K_{OW} 1.0–3.7) reaching an equilibrium in *Lagarosiphon major* within 24 h of exposure (de Carvalho et al. 2007b). The uptake of herbicides by aquatic plants occurs often by partitioning of the compound over the cell membrane (Hsu and Kleier 1996). Accumulation of herbicides in aquatic plants is described well for most non-ionized compounds by equilibration into the aqueous phase in the plant cells together with partitioning onto the plant solids; however, the uptake of some herbicides (isoproturon and chlorotoluron) was better explained using solvation descriptors (de Carvalho et al. 2007b). These herbicides are taken up by specific binding at their site of action in the plant. The uptake of the herbicide isoproturon was ascribed to specific binding to the D1 protein of the photosynthetic PSII complex (Feurtet-Mazel et al. 1996). According to Knuteson et al. (2002), the age of the plant also influences the uptake rate of herbicides, since 4-week-old aquatic plants took up more simazine than 2-week-old plants. However, the tissue burden normalized for plant biomass was lower in the older plants (Knuteson et al. 2002).

Rooted aquatic plants can take up herbicides via both the roots and the leaves, with herbicide-specific differences in relative uptake rates between shoot and root (Turgut and Fomin 2002; Turgut 2005). The uptake by the roots was related linearly to the external herbicide concentrations over a wide concentration range, implying that transport across the membrane proceeds via non-facilitated diffusion (Devine et al. 1987). Briggs et al. (1982) reported a very strong relationship between the lipophilicity (log K_{OW}) of compounds and the transpiration stream concentration factor (TSCF). However, this was only applicable to emergent aquatic macrophytes, since submerged aquatic plants do not experience leaf transpiration (Turgut 2005). Still, a high K_{OW} value increased the uptake rate of sediment-associated herbicides via the pore water due to the high lipid content of macrophytes (Jones and Winchell 1984; Guilizzoni 1991; Cedergreen et al. 2005). In contrast, the more polar herbicides are rapidly taken up by macrophyte roots directly from the pore water (Burešová et al. 2013).

Translocation of nutrients and energy, but also other compounds, plays an important role in the exchange between shoots and roots of macrophytes. After the contact of herbicides to macrophytes has been established, they can either act as contact herbicides (e.g. diquat) and be non-mobile, i.e. only affecting the part of the organisms that it comes into contact with, or act as systemic herbicides (e.g. glyphosate and imazapyr) and be mobile, i.e. can be translocated through the organisms via the phloem or xylem (Netherland 2014). Contact herbicides only influence the plant parts directly exposed to the herbicide, like floating and emergent parts when exposed to herbicide spraying (Lockhart et al. 1989), with potential regrowth possible from non-exposed plant parts. Translocation through the plant via the phloem or xylem enables the systemic herbicides to affect all parts of the plant, limiting recovery or regrowth from stored resources in belowground parts. After a rapid uptake of linuron by *Elodea canadensis* and *Myriophyllum spicatum* shoots, translocation to the roots of this herbicide occurred within 1–3 days (Diepens et al. 2014a). After atrazine exposure of *Hydrilla verticillata* in solution, Hinman and Klaine (1992) observed that uptake and release approached equilibrium within 1 and 2 h for shoot and root tissue, respectively. Translocation of compounds through the plant is directly related to their water solubility (Hinman and Klaine 1992). Translocation of three analogues of phenylurea herbicides in *Myriophyllum aquaticum* was passive and reached optimal efficiency for herbicides with a log K_{OW} value of around 1.8 (de Carvalho et al. 2007a). Heine et al. (2015) developed a mechanistic model of toxicokinetic processes to predict the uptake and the elimination of herbicides, as well as the distribution processes between plant compartments (leaves, stems, roots) of *M. spicatum*. Their results showed that toxicokinetic patterns were mainly based on two chemical-specific parameters: the cuticular permeability and the plant/water partition coefficient.

Besides translocation of herbicides to different plant parts or cell structures, detoxification can occur after the uptake of herbicides by aquatic primary producers. Uptake by aquatic plants can accelerate degradation of the herbicide by metabolic processes (Fernandez et al. 1999; de Carvalho et al. 2007b). Glutathione-S-transferases are the main group of enzymes involved in this process by conjugating herbicides with tripeptide glutathione (Dhir et al. 2009). The biodegradation mechanism for metabolism of simazine probably involves dealkylation into hydroxysimazine followed by storage of end products in vacuoles (Knuteson et al. 2002). In this way, there is an interaction between the influence of exposure of aquatic primary producers to herbicides and the removal of herbicides by these species. Differences in sensitivity and mechanisms to deal with herbicides can therefore influence overall species composition in areas prone to herbicide exposure (Gomes and Juneau 2017).

Toxicokinetic/toxicodynamic (TKTD) models provide a conceptual framework to better understand the causes for species-specific sensitivities to a single compound, as well as the causes for different toxicities of different compounds to a single species (Ashauer and Escher 2010). TKTD models are based on the principle that processes influencing internal exposure of an organism (TK) are separated from the processes that lead to damage and effects (TD) (EFSA PPR 2018). TKTD models appear furthermore advantageous in terms of gaining a mechanistic understanding of the chemical mode of action and deriving time-independent parameters (Baudrot and Charles 2019). This is especially relevant since exposure time is an important source of uncertainty, which is associated with chemical-specific toxicokinetic and toxicodynamic characteristics (Wu et al. 2020). Different types of TKTD models have been successfully developed, including the general unified threshold model of survival (GUTS) and models for primary producers (EFSA PPR 2018; Baudrot and Charles 2019). For aquatic primary producers exposed to pesticides, TKTD models have been developed for algae, *Lemna* and *Myriophyllum* (EFSA PPR 2018). Although TKTD models are species- and compound-specific, toxicity data can be used derived from both standard test species and additional species for model calibrations. However, for validation of TKTD models, compound-specific and species-specific datasets from independent refined-exposure experiments are required.

3 Toxicity of Herbicides to Aquatic Primary Producers

3.1 Mode of Action of Herbicides

There is a wide diversity of herbicides that have been synthesized to attack specific biochemical targets in plants. In an attempt to classify herbicides by mode of action, a system of 22 different categories is often used (Sherwani et al. 2015). Here we present a simplified classification specifying only eight categories (Plant and Soil Sciences eLibrary 2019; Table 2). Inhibition of photosynthesis can occur through disruption of various steps in the photosynthetic process (Vonk et al. 2009). Triazine herbicides, like atrazine, simazine, metribuzin and phenylureas, like diuron, linuron and isoproturon block the electron transfer in the PSII system (Feurtet-Mazel et al. 1996; Van den Brink et al. 2006), while the herbicide isoproturon reduces the carbon fixation and oxygen production (Feurtet-Mazel et al. 1996). Plants can also repair the oxidative damage caused by photosynthesis-inhibiting herbicides, which reduces the negative effects of these herbicides (Cedergreen et al. 2005). Even a fast reversibility of photosynthesis inhibition (within hours) has been demonstrated for several photosynthesis-inhibiting herbicides (e.g. Snel et al. 1998). Plant hormone-disrupting herbicides, comprised of 2,4-D, 2,4,5-T, picloram, clopyralid and

Table 2 Classification of herbicides by mode of action

No.	Class (mode of action)	Examples of compound groups	Example of active ingredient
1	Amino acid synthesis inhibitors	Sulfonylureas, imidazolones, triazolopyrimidines, epsp synthase inhibitors	Glyphosate
2	Seedling growth inhibitors	Carbamothiates, acetamides, dinitroanilines	EPTC
3	Growth regulators (interfere with plant hormones)	Phenoxy-acetic acids, benzoic acid, carboxylic acids, picolinic acids	2,4-D
4	Inhibitors of photosynthesis	Triazines, uracils, phenylureas, benzothiadiazoles, nitriles, pyridazines	Atrazine
5	Lipid synthesis inhibitors	Aryloxyphenoxypropionates, cyclohexanediones	Sethoxydim
6	Cell membrane disrupters	Diphenyl ethers, aryl triazolinones, phenylphthalamides, bipyridilium	Paraquat
7	Inhibitors of protective pigments	Isoxazolidinones, isoxazoles, pyridazinones	Clomazone
8	Unknown	Compounds with proven herbicide efficacy but unknown mode of action	Ethofumesate

triclopyr (Van den Brink et al. 2006), are especially hazardous to vascular plants, having auxin hormones that regulate their growth, in contrast to other groups of primary producers, like unicellular algae, that lack these hormones (Belgers et al. 2011). Since many of the herbicides that influence the plant hormone system are auxin stimulators, exposure to these herbicides might initially increase the growth rate of plants instead of decreasing it (Van den Brink et al. 2006).

3.2 Standardized Toxicity Tests with Aquatic Primary Producers

Most herbicides have been developed to be selective, i.e. to be phytotoxic to the competing non-crop plants, but not to the crop plants. This resulted in a wide variety of modes of action (Table 2). Accordingly, significant differences in toxicity to aquatic primary producer species are to be expected. Consequently, appropriate test species should be proposed, covering all presently known modes of action of the currently applied herbicides. Several standardized guidelines were proposed by organizations such as the OECD (Organisation for Economic Co-operation and Development), ASTM (American Society for Testing and Materials), USEPA (United States Environmental Protection Agency) and ISO (International Organization for Standardization), which are globally used for hazard and risk assessment. Most of these guidelines outline toxicity tests to determine the effects of hazardous herbicides on single species. For regulatory purposes, the majority of the toxicity tests are done according to freely available OECD or USEPA guidelines. However, the guidelines of the ISO and the ASTM were not freely available. Therefore, the guidelines from these organizations could not be evaluated completely, and only limited information about the species, endpoints and test methods were available. Among the standard guidelines, 18 tests consider aquatic primary producers (Table 3). In 9 of the 18 standardized guidelines with aquatic primary producers provided by the USEPA, ISO, OECD and the ASTM, the standard test species were algae, including diatoms, green algae and cyanobacteria. In five tests floating macrophytes have been selected as test organisms, all consisting of duckweed species. Submerged macrophytes have been selected in four tests and emergent macrophytes in only one test (Table 3). In addition, only two tests included sediment toxicity by selecting rooting plant species. Hence, among the available tests, there is a bias towards algae compared to macrophytes, while the few available macrophyte tests largely ignore the sediment as environmental compartment of concern. One reason for the relative lack of sediment tests is the usually perceived lower toxicity of herbicides in sediment tests compared to water-only tests. However, partitioning of herbicides to the sediment can result in exposure via root uptake (OECD 2014b) and enhanced toxicity in sediment tests compared to water-only tests. Hence, the paucity of tests with rooting macrophytes leaves the effect of contaminated sediments on aquatic primary producers largely unknown. Another knowledge gap concerns

Table 3 Standard guidelines for testing the effect of hazardous compounds in the water/sediment on various species of aquatic primary producers

Aquatic primary producer	Species	Compartment	System	Organization	Test number	Reference
Microalgae	N.A.	W	F	ASTM	E1218 – 04	ASTM (2012d)
	Selenastrum capricornutum	W	F	ASTM	D3978 – 04	ASTM (2012e)
	N.A.	W	F	OECD	201	OECD (2011)
	Anabaena flos-aquae	W	F	USEPA	850.4550	USEPA (2012d)
	N.A.	W	F	USEPA	850.4500	USEPA (2012a)
	N.A.	W	F	ISO	8,692	ISO (2012)
	Skeletonema sp./*Phaeodactylum tricornutum*	W	M	ISO	10,253	ISO (2016)
	Ceramium tenuicorne	W & S	B & M	ISO	10,710	ISO (2010)
Floating macrophytes	*Lemna minor*	W	F	ISO	20,079	ISO (2005)
	Spirodela polyrhiza	W	F	ISO	20,227	ISO (2017)
	Lemna gibba	W	F	ASTM	E1415 – 91	ASTM (2012c)
	Lemna sp.	W	F	OECD	221	OECD (2006b)
	Lemna spp.	W	F	USEPA	850.4400	USEPA (2012b)
Submerged macrophytes	*Champia parvula*/*Fucus edentatus*/ *Laminaria saccharina*/*Macrocystis pyrifera*	W	M	ASTM	E1498 – 92	ASTM (2012b)
	Myriophyllum aquaticum	S	F	ISO	16,191	ISO (2013)
	Myriophyllum spicatum	W	F	OECD	238	OECD (2014a)
	Myriophyllum spp./*Glyceria maxima*	W & S	F	OECD	239	OECD (2014b)
Emergent macrophytes	N.A.	W & S	F	ASTM	E1841 – 04	ASTM (2012a)
Aquatic plants*	N.A.	W	F	USEPA	850.4450	USEPA (2012c)

Standardized guidelines are available for exposure in different compartments (W = water; S = sediment) and systems (F = freshwater; B = brackish; M = marine). All guidelines are designed for toxicity testing, unless noted (* = field study) (N.A. is not available) marine species that are often neglected. Only three standard guidelines were proposed to test the effects of polluted marine waters on primary producers (Table 3). Moreover, no standard guidelines at all were proposed to test the effect of polluted marine sediments.

Outdoor microcosms and mesocosms can be an important tool in bridging the gap between lower-tier and higher-tier laboratory studies (single-species and multi-species) and in attempting to understand, predict and confirm what may occur in the natural environment upon herbicide exposure (Coors et al. 2006; OECD 2006c). Various guidance documents have been developed for summarizing and harmonizing the results of micro- and mesocosm studies (e.g. Giddings et al. 2002; OECD 2006c; De Jong et al. 2008), because of the unique nature of each microcosm or mesocosm study in at least some aspects of the experimental design (OECD 2006c). In comparison to standardized toxicity tests, microcosm and mesocosm studies can include (1) multiple species, functional groups or habitat types, (2) more environmentally realistic exposure conditions and (3) the impact on structural and functional attributes of natural ecosystems (OECD 2006c). When studying the impact of herbicides on aquatic macrophytes, special efforts are required to establish a diverse and representative community (Giddings et al. 2002). Still, not all ecological relevant processes can be included in mesocosm studies. Due to the isolate character of mesocosms, external recovery and avoidance will not be taken into account (De Jong et al. 2008). Finally, the chosen environmental conditions in mesocosms, such as nutrient availability and substrate, can influence the effects of herbicides (cf. Dalton et al. 2015).

3.3 *Selected Endpoints in Standardized Toxicity Tests with Aquatic Primary Producers*

An obvious condition for herbicides to be effective is that they are actually taken up by the primary producers. Accumulation after uptake and translocation to specific cell organelles or plant tissue can result in increased herbicide concentrations at target sites in primary producers. Although elevated concentrations in primary producers are indicative of the presence of bioavailable herbicides, this does not necessarily imply that adverse effects on these organisms occur. Measurements assessing the accumulation of herbicides in aquatic primary producers can therefore be best combined with one or more biological endpoint assessments. The most frequently used endpoints in toxicity tests with primary producers are growth-related effects. These endpoints are the most relevant for ecological risk assessment and are independent of the herbicides' mode of action. Other endpoints like enzyme activities or photosynthesis provide insight into the mode of action of the herbicide, but may be less relevant for ecological risk assessment. Yet, photosynthesis is the most essential metabolic pathway for primary producers, and therefore photosynthesis inhibition is the mode of action of many herbicides, whereby different steps in the photosynthetic pathway can be targeted. Hence, photosynthesis is relevant for assessing acute effects on the chlorophyll electron transport and can be assessed using pulse-amplitude modulation (PAM) fluorometry or from oxygen production or carbon fixation.

Growth represents the accumulation of biomass of primary producers. Growth inhibition is the most important endpoint in test with primary producers, since this endpoint integrates responses of a wide range of metabolic effects into a whole organism or a population response. However, it takes longer to assess, especially for larger primary producers. Cell counts; increase in size over time for either leaves, roots or whole organisms; and (bio)mass (fresh weight and dry weight) are the growth endpoints mostly used. Although area under the growth curve based on cell counts is a sensitive endpoint for both freshwater and marine algae (Hampel et al. 2001), assessing inhibition of growth rate is preferred over inhibition of biomass, since the latter is more affected by deviations in test conditions among studies (Bergtold and Dohmen 2011). For vascular aquatic plants, not only growth is a relevant endpoint but also endpoints specifically related to various life stages. Flowering and seed production are relevant endpoints for certain floating and emergent plant species, although vegetative reproduction is omnipresent in aquatic primary producers. Seedling emergence and early development of seedlings into plants are especially relevant for perennial and biannual aquatic plants (Muller et al. 2001). Successful germination of aquatic plants after seed dispersal can help to disperse species and to maintain healthy populations. For terrestrial plants seedling emergence tests are available (e.g. OECD 2006a; USEPA 2012e); however, no standardized seedling emergence test is currently available for aquatic plants. Other relevant endpoints for aquatic primary producers include elongation of different plant parts (e.g. roots), necrosis of leaves and disturbances in plant-microbial symbiont relationships (e.g. Mynampati et al. 2015).

Since the selected endpoint can influence the outcome of the toxicity test (Eklund and Kautsky 2003; Cedergreen et al. 2005), it is recommended to combine several endpoints in a single test. After exposure to herbicides influencing plant elongation (e.g. auxin stimulators), shoot length can be increased compared to control plants (Van den Brink et al. 2006), which is not especially beneficial to aquatic plants since this my limit their hydrodynamic resistance and further development. Growth and change in biomass or abundance are therefore generally considered to be the most robust endpoints (Knauer et al. 2006; Maltby et al. 2009; Bergtold and Dohmen 2011), showing the overall result of alterations in plant metabolic pathways by herbicides. An additional advantage is that growth can be calculated for any species, including population growth in the case of algae, facilitating the comparison of species-specific sensitivities between aquatic primary producers. Challenges to improve ecotoxicity tests with aquatic primary producers would be to include more sensitive and early response endpoints and to relate these endpoints to impact on growth, development and biomass of aquatic primary producers. Also, the development of ecotoxicogenomic endpoints (e.g. metabolomics) in the field of plant ecotoxicity tests would enable us to determine effects on a wider range of plant metabolic pathways. However, quantifying the effects on these metabolic pathways in terms of overall productivity of primary producers is not yet possible.

The OECD proposed growth inhibition and yield of total shoot length, fresh weight and dry weight as endpoints for a sediment-free test and additionally qualitative observations of symptoms such as chlorosis, necrosis and growth deformities for a water-sediment test with rooting macrophytes (OECD 2014a, b). For this group of primary producers, somatic endpoints like total plant length, main shoot length, fresh weight and root length are more sensitive than pigment endpoints, similar as for floating macrophytes (Hanson et al. 2003; Brain et al. 2004; Knauer et al. 2006). For soil and sediment exposure of aquatic plants to herbicides, development of endpoints related to root morphology and root metabolism could provide insights into early impact of herbicides on exposed plant parts. For auxin-type acting herbicides, root endpoints are the most sensitive somatic endpoints for rooting macrophytes (Hanson et al. 2003; Arts et al. 2008). However, development of belowground endpoints is still challenging since root development is also strongly impacted by available nutrients and redox conditions in the sediment (Barko et al. 1991; Boros et al. 2011).

3.4 Sensitivity of Aquatic Primary Producers to Herbicides

All herbicides are extensively tested before they can be applied in the environment. For this review, we merged the available EC50 data of aquatic primary producers used for the regulatory assessment of herbicides in Europe, mainly from the EFSA website (European Food and Safety Authority; http://www.efsa.europa.eu/; accessed Feb 2020) and from the USEPA ECOTOX knowledgebase (https://cfpub.epa.gov/ecotox/, accessed Feb 2020). The selected herbicides were the most commonly encountered herbicides mentioned in Table 1 and supplemented with 2,4-D (CAS 94757), dicamba (CAS 1918009) and triclopyr (CAS 55335063), three commonly analysed herbicides in the environment which act as synthetic auxin growth regulators (Ensminger et al. 2013). On the EU regulatory websites, limited or no data were present for the herbicides that were not approved or even banned (atrazine, irgarol, metolachlor, simazine, simetryn and terbutryn) in Europe. From the USEPA ECOTOX database, we first selected laboratory tests on plant species with water as exposure medium (freshwater and marine) and EC50 values at the individual or the population level (abundance, (bio)mass and (population) growth rate), excluding short-term physiological endpoints like photosynthetic activity. Exposure types ‘renewal’ and ‘flow through’ as well as all EC50 values reported as ‘NR’ were removed. To use as much of the available data as possible, no distinction was made between nominal, initial measured and mean measured concentrations during the test. Incorrectly mentioned media types for some species (wrongly placed in either saltwater or freshwater) were corrected, and in the case of multiple EC50 values from a single combination of species and study, the average EC50 was calculated. The available effect concentrations were grouped by generic endpoint, e.g. growth included length, yield and biomass. Species were then divided into freshwater (§4.4.1; Supplement Table S1) and marine (§4.4.2; Supplement Table S2). For sediment-associated herbicide exposure, we searched for aquatic tests on plant species and terrestrial tests on algae, in both cases using sediment and soil as exposure medium, respectively, applying the same criteria as mentioned above.

3.4.1 Sensitivity of Freshwater Primary Producers to Herbicides

The inventory of the available ecotoxicity data, expressed as EC50 values with abundance, (bio)mass and (population) growth rate as endpoints, revealed that the most frequently tested herbicides were atrazine, simetryn, diuron and metolachlor, followed by irgarol, isoproturon, simazine, 2,4-D, acetochlor and MCPA (Table 4). In total, 109 freshwater taxa belonging to 66 genera were tested, the most frequently selected test genera being the algae *Pseudokirchneriella* (synonym of *Raphidocelis*, previously also classified as *Selenastrum* or *Ankistrodesmus*; www.algaebase.org) and *Chlorella* and the floating macrophyte *Lemna*. The toxicity of each herbicide varied substantially (Table 4), with the lowest effect concentration observed for irgarol (E_bC50 0.09 μg/L) and the highest for mecoprop (E_rC50 729 mg/L). Toxicity data varied most for acetochlor, ranging from 0.0003 mg/L to 110 mg/L, hence a six orders of magnitude difference, followed by atrazine, irgarol and mecoprop with a five orders of magnitude difference between the lowest and highest EC50. But also for other herbicides (2,4-D, metazachlor and metolachlor), an around four orders of magnitude difference between the highest and lowest effect concentration was not uncommon. Only for bentazon the range in effect concentrations was quite small, and these EC50 values were all relatively high (3.88–42.5 mg/L). In spite of these wide ranges in effect concentrations, we calculated the median of the available data, which allowed a general ranking of the toxicity of the herbicides. Based on median EC50 values, irgarol, terbutryn, terbuthylazine, flurtamone and simetryn were the most toxic herbicides (Table 4). On the other hand, the highest median effect concentrations were obtained for mecoprop, triclopyr, MCPA, 2,4-D and bentazon, indicating that these herbicides were the least toxic to aquatic primary producers.

Considering the species-specific sensitivities to the 18 herbicides included in our analyses, hardly any pattern was observed. Generally, the most sensitive as well as the least sensitive species differed per herbicide. *Pseudokirchneriella subcapitata* (=*Selenastrum capricornutum*) was the most sensitive and the least sensitive species for one third of herbicides (i.e. six) included in our study. *Chlorella* sp. was least sensitive to three herbicides, but most sensitive to isoproturon, while *Anabaena flos-aquae* was most sensitive to two herbicides and least sensitive to one herbicide. For five herbicides, macrophytes showed the highest sensitivities, while for two herbicides, macrophytes were the least sensitive aquatic primary producers. Dividing the EC50 values obtained for aquatic primary producers into algae and macrophytes showed a large difference in available data, i.e. 456 values for algae but only 95 values for macrophytes. Consequently, most of the general patterns for aquatic primary producers described above related to the responses of algae. In fact, only for

Table 4 Overview of the sensitivity of freshwater primary producers to herbicides expressed as EC50 values based on measured abundance, (bio)mass or population growth (Overview of the studies and species included in the SSDs in Supplement Table S1)

	Freshwater primary producers					Freshwater algae			Freshwater macrophytes		
			ExC50 (mg/L)			ExC50 (mg/L)			ExC50 (mg/L)		
Herbicide	Genera (#)	Taxa (#)	(#)	Median	Range	(#)	Median	Range	(#)	Median	Range
2,4-D	16	20	27	21	0.011–582	22	52	0.055–582	5	0.70	0.011–100
Acetochlor	8	11	23	1.3	0.0003–110	21	1.4	0.0003–110	2	0.0034	0.0027–0.0041
Atrazine	35	60	171	0.13	0.0039–64	144	0.13	0.0039–64	27	0.097	0.021–14
Bentazon	4	4	10	12.7	4.2–33	7	17	4.2–33	3	7.9	5.4–15
Dicamba	7	9	16	3.7	0.45–42	10	4.0	1.8–42.4	6	2.7	0.45–3.7
Diuron	16	23	38	0.033	0.0007–0.54	34	0.035	0.0007–0.54	4	0.027	0.018–0.035
Flurtamone	4	4	8	0.023	0.0080–0.12	4	0.023	0.011–0.053	4	0.071	0.0080–0.12
Irgarol	17	20	29	0.0018	0.0001–0.011	24	0.0018	0.0001–0.25	6	0.0023	0.0002–0.011
Isoproturon	8	12	28	0.059	0.0050–0.35	21	0.047	0.0050–0.19	7	0.080	0.041–0.35
MCPA	13	16	21	22	0.12–392	20	27	0.12–392	1	0.17	–
Mecoprop	5	6	12	57	1.6–729	8	93	16.2–729	4	21	1.6–56
Metazachlor	5	5	10	0.031	0.0023–73	8	6.9	0.0088–73	2	0.0047	0.0023–0.0071
Metolachlor	16	25	38	0.30	0.0080–57	26	0.31	0.0080–57	12	0.30	0.023–3.0
Simazine	12	19	26	0.23	0.034–2.2	22	0.24	0.034–2.2	4	0.22	0.14–0.28
Simetryn	30	39	62	0.024	0.0079–0.70	62	0.024	0.0079–0.70	–	–	–
Terbuthylazine	6	7	18	0.016	0.0032–0.41	13	0.016	0.0032–0.10	5	0.016	0.013–0.41
Terbutryn	3	3	5	0.0048	0.0020–0.0078	5	0.0048	0.0020–0.0078	–	–	–
Triclopyr	6	6	9	23	2.0–181	6	29	2.0–181	3	18	8.2–23

11 herbicides, at least 4 EC50 values were available for macrophytes. However, ranking these herbicides based on median EC50 values showed a similar ranking for algae and macrophytes.

The wide variety in effect concentrations per herbicide are due to species-specific sensitivities, but also due to variation in effect concentrations within the same species, among others caused by differences in exposure time between the various studies (Thompson and Couture 1991), but also on the lack of information on the used exposure metrics (nominal, measured initial or mean concentration). To distinguish these two sources of variation, effect concentrations may be best compared per herbicide and per exposure time between species. This reduces the accompanying margins of uncertainty extensively, as shown for atrazine, the herbicide for which most toxicity data are available. Generally, at a given exposure time, the maximal variability in effect concentrations for a specific herbicide per species was reduced to approximately a factor of 10. Moreover, considering the toxicity of the herbicides per exposure time also allowed to evaluate if and how much the toxicity of the herbicides increases with increasing exposure time, although this may be masked by the use of different exposure metrices.

If enough toxicity data are available for a specific herbicide at a given exposure time, these can best be visualized and evaluated by species sensitivity distributions. A SSD is a distribution describing the variance in sensitivity of multiple species exposed to a hazardous compound. A SSD curve can be used to derive a so-called hazardous concentration on the X-axis: a benchmark concentration that can be used as regulatory criterion to protect the environment. By selecting a protection level on the Y-axis, representing a certain fraction of species affected (e.g. 5%), one derives the compound-specific hazardous concentration 5 (HC5). The obtained EC50 values (Supplement Table S1) were combined to construct SSDs using a SSD generator (USEPA 2016). The available effect concentrations were grouped by generic endpoint, e.g. growth rate (ErC50), yield (EyC50) and biomass (EbC50). Since algal ecotoxicity data were significantly more available than macrophyte data, we first constructed SSDs based on algae. In addition, we could also construct SSDs for macrophytes for atrazine and metolachlor. An overview of the calculated HC5 concentrations for the most frequently observed herbicides per exposure time is provided in Table 5.

For nine herbicides (acetochlor, atrazine, diuron, irgarol, isoproturon, MCPA, metolachlor, simetryn and simazine), enough ecotoxicity data (either EbC50, ErC50 or EyC50) were available to construct SSD curves for 4 days of exposure, the exposure time that had most herbicides in common (Table 5). Comparing the HC5 values derived from these SSDs allowed a clear ranking of the herbicides (Fig. 2), with irgarol being the most toxic one (HC5 0.31 μg/L), followed by diuron (0.35 μg/L), isoproturon (4.4 μg/L), simetryn (5.4 μg/L), atrazine (6.9 μg/L), acetochlor (11.0 μg/L), simazine (35.4 μg/L), metolachlor (97.3 μg/L) and MCPA (11.6 mg/L). This ranking only partly matched the one based on the rough estimates derived from Table 4, underlining that the precise and detailed analysis of the

Table 5 Overview of calculated HC5 values for aquatic primary producer communities for commonly analysed herbicides in freshwater and marine ecosystems based on EC50 values

				SSD		HC5	
Environment	Herbicide	Group	Exposure (d)	Species (#)	R^2	Median (µg/L)	0.05–0.95 CI (µg/L)
Freshwater	2,4-D	A	2	7	0.98	36.3	25.2–52.4
Freshwater	Atrazine	A	1	5	0.94	15.2	5.5–41.9
Freshwater	Atrazine	A	2	13	0.98	23.8	17.5–32.3
Freshwater	Atrazine	A	3	12	0.92	4.4	1–19.9
Freshwater	Atrazine	A	4	24	0.87	6.9	1.7–28.2
Freshwater	Atrazine	A	5	5	0.92	32.6	13.8–77.1
Freshwater	Atrazine	B	7	10	0.98	23.5	12.8–43.1
Freshwater	Atrazine	M	14	8	0.73	8.5	2.4–30.6
Freshwater	Acetochlor	A	4	7	0.88	11.0	0.6–196
Freshwater	Diuron	A	2	9	0.95	2.98	1–8.6
Freshwater	Diuron	A	4	9	0.89	0.35	0.07–1.8
Freshwater	Irgarol	A	3	5	0.96	0.33	0.16–0.68
Freshwater	Irgarol	A	4	7	0.89	0.31	0.14–0.7
Freshwater	Isoproturon	A	3	6	0.88	24.3	11.9–49.7
Freshwater	Isoproturon	A	4	5	0.78	4.4	1.1–16.7
Freshwater	MCPA	A	2	7	0.99	113.3	88.5–145
Freshwater	MCPA	A	4	6	0.92	11,588	4,658–28,827
Freshwater	Metolachlor	A	4	11	0.94	97.3	39.4–240
Freshwater	Metolachlor	M	14	6	0.91	10.8	1.7–67
Freshwater	Simazine	A	2	5	0.95	32.1	16.2–63.6
Freshwater	Simazine	A	4	5	0.64	35.4	10.2–122
Freshwater	Simetryn	A	4	19	0.93	5.35	3.1–9.2
Freshwater	Simetryn	A	7	37	0.92	7.14	4.2–12.2
Marine	Atrazine	A	3	8	0.96	15.2	10–23.1

Marine	Atrazine	A	4	8	0.93	34.8	26.7–45.3
Marine	Irgarol	A	3	5	0.97	0.082	0.05–0.12
Marine	Irgarol	A	4	6	0.93	0.123	0.04–0.36

SSD were constructed using the SSD calculator (USEPA 2016) based on at least five different species to obtain HC5 median and 90% confidence interval values for combinations of herbicides and exposure times for either algae (A), macrophytes (M) or both groups (B). (Overview of the studies and species included in the SSDs in Supplement Tables S1 and S2)

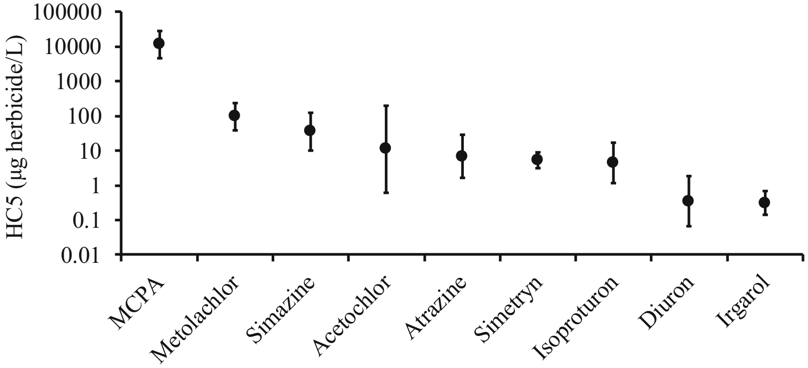

Fig. 2 Order of increasing toxicity of herbicides to freshwater algae, based on HC5 values (median ± 90% CI) derived from ecotoxicity tests after 4 days of exposure to the compound (Overview of the studies and species included in the SSDs in Supplement Table S1)

ecotoxicity data by means of constructing SSD curves is the only reliable way to compare herbicides and exposure times. Yet, SSDs are data hungry, requiring preferably at least EC50 values for eight different species (EFSA PPR 2013), although for the present study we went down to five data points.

Since atrazine was the most frequently studied herbicide, enough algae data were available to construct SSDs for 1, 2, 3, 4 and 5d of exposure. The median HC5 values derived from these SSD curves ranged from 4.4 to 32.6 µg/L (Fig. 3a), but these values were not related to the exposure time (ANOVA $F_{1,4} = 1.257$, $p = 0.69$). Although only algal species were included in this analysis, differences in test species per exposure times could have contributed to the variation in these median HC5 values. For six other herbicides, we could calculate HC5 values based on algal species for two different exposure times. As for atrazine, no difference in HC5 values between exposure times was observed for simazine (Fig. 3f), simetryn (Fig. 3g) and irgarol (Fig. 4B). This is most likely due to the direct mode of action of these herbicides, all interfering with photosynthesis. Apparently, the herbicide concentration at the target site and the expression of the toxic effect takes already place within the shortest exposure time (1 d). In contrast, for herbicides that need more time to build up lethal concentrations and that are characterized by slower time-to-events EC50 values, SSD curves and HC5 values decrease with increasing exposure time (Schroer et al. 2004; Roessink et al. 2006). In the present study, this decrease in HC5 values was observed for the herbicides diuron (Fig. 3b) and isoproturon (Fig. 3c). For MCPA, a contrasting pattern in HC5 values was obtained (Fig. 3d). Finally, comparing HC5 values for different groups of aquatic primary producers showed that the sensitivity to atrazine was comparable for macrophytes after 14d exposure and algae after 1d to 5d exposure (Fig. 3A). This is also reflected by the HC5 values obtained from both groups after 7d exposure. Contrastingly, sensitivity of macrophytes to metolachlor (14d exposure) was around one order of magnitude higher compared to algae (4d exposure; Fig. 3E).

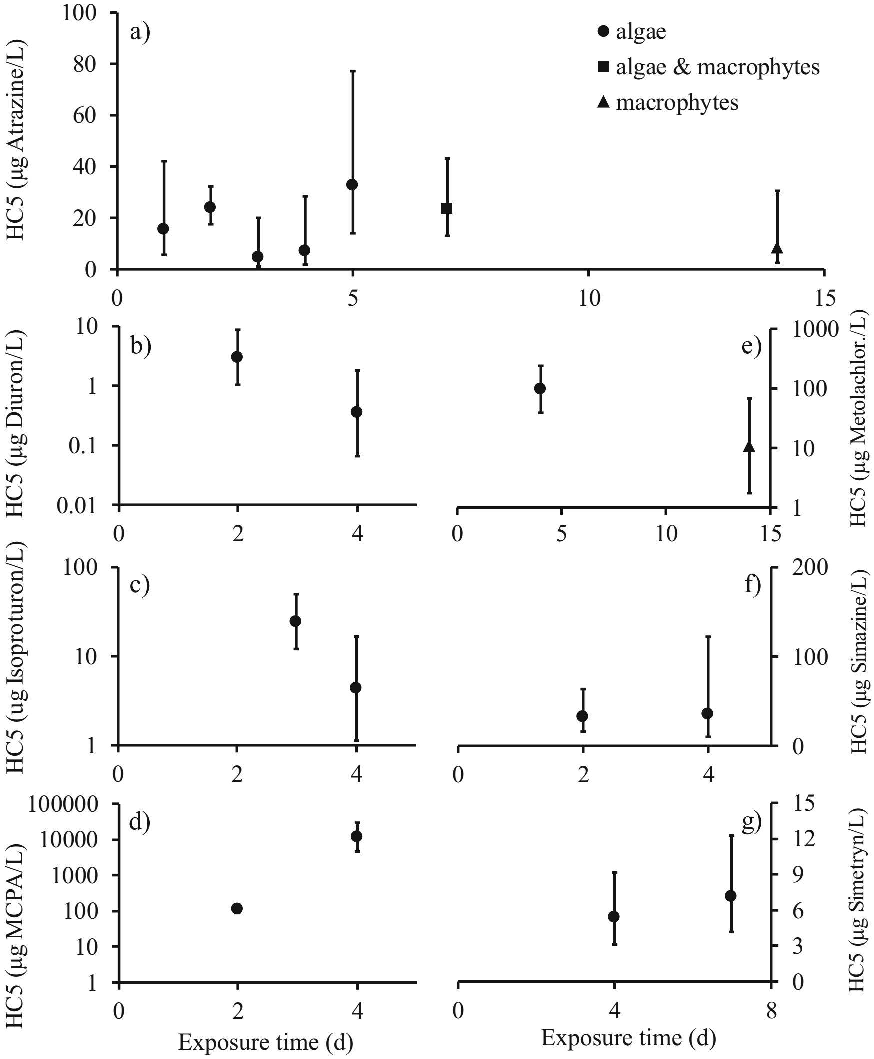

Fig. 3 Overview of HC5 values (median ± 90% CI) derived from SSD curves per exposure time for (**a**) atrazine, (**b**) diuron, (**c**) isoproturon, (**d**) MCPA, (**e**) metolachlor, (**f**) simazine and (**g**) simetryn. (Overview of the studies and species included in the SSDs in Supplement Table S1)

The wide range of effect concentrations per herbicide and the rather random distribution of the species being the most or the least sensitive one underline the urgent need to test different species, certainly more than one. The OECD and USEPA guidelines contain standard information on parameters like temperature and light conditions, but these may vary between the reported studies. The observed

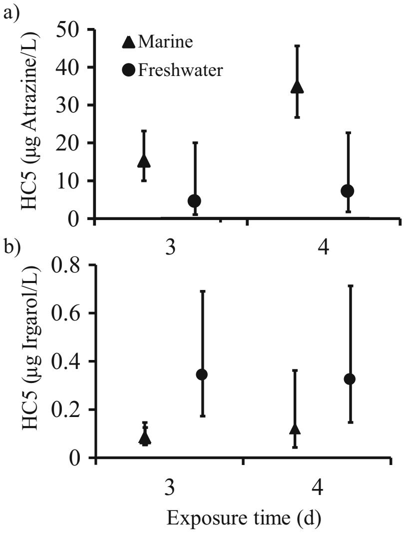

Fig. 4 Comparison HC5 values (median ± 90% CI) for marine and freshwater algae for (**a**) atrazine and (**b**) irgarol. (Overview of the studies and species included in the SSDs in Supplement Tables S1 and S2)

species-specific sensitivities can therefore also at least partly be attributed to the testing methods. For example, light conditions can have a strong influence on the sensitivity of aquatic primary producers, but this confounding effect differs between herbicides. The extent of the light-saturated region of photosynthesis of a species is modulated by a number of factors (e.g. availability of carbon dioxide, temperature, developmental stage, etc.), and these factors also influence the sensitivity of aquatic primary producers to herbicides (Snel et al. 1998). Comparing the sensitivity of ten aquatic macrophytes under low light intensity (irradiance 200 µmol/m^2/s) and high light intensity (irradiance 550 µmol/m^2/s), Cedergreen et al. (2004) showed that the sensitivity of the macrophytes, expressed as mean HC5 values based on EC50 values 14d of repeated exposure, decreased for terbuthylazine (11 and 39 µg/L, respectively), but increased for metsulfuron-methyl (0.031 and 0.014 µg/L, respectively). In situ, this means that an individual plant in full sunlight might be nearly unaffected, while another plant of the same species in the shade might be affected to a much greater extent by a single herbicide with a photosynthesis II inhibition mode of action (Snel et al. 1998). Also, Sjollema et al. (2014) showed that the toxicity of diuron and irgarol to the marine flagellate was higher under simulated spring irradiance than under autumn irradiance, which indicates that herbicide toxicity in the field is also seasonally variable. This clearly shows that the sensitivity of aquatic primary producers to herbicides is also depending on their metabolic activity, hence the strict set of standardized test conditions used in regulatory assessment of herbicides.

3.4.2 Sensitivity of Marine Primary Producers to Herbicides

For marine primary producers, 98 EC50 values for the endpoints abundance (EyC50), biomass (EbC50) and growth rate (ErC50) of mainly algae were obtained for 11 herbicides, and only a single macrophyte was tested (Supplement Table S2). Hence, far less studies have tested the effects of a lower diversity of herbicides on marine macrophytes and algae (Table 6) compared to freshwater primary producers. The only macrophyte included was *Zostera marina*, which was tested for only two herbicides (irgarol and diuron) (Chesworth et al. 2004), while microalgae were much more frequently represented. Consequently, only the sensitivities of algae to the most frequently detected and studied herbicides could be compared. Moreover, for several herbicides, data for only one or two marine species were available (acetochlor, bentazon, dicamba, metolachlor and terbuthylazine), leaving only five herbicides that were tested on more than one species. This strongly hampers the identification of species-specific and herbicide-specific sensitivities in the marine environment.

The inventory of the available marine ecotoxicity data revealed that the only extensively tested herbicides were 2,4-D, atrazine, diuron, irgarol and simazine (Table 6). In total 28 marine taxa belonging to 25 genera were tested, about a quarter of the numbers of freshwater taxa tested. Moreover, the marine genera were represented by fewer species than the freshwater genera. The only frequently selected test species (>15 tests) were the algae *Skeletonema costatum* and *Dunaliella tertiolecta* (Supplement Table S2). Also for marine test species, the toxicity of each herbicide varied substantially (Table 6). The lowest effect concentration was observed for irgarol (0.1 μg/L), the same value as the lowest effect concentration observed in the freshwater tests. Similar to freshwater, the highest effect

Table 6 Overview of the sensitivity of marine primary producers to herbicides expressed as EC50 values based on measured abundance, (bio)mass or population growth (Overview of the studies and species included in the SSDs in Supplement Table S2)

	Marine algae				
			ExC50 (mg/L)		
Herbicide	Genera (#)	Taxa (#)	(#)	median	range
2,4-D	5	5	8	48	0.68–75
Acetochlor	1	1	1	0.0051	–
Atrazine	17	17	43	0.069	0.017–0.43
Bentazon	1	1	1	10.1	–
Dicamba	1	1	1	0.49	–
Diuron	11	11	15	0.008	0.0006–0.02
Irgarol	13	14	19	0.0004	0.0001–0.01
Isoproturon	2	2	2	0.04	0.027–0.053
Metolachlor	1	1	1	0.061	–
Simazine	6	6	6	1.8	0.11–12.5
Terbuthylazine	1	1	1	0.031	–

concentration was observed for 2,4-D (75 mg/L), but this concentration was lower than the highest effect concentration observed in the freshwater tests (729 mg/L).

Toxicity data varied most for 2,4-D and simazine, for which an around two orders of magnitude difference for both herbicides was observed. Yet, this range was substantially smaller than the six orders of magnitude difference observed for MCPA in freshwater. This is potentially due to the lack of data on marine macrophytes, causing the dataset to consist of algae only. Especially for 2,4-D, the range in effect concentrations was much smaller compared to freshwater primary producers, and the values were relatively high (EC50 range 0.68–75 mg/L). This indicates that 2,4-D may be considered to be one of the least toxic herbicides to marine algae, because they are not sensitive to the auxin mode of action of this herbicide. Given the paucity and the wide range in marine effect concentrations, we refrained from ranking the herbicides based on their effects on marine primary producers. Moreover, considering the species-specific sensitivities for the five herbicides, also hardly any pattern was observed.

Given the limited marine ecotoxicity data, only for atrazine and irgarol, SSD curves could be constructed for 3 and 4d of exposure (Table 5). Similar to freshwater, no clear relationship was observed between exposure time and the HC5 values derived from these SSD curves (Fig. 4), with no difference for irgarol and even an increase in HC5 values for atrazine. Both the 3 and 4d SSD curves showed that irgarol was at least ten times more toxic to marine algae than atrazine, following the trend observed for freshwater algae. These HC5 values also showed that irgarol was more toxic to marine species, whereas atrazine was more toxic to freshwater species. This shows that the toxicity of herbicides may differ between environmental compartments, although this statement is based on two herbicides only and is possibly biased by testing different taxonomic groups, e.g. more green algae and in freshwater and more brown and red algae in marine environments. Due to the lack of data, the ranking of the other herbicides based on their toxicity to marine primary producers can only be based on the relatively rough estimates listed in Table 5. It is concluded that toxicity data for herbicides on marine primary producers, especially macrophytes, lag behind that of freshwater species and more research is warranted.

3.4.3 Sensitivity of Aquatic Primary Producers to Sediment-Associated Herbicides

In comparison to exposure through surface water, there is very limited information available on the sensitivities of aquatic primary producers to exposure to herbicides via the sediment. Yet, given the accumulation of herbicides in sediments (Haynes et al. 2000; Devault et al. 2009), rooting macrophytes are expected to be exposed much more to this source of herbicides than algae or free-floating plants (Lovett-Doust et al. 1994). Although various rooting macrophytes have been tested, the main exposure pathway was still often via surface water (e.g. Kemp et al. 1985; Wilson and Wilson 2010; Ratte and Ratte 2014), and reported differences in sensitivity to herbicides between rooting macrophytes and other aquatic primary producers were consequently often based on surface water exposure. The main species currently used in standardized sediment toxicity testing is the rooting dicotyledonous *Myriophyllum* spp., while monocotyledonous species are mainly mentioned as suitable test species but not actually tested (Davies et al. 2003; OECD 2014b). In the USEPA ECOTOX database, there were only a few studies reporting the sensitivity of rooting macrophytes to exposure to herbicides through sediment (e.g. Burešová et al. 2013).

Given the low number of available studies, the sensitivity of aquatic primary producers to contaminated sediments is hard to compare with the sensitivity to contaminated waters. Burešová et al. (2013) reported the effects of linuron on *M. spicatum* in sediment-dosed test systems, with EC50 values for various endpoints ranging from 11.6 to 16.9 mg linuron/kg sediment. Since *Myriophyllum* can take up linuron through the roots, pore water effect concentrations provided relevant values for describing the effects on this rooting aquatic macrophyte and allowed a comparison of sediment pore water and surface water effect concentrations (Burešová et al. 2013). This comparison showed that the mean effect concentration (EC50) for plant biomass was about one order of magnitude higher in pore water in sediment-dosed systems (1,115 μg/L; Burešová et al. 2013) compared to the overlying water in water-dosed test systems (137 μg/L; Kemp et al. 1985). Yet, taken into account the much lower root biomass (5–20% of plant biomass for *M. spicatum*; Cao et al. 2012) compared to the shoot biomass (80–95%), the total exposed plant biomass was about one order of magnitude lower in the sediment-dosed test systems.

Responses of rooting plants to herbicide exposure through the sediment are expected to be most strongly in their belowground parts, since in this case these parts of the plant are most directly exposed to the herbicide. Sensitivity of *Vallisneria americana* to sediment-associated contaminants could be assessed by changes in their shoot-to-root ratios, with plants grown in sediments contaminated with organic compounds having larger shoot-to-root ratios compared to plants grown in cleaner sediments (Biernacki et al. 1997). Although root endpoints were more sensitive than shoot endpoints for *M. spicatum* exposed to linuron via sediment, shoot biomass declined more (1.8x lower than control) compared to root biomass (1.5x lower; Burešová et al. 2013). Generally, *Myriophyllum* species appear to have a large variation in shoot-to-root ratios, also strongly influenced by the type of sediment used, the length of the initial cutting and the incubation time (Knauer et al. 2006, 2008). Examples for emergent rooting plants are scarce, with rice (*Oryza sativa*) showing a more sensitive response in the shoots compared to the roots to sediment-associated herbicides (Brinke et al. 2015).

Benthic biofilms and microalgae living on the top layer of the sediment are exposed via the overlaying water and to sediment-associated herbicides. The uptake of herbicides from the sediment by microalgae is even more direct than that by higher organisms (Diepens et al. 2014b). The uptake of herbicides from the sediment matrix is diffusion-driven and relatively fast for microalgae due to the much higher surface area-to-volume ratio compared to macrophytes. This pathway of uptake also implies that freely dissolved pore-water concentrations are the most relevant dose metric for tests with benthic microalgae (Diepens et al. 2014b). Only a few studies compared the herbicide sensitivity of algae living on the top layer of sediments, but some information is available for microalgae living in agricultural soils. Pipe and Cullimore (1984) showed that diuron, monuron and chloroxuron were more toxic to the soil diatom *Hantzschia* than chlortoluron and linuron. Atrazine application changed the species composition of the soil diatom communities in agricultural fields, with short-term ecotoxicity tests showing that the communities that had developed under herbicide stress were more tolerant to further atrazine application than the control communities (Bérard et al. 2004). Diatoms living on top of the sediment are the main aquatic primary producers in streams, but their exposure to herbicides has focused entirely on surface water contaminants (Debenest et al. 2010). Eutrophic and small diatom species were the most tolerant growth forms to atrazine, irgarol and isoproturon exposure (Debenest et al. 2010). Furthermore, diatom communities that include species capable of switching from autotrophic to heterotrophic modes when photosynthesis is inhibited (e.g. after herbicide exposure) can continue to grow, even in the presence of high concentrations of herbicides (Debenest et al. 2010).

It is concluded that the largest knowledge gap concerns the effects of sediment-associated herbicides on primary producers. This is remarkable, since chemical pollution of water bodies in the past resulted in high concentrations of toxicants in sediments (De Deckere et al. 2011), and where regulations strongly improved chemical water quality (De Deckere et al. 2011), sediments are considered to be the largest chemical repositories on earth (Borja et al. 2004). Consequently, sediments are the most relevant environmental compartment to link adverse effects on biota to toxicants (Borja et al. 2004). Although a proposal for a risk assessment of sediment-associated herbicides is provided by the EFSA PPR (2015), an extensive catch-up must be made concerning contaminated sediment and sediment-associated herbicide toxicity to primary producers.

3.5 Mixture Toxicity of Herbicides to Aquatic Primary Producers

Mixture toxicity should be taken into account, since herbicides are frequently applied in mixtures and mostly occur jointly in the aquatic environment (Schreiner et al. 2016; Moser et al. 2018). Various studies have evaluated the relative contribution of different pesticide groups to risks to aquatic communities. Although insecticides (especially the highly toxic pyrethroids) generally play a large role in the direct effects of mixtures on aquatic communities, herbicides also contribute substantially. From a nationwide screening of rivers in Swiss using liquid chromatography-high-resolution mass spectrometry, Moschet et al. (2014) calculated that herbicide mixtures made up 60–80% of the total risk of pesticides together in the rivers. However, the pyrethroids were not included in the analysis, while fungicides were not considered in the risk assessment based on three organism groups (plants, vertebrates and invertebrates). Mixture effects of herbicides and fungicides on aquatic primary producers should also be taken into account, since fungicides may affect algae as well (Guida et al. 2008) and their risk to aquatic primary producers may be underestimated (Reilly et al. 2012).

For herbicides with the same mode of action, concentration addition has been observed for algal community responses (Arrhenius et al. 2004). Hence, the only difference between the herbicides in the mixture is the relative potency of the compounds, and a mixture of herbicides with the same mode of action thus poses a concentration additive effect on primary producers (Backhaus et al. 2004). Deviations from concentration addition can be seen as a first indication of the herbicides in the mixture having a different mode of action. Herbicides with the same mode of action often act on a set of biological pathways related to a specific metabolic process, e.g. photosynthesis. Still there are many pathways involved in most metabolic processes, so herbicides with a specific mode of action (e.g. photosynthesis inhibition) can act on different molecular targets. Different photosynthesis-inhibiting herbicides can thus still have different mechanisms of action (Busch et al. 2016). For photosynthesis-inhibiting herbicides, this mechanism is often known, but for many other types of herbicides, it is often difficult to assess the exact mechanism of action in different groups of aquatic primary producers (Vonk et al. 2009).

The effects of herbicide mixtures on aquatic primary producers show variation, depending on the used herbicide combinations, test species and endpoints assessed. We have separated here studies using growth or biomass as endpoint and studies using various endpoints related to photosynthetic activity. Faust et al. (1993) tested 29 binary mixtures of 9 different herbicides on the unicellular green algae *Chlorella fusca* over 24 h development, and for 85% of the mixtures, results were consistent with concentration additivity. This was also observed for growth inhibition in *Pseudokirchneriella subcapitata* following exposure to mixtures of diuron and hexazinone, while the independent action model underestimated the combined effect (Hasenbein et al. 2017). Contrary, the independent action model fitted best the effects of a mixture of atrazine and sulfentrazone on the same microalgae (*P. subcapitata*) and on the floating macrophyte *Lemna minor* (Thorngren et al. 2017), indicating different mechanisms of action for these herbicides.

Results from studies assessing mixture toxicity of herbicides to aquatic primary producers using photosynthesis endpoints are also providing variable results. Whether additive responses, synergism or antagonism occurred depended on the mode of action of herbicides and the relative concentrations of the herbicides in the mixture. Binary mixtures of herbicides (diuron, tebuthiuron, atrazine, simazine and hexazinone) exhibited additive toxicity to the microalgae *Navicula* sp., *Cylindrotheca closterium*, *Nephroselmis pyriformis* and *Phaeodactylum tricornutum* (Magnusson et al. 2010). Sjollema et al. (2014) tested the effect of an equitoxic mixture of the herbicides irgarol and diuron on photosynthesis of *Dunaliella tertiolecta*. Although the mode of action of both herbicides was inhibition of photosynthesis, a more than additive effect of the herbicides in the mixture was observed. Photosynthetic activity of the marine cyanobacterium *Arthrospira maxima* showed both additive and antagonistic effects when exposed to the herbicides diuron and irgarol, depending on the relative concentrations of the herbicides in the mixture (Kottuparambil et al. 2013). Also for the floating macrophyte *Lemna* sp., binary herbicide mixtures (atrazine, diuron, simazine and hexazinone) resulted in both additive and antagonistic effects on photosynthesis (Kumar and Han 2011). Using a herbicide mixture of atrazine, diuron and isoproturon, Knauert et al. (2010) observed concentration additive effects on photosynthetic efficiency in *Myriophyllum spicatum* exposed to equitoxic herbicide concentrations.

Besides herbicide mixtures, also a wide variety of other pesticides can be present in the aquatic environment (e.g. Ensminger et al. 2013). These pesticide mixtures can exhibit toxic effects on aquatic primary producers. Faure et al. (2012) showed synergistic phytotoxic effects of a mixture of organochlorines (lindane (HCH), monochlorobenzene (MCB), 1,4-dichlorobenzene (DCB) and 1,2,4-trichlorobenzene (TCB)) on the aquatic emergent macrophyte *Phragmites australis*. Applied herbicides are often products with two or three different active ingredients with information available on their mixture toxicity from regulatory testing. However, in aquatic ecosystems, different events of herbicides application can easily result in different combinations of active herbicides and potential mixture effects on aquatic primary producers.

4 Retrospective Site-Specific Risks Assessment of Herbicides for Aquatic Primary Producers

The application of pesticides always involves exposure of non-target organisms, which can be reduced by increasing the specificity of the pesticides. In the case of herbicides, animals can be spared at least to some extent if the herbicides have a plant-specific mode of action, like most of the categories listed in Table 2, with photosynthesis inhibition being the most obvious one (Van den Brink et al. 2006). Yet, non-target primary producers remain equally affected as the target ones, causing aquatic primary producers to be permanently at risk of herbicide exposure. In a retrospective site-specific risk assessment, these risks may be substantiated by comparing and weighing effect concentrations and measured environmental concentrations. A refinement of this method can be applied if for a specific herbicide enough ecotoxicity data are available to construct SSD curves. In this case, one can derive the fraction of species probably affected at a measured ambient concentration (X to Y in the SSD).

The major drawback of the abovementioned methodologies is that they are based on single herbicides. Yet, in heavily anthropogenically exploited areas, risks to aquatic primary producers are generally caused by mixtures of a myriad of (un)-known compounds, with estimates of up thousands of compounds being present in large European rivers (Loos et al. 2009; Altenburger et al. 2015; Storck et al. 2015). Thus, a large portion of toxic risks in surface waters cannot be attributed to compounds measured by water authorities. To meet these challenges, the SSD approach can be further refined by deriving a multi-substance potentially affected fraction of species (msPAF). The msPAF model is designed to assess the risk of mixtures of toxicants using the SSD principles (Traas et al. 2002; de Zwart and Posthuma 2005). This model applies first concentration addition to calculate a single risk value for substances that have a shared toxic mode of action and then applies response addition to sum the toxicity risks of each mode of action. The resulting msPAF value describes the potentially affected fraction of species from exposure to a complex mixture (Traas et al. 2002; de Zwart and Posthuma 2005). This approach has been successfully applied to assess the risk of a mixture of pesticides, including many herbicides, in different regions (e.g. Wilson and Wilson 2011; Rämö et al. 2018).

Alternatively, understanding of the risks of herbicide exposure for aquatic primary producers can also be achieved by a shift towards new monitoring methods that do not depend on chemical analysis of priority substances solely, but consider the biological effects of the entire micro-pollutant mixture first. Therefore, there is a need for effect-based monitoring strategies that employ bioassays to identify environmental risk (e.g. De Baat et al. 2018). Responses in bioassays are caused by all bioavailable (un)known compounds and their metabolites, whether or not they are listed as priority substances. All toxicity tests described in §3.2 can be employed as bioassays, in which the responses of the primary producers to contaminated water and sediments samples can be determined, providing a direct indication of the potential ecological risks. Likewise, all the different endpoints described in §3.3 can be assessed in such bioassays, including survival, growth, reproduction, photosynthesis, etc. Applying bioassays enables an efficient and effective assessment of the toxicity of environmental samples to primary producers because it (1) identifies the presence of herbicides that would be overlooked by routine chemical WFD monitoring and (2) avoids redundant chemical analyses by focusing only on (non-) target screening in samples with demonstrated effects (De Baat et al. 2018). Major drawbacks in applying bioassays are the difficulties in relating the observed effects to specific compounds and the effects of confounding factors, like a poor nutritional value of the field samples, causing false positives.

4.1 Risk Assessment of Aqueous Herbicides for Aquatic Primary Producers

Monitoring efforts may vary widely between countries, the Netherlands being one of the few countries for which an open online platform on pesticide monitoring is publicly available (Vijver et al. 2008). Consulting this atlas revealed that for atrazine, diuron, isoproturon, MCPA, metolachlor and simazine, the measured environmental concentrations are all in the low ng/L range, hence generally at least three orders of magnitude lower than the HC5 values listed in Table 5 that generally fall in the μg/L range. This suggests that in the Netherlands, there is no actual risk of waterborne herbicides to aquatic primary producers. However, a number of considerations should be taken into account, mixture toxicity being the most obvious one. Yet, if effect concentrations and field concentrations differ a factor thousand, then only mixtures consisting of thousands of compounds may in the end come close to the effect concentrations. This may only be the case in the most downstream part of large rivers, but their concentrations are also generally further diluted. Ten to 20 years ago, herbicide concentrations were substantially higher, about a factor of 10 (www.bestrijdingsmiddelenatlas.nl; Vijver et al. 2008), but even then the difference between environmental concentrations and effect concentrations was still a factor hundred. Also, peak discharges may be missed by routine grab sampling monitoring, but this strongly depends on the monitoring frequency and intensity. Alternatively, passive sampling may be employed, strongly diminishing the chance of missing these peaks, but on the other hand, the final time integrated concentrations in the passive samplers also dampen these peaks. Munz et al. (2017) screened 24 Swiss WWTPs for almost 400 chemically synthesized pesticides and pharmaceuticals. Detected herbicide concentrations were several orders of magnitude lower than the HC5 values derived in the present review, confirming the low risk of herbicides to aquatic primary producers.

Fang et al. (2019) reported the minimum, median and maximum concentrations of a wide range of pesticides in Europe, China and the USA. For acetochlor, irgarol, isoproturon, MCPA, metolachlor and simazine, even the maximum concentrations were still at least a factor of 10 below the HC5 values. In contrast, for atrazine the maximum concentrations measured in China and the USA were very similar to the HC5 values listed in Table 5, suggesting an actual risk to aquatic primary producers. For diuron, the HC5 values varied, but nevertheless the maximum concentrations measured in the USA (1.36 μg/L) were half of the median 2d HC5 value (2.98 μg/L) and even around four times higher than the median 4d HC5 values (0.35 μg/L), indicating serious risks. Exceptional high risks would be anticipated based on the diuron concentrations measured by Hermosin et al. (2013) in Spain. The median (0.6 μg/L) and mean concentration (2.36 μg/L) that they reported are very similar to the HC5 ranges (overall 0.07–8.6 μg/L) calculated in the present review. Moreover, the maximum concentration that Hermosin et al. (2013) measured (21 μg/L) is even ten- to a hundred-fold higher than the median HC5 values for diuron. The latter would imply that approximately 60% of the EC50 values plotted in the SSD would be exceeded. Moreover, in such cases, mixture toxicity would likely play a role as well. An appropriate risk assessment of the generally occurring mixtures of compounds is, however, hampered by the compound approach involved in using SSDs. A reliable estimation of the actual risks at contaminated sites can therefore only be obtained by employing bioassays that respond to the entire mixture of bioavailable (un)known herbicides present in the environmental samples.

De Baat et al. (2018) employed an algal photosynthesis bioassay on a nationwide scale in the Netherlands to identify surface water toxicity to algae and subsequently to identify the causing compound(s). Out of 39 surface water locations, toxicity was observed at only one location. Chemical screening for 151 commonly applied pesticides identified 3 suspect herbicides (linuron, dimethenamid and the metabolite desethylterbuthylazine) that were present in the water sample above their respective quality standards. Generating EC50 values revealed that linuron was solely responsible for the observed effects at this location. Neale et al. (2017) applied chemical analysis and bioanalysis to assess the micro-pollutant burden during low flow conditions upstream and downstream of three wastewater treatment plants (WWTPs) discharging into small streams in the Swiss Plateau. They could explain that the observed effects on the photosystem II inhibition bioassays by ten detected herbicides, with main contributions by diuron and terbuthylazine). This was in contrast to the observed effects for most other bioassays, including activation of the aryl hydrocarbon receptor, activation of the androgen receptor, activation of the oestrogen receptor and acetylcholinesterase inhibition.

The success of surface water screenings relies largely on the endpoint specificity and scale of the selected bioassays, with in vitro or small-scale in vivo bioassays with specific drivers of adverse effects allowing for focused identification of toxicity and subsequent confirmation of the toxic compounds (Leusch et al. 2014; Brack et al. 2016). Microalgal photosynthesis is a sensitive and well-studied bioassay endpoint to identify hazardous effects of herbicides in surface waters (e.g. Ralph et al. 2007; Sjollema et al. 2014; Booij et al. 2015). Adequate selection of bioassays employed in water quality monitoring can thus greatly aid in narrowing down the identification of compound(s) that cause environmental risks (De Baat et al. 2018). The bioassays targeting photosynthesis inhibition by herbicides are often successful due to the specific mode of action and the sensitivity of PSII inhibition as an endpoint (Neale et al. 2017). Yet, herbicides with a different mode of action, like commonly observed auxin stimulating herbicides (e.g. Ensminger et al. 2013), are not detected using such microalgae bioassays.

4.2 Risk Assessment of Sediment-Associated Herbicides for Aquatic Primary Producers

While knowledge regarding the analysis and improvement of water quality is increasing, knowledge considering sediments and sediment-water-plant interactions specifically remains relatively scarce. Hence, more insight into the impact of changes induced by human activities on sediment and sediment-inhabiting organisms is required, since sediments are the largest chemical repositories on earth (Borja et al. 2004; Babut et al. 2005). Moreover, sediments nowadays act as a source of pollutants rather than as a sink, releasing a variety of stored toxicants and other detrimental components (Brils 2002; Förstner 2004; Chon et al. 2012). Despite the importance of contaminated sediments considering water quality assessment and risks for aquatic (primary producer) communities, the European Water Framework Directive (WFD) has focused primarily on compounds in the water column, mentioning water 373 times and sediment only 7 times (Borja et al. 2004). Moreover, the risks of herbicides accumulated in the sediments are strongly linked to the presence of other hazardous compounds, since in agricultural and urban areas, rooting primary producers are often influenced by mixtures of herbicides, heavy metals and many other unmonitored compounds in the sediment (Kronvang et al. 2003).

Microalgae generally have a short life-span and reproduction occurs often through simple cell division. Exposing microalgae for a couple of days to a few weeks, timeframes possible within the available ecotoxicity tests, will therefore also include reproduction of the species. Also for *Lemna* species, one can argue that the whole life-cycle is covered by the available toxicity test. However, assessing the risk for larger macrophytes is complicated, particularly when taking into account the seasonal growing and decay phase (Hill et al. 1994). Given the longer life-span of most (rooting) macrophytes (few months to even years; Cronk and Fennesy 2001), no standardized ecotoxicity test includes the entire life-cycle of these vascular plants. Hence, there is limited information available on the effects of herbicides on germination, flowering, seed formation and resource allocation during senescence of macrophytes (but see Moore et al. 1999, Gao et al. 2011; Moore and Locke 2012). Especially in the early life stages (seed germination) and during senescence and reallocation of resources to belowground parts, aquatic plants could be sensitive to sediment-associated herbicides. Mesocosm studies can be used to determine long-term effects of pesticides on aquatic primary producers, since both direct and indirect effects are taken into account in these studies (Müller et al. 2019). Still, mostly endpoints related to species composition and plant biomass are reported with less information on endpoints related to flowering, seed production and belowground storage of resources.

In the marine environment, suspicions regarding the risks of contaminated sediments are hard to confirm, since there are no standardized ecotoxicity tests using marine rooting macrophytes available. Assays for marine macrophytes (e.g. using leaves of the seagrass *Halophila ovalis*; Wilkinson et al. 2015) are currently being developed, but these still often focus on exposure through surface water only. Hence, it cannot be determined whether marine primary producers are affected by sediment-bound herbicides. Located in the coastal zones and influenced by rivers, seagrass meadows are contaminated by herbicides transported through the catchment to the sea (e.g. Scarlett et al. 1999; Haynes et al. 2000). For example, the modelled discharge of six widely used herbicides (atrazine, tebuthiuron, simazine, ametryn, diuron and hexazinone) to the Great Barrier Reef was on average 17,000 kg per year with the main risks for this area (Brodie et al. 2013, 2017). Although detected concentrations of herbicides in sediments of the Great Barrier Reef were relatively low (below 1 μg/kg sediment; Haynes et al. 2000), risk assessment of pesticides in sediments is restricted because the Australian sediment quality guidelines are limited in their scope to evaluate pesticide bioavailability (Brodie and Landos 2019). Seagrasses are exposed to herbicides and their degradation products through both the surface water (leaves) and the sediment (roots). Although a few studies have reported the impact of herbicides on seagrasses (see Devault and Pascaline (2013) for an overview), most studies reported impact on plant physiological endpoints (photosynthesis) only and not on overall growth. Seagrass vulnerability to short exposures of high concentrations of herbicides has been observed (Macinnis-Ng and

Ralph 2004), and the combined effects of high temperatures and the herbicide atrazine were more harmful to seagrass compared to a single pressure (Gao et al. 2017). However, the risk of herbicides through long-term exposure to mixtures of compounds generally present in the sediment of contaminated coastal areas remains unknown. Adjustments of environmental quality standards may therefore be needed in order to increase the protection level of marine species to herbicides. Priority should be given to evaluate if marine primary producers are currently sufficiently protected against the risks of exposure to hazardous concentrations of herbicides.

Comparable to surface water screenings, a reliable estimation of the actual risks at contaminated sediment sites can only be obtained by employing bioassays that respond to the entire mixture of bioavailable (un)known compounds present in the sediment and the interstitial water. Magnusson et al. (2013) compared the phytotoxicity of interstitial water extracts from sediments on benthic microalgae to the expected phytotoxicity of compounds detected in the overlying water. The herbicide concentrations in the interstitial water explained most of the phytotoxicity measured in the bioassay, and this photoinhibition was even higher than expected, indicating the presence of unidentified phytotoxins in the sediment pore water. Rooting macrophyte species have also been used in bioassays to assess sediment quality. In estuaries, Lewis et al. (2001) observed significant stimulatory and inhibitory effects on early seedling growth of *Scirpus robustus* (saltmarsh bulrush) and *Spartina alterniflora* (saltmarsh cordgrass), relative to a reference sediment. However, only in 3 of the 15 tests, these effects were related to pesticides (Lewis et al. 2001). Feiler et al. (2004) showed that growth of the freshwater macrophyte *Myriophyllum aquaticum* was depending on the origin of the sediment tested, with contamination in the sediments causing adverse effects on the plants. Successful application of bioassays to assess the toxicity of sediment-associated herbicides and to identify compounds of concern relates to (1) the identification of sensitive plant species and suitable response parameters; (2) the determination of the influence of sediment chemical and physical characteristics on plant growth; and (3) the quantification of the (bio)available concentrations of herbicides and other phytotoxins in the sediment-pore water matrix.

5 Conclusions

The aim of the present review was to give an overview of the current state of science concerning herbicide exposure and toxicity to aquatic primary producers. Assessing the open literature revealed that the unintentional as well as intentional sources of herbicides in the aquatic environment are numerous, evidently leading to the widespread presence of herbicides, inevitably leading to the exposure of non-target primary producers. The fate of herbicides in the environment is determined by the combination of the chemical properties and the formulation of the herbicides, the local environmental conditions and the timing, rate and method of application.

Overall, this results in exposure concentrations showing strong temporal and spatial variations and consisting of mixtures of herbicides.

Among the available toxicity tests with aquatic primary producers, there are a bias towards algae compared to macrophytes and a bias to water compared to sediment exposure. In response to ignoring the sediment as environmental compartment of concern, the OECD guideline for the macrophyte *Myriophyllum* has been extended with rooting plants allowing to test the toxicity of sediment-associated herbicides, while a test with the rooted emergent macrophyte *Glyceria* is currently being developed. Based on the outcome of the available ecotoxicity tests, it was concluded that the most sensitive as well as the least sensitive species differed per herbicide and that the observed effect concentrations for herbicides were rather similar independent from the exposure time. To come to a reliable hazard assessment for the effects of herbicides on primary producers, extensive ecotoxicity testing is required, especially considering macrophytes and marine herbicide toxicity. Yet, it is concluded that the largest knowledge gap concerns the effects of sediment-associated herbicides on primary producers.

Comparing environmental concentrations and effect concentrations demonstrated that generally there is no actual risk of waterborne herbicides to aquatic primary producers. Still, median concentrations of atrazine and especially of diuron measured in China, the USA and Europe represented moderate risks for primary producers. Maximum concentrations due to misuse and accidents may even cause the exceedance of almost 60% of the effect concentrations plotted in SSDs. Applying bioassays to detect the impact of unknown herbicide mixtures and to identify the herbicide of concern is a successful approach, especially for the photosynthesis-inhibiting herbicides. However, for herbicides with other modes of action, the use of bioassays remains challenging. It is concluded that to come to a reliable herbicide hazard and risk assessment, an extensive catch-up must be made concerning macrophytes, the marine environment and especially sediment as overlooked and understudied environmental compartment.

6 Summary

The aim of the present review was to give an overview of the current state of science concerning herbicide exposure and toxicity to primary producers. To this end we assessed the open literature, revealing the widespread presence of (mixtures of) herbicides, inevitably leading to the exposure of non-target primary producers. Yet, herbicide concentrations show strong temporal and spatial variations. Concerning herbicide toxicity, it was concluded that the most sensitive as well as the least sensitive species differed per herbicide and that the observed effect concentrations for some herbicides were rather independent from the exposure time. More extensive ecotoxicity testing is required, especially considering macrophytes and marine herbicide toxicity. Hence, it was concluded that the largest knowledge gap concerns the effects of sediment-associated herbicides on primary producers in

the marine/estuarine environment. Generally, there is no actual risk of waterborne herbicides to aquatic primary producers. Still, median concentrations of atrazine and especially of diuron measured in China, the USA and Europe represented moderate risks for primary producers. Maximum concentrations due to misuse and accidents may even cause the exceedance of almost 60% of the effect concentrations plotted in SSDs. Using bioassays to determine the effect of contaminated water and sediment and to identify the herbicides of concern is a promising addition to chemical analysis, especially for the photosynthesis-inhibiting herbicides using photosynthesis as endpoint in the bioassays. This review concluded that to come to a reliable herbicide hazard and risk assessment, an extensive catch-up must be made concerning macrophytes, the marine environment and especially sediment as overlooked and understudied environmental compartments.

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References

Altenburger R, Ait-Aissa S, Antczak P et al (2015) Future water quality monitoring – adapting tools to deal with mixtures of pollutants in water resource management. Sci Total Environ 512–513:540–551. https://doi.org/10.1016/j.scitotenv.2014.12.057

Anudechakul C, Vangnai AS, Ariyakanon N (2015) Removal of chlorpyrifos by water hyacinth (*Eichhornia crassipes*) and the role of a plant-associated bacterium. Int J Phytoremediation 17:678–685. https://doi.org/10.1080/15226514.2014.964838

Arrhenius Å, Grönvall F, Scholze M et al (2004) Predictability of the mixture toxicity of 12 similarly acting congeneric inhibitors of photosystem II in marine periphyton and epipsammon communities. Aquat Toxicol 68:351–367. https://doi.org/10.1016/j.aquatox.2004.04.002

Arts GH, Belgers JDM, Hoekzema CH, Thissen JT (2008) Sensitivity of submersed freshwater macrophytes and endpoints in laboratory toxicity tests. Environ Pollut 153:199–206. https://doi.org/10.1016/j.envpol.2007.07.019

Ashauer R, Escher BI (2010) Advantages of toxicokinetic and toxicodynamic modelling in aquatic ecotoxicology and risk assessment. J Environ Monit 12:2056–2061. https://doi.org/10.1039/C0EM00234H

ASTM (American Society for Testing and Materials) (2012a) Standard guide for conducting renewal phytotoxicity tests with freshwater emergent macrophytes. ASTM international E1841-04

ASTM (American Society for Testing and Materials) (2012b) Standard guide for conducting sexual reproduction tests with seaweeds. ASTM international E1498-92

ASTM (American Society for Testing and Materials) (2012c) Standard guide for conducting static toxicity tests with *Lemna gibba* G3. ASTM international E1415-91

ASTM (American Society for Testing and Materials) (2012d) Standard guide for conducting static toxicity tests with microalgae. ASTM international E1218-04

ASTM (American Society for Testing and Materials) (2012e) Standard practice for algal growth potential testing with *Pseudokirchneriella subcapitata*. ASTM international D3978-04

Babut MP, Ahlf W, Batley GE et al (2005) International overview of sediment quality guidelines and their uses. In: Wenning RJ, Batley GE, Ingersoll CJ, Moore DW (eds) Use of sediment quality guidelines and related tools for the assessment of contaminated sediments. Society of Environmental Toxicity and Chemistry, Pensacola, pp 345–382

Backhaus T, Faust M, Scholze M et al (2004) Joint algal toxicity of phenylurea herbicides is equally predictable by concentration addition and independent action. Environ Toxicol Chem 23:258–264. https://doi.org/10.1897/02-497

Bakker ES, Wood KA, Pagès JF et al (2016) Herbivory on freshwater and marine macrophytes: A review and perspective. Aquat Bot 135:18–36. https://doi.org/10.1016/j.aquabot.2016.04.008

Barko JW, Gunnison D, Carpenter SR (1991) Sediment interactions with submersed macrophyte growth and community dynamics. Aquat Bot 41:41–65. https://doi.org/10.1016/0304-3770(91)90038-7

Baudrot V, Charles S (2019) Recommendations to address uncertainties in environmental risk assessment using toxicokinetic-toxicodynamic models. Sci Rep 9:11432. https://doi.org/10.1038/s41598-019-47698-0

Belgers JDM, Aalderink GH, Arts GHP, Brock TCM (2011) Can time-weighted average concentrations be used to assess the risks of metsulfuron-methyl to *Myriophyllum spicatum* under different time–variable exposure regimes? Chemosphere 85:1017–1025. https://doi.org/10.1016/j.chemosphere.2011.07.025

Bérard A, Rimet F, Capowiez Y et al (2004) Procedures for determining the pesticide sensitivity of indigenous soil algae: a possible bioindicator of soil contamination? Arch Environ Contam Toxicol 46:24–31. https://doi.org/10.1007/s00244-003-2147-1

Bergtold M, Dohmen GP (2011) Biomass or growth rate endpoint for algae and aquatic plants: relevance for the aquatic risk assessment of herbicides. Integr Environ Assess Manage 7:237–247. https://doi.org/10.1002/ieam.136

Biernacki M, Lovett-Doust J, Lovett-Doust L (1997) Laboratory assay of sediment phytotoxicity using the macrophyte *Vallisneria americana*. Environ Toxicol Chem 16:472–478. https://doi.org/10.1002/etc.5620160312

Birk S, Bonne W, Borja A et al (2012) Three hundred ways to assess Europe's surface waters: an almost complete overview of biological methods to implement the water framework directive. Ecol Indic 18:31–41. https://doi.org/10.1016/j.ecolind.2011.10.009

Booij P, Sjollema SB, Van der Geest HG et al (2015) Toxic pressure of herbicides on microalgae in Dutch estuarine and coastal waters. J Sea Res 102:48–56. https://doi.org/10.1016/j.seares.2015.05.001

Borja A, Valencia V, Franco J et al (2004) The water framework directive: water alone, or in association with sediment and biota, in determining quality standards? Mar Pollut Bull 49:8–11. https://doi.org/10.1016/j.marpolbul.2004.04.008

Boros G, Søndergaard M, Takács P, Vári A, Tátrai I (2011) Influence of submerged macrophytes, temperature, and nutrient loading on the development of redox potential around the sediment–water interface in lakes. Hydrobiologia 665:117–127. https://doi.org/10.1007/s10750-011-0609-4

Boxall ABA, Sinclair CJ, Fenner K et al (2004) When synthetic chemicals degrade in the environment. Environ Sci Technol 38:368A–375A. https://doi.org/10.1021/es040624v

Brack W, Ait-Aissa S, Burgess RM et al (2016) Effect-directed analysis supporting monitoring of aquatic environments – an in-depth overview. Sci Total Environ 544:1073–1118. https://doi.org/10.1016/j.scitotenv.2015.11.102

Brain RA, Johnson DJ, Richards SM et al (2004) Microcosm evaluation of the effects of an eight pharmaceutical mixture to the aquatic macrophytes *Lemna gibba* and *Myriophyllum sibiricum*. Aquat Toxicol 70:23–40. https://doi.org/10.1016/j.aquatox.2004.06.011

Briggs GG, Bromilow RH, Evans AA (1982) Relationship between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. Pestic Sci 13:495–504. https://doi.org/10.1002/ps.2780130506

Brils J (2002) The SedNet mission. J Soils Sed 2:2–3. https://doi.org/10.1007/BF02991243

Brinke A, Buchinger S, Reifferscheid G, Klein R, Feiler U (2015) Development of a sediment contact test with rice for the assessment of sediment-bound pollutants. Environ Sci Pollut Res 22:12664–12675. https://doi.org/10.1007/s11356-015-4452-4

Brodie J, Landos M (2019) Pesticides in Queensland and great barrier reef waterways – potential impacts on aquatic ecosystems and the failure of national management. Estuar Coast Shelf Sci 230:106447. https://doi.org/10.1016/j.ecss.2019.106447

Brodie JE, Waterhouse J, Schaffelke B et al (2013) Reef water quality scientific consensus statement 2013. Queensland Government, Department of the Premier and Cabinet, Brisbane

Brodie JE, Lewis SE, Collier CJ et al (2017) Setting ecologically relevant targets for river pollutant loads to meet marine water quality requirements for the great barrier reef, Australia: a preliminary methodology and analysis. Ocean Coast Manage 143:136–147. https://doi.org/10.1016/j.ocecoaman.2016.09.028

Burešová H, Crum SJH, Belgers JDM et al (2013) Effects of linuron on a rooted aquatic macrophyte in sediment-dosed test systems. Environ Pollut 175:117–124. https://doi.org/10.1016/j.envpol.2012.12.030

Busch W, Schmidt S, Kühne R et al (2016) Micropollutants in European rivers: a mode of action survey to support the development of effect-based tools for water monitoring. Environ Toxicol Chem 35:1887–1899. https://doi.org/10.1002/etc.3460

Campos MMC, Faria VHF, Teodoro TS et al (2013) Evaluation of the capacity of the cyanobacterium *Microcystis novacekii* to remove atrazine from a culture medium. J Environ Sci Health Part B 48:101–107. https://doi.org/10.1080/03601234.2013.726891

Cao JJ, Wang Y, Zhu ZL (2012) Growth response of the submerged macrophyte *Myriophyllum spicatum* to sediment nutrient levels and water-level fluctuations. Aquat Biol 17:295–303. https://doi.org/10.3354/ab00484

Casado J, Brigden K, Santillo D, Johnston P (2019) Screening of pesticides and veterinary drugs in small streams in the European Union by liquid chromatography high resolution mass spectrometry. Sci Total Environ 670:1204–1225. https://doi.org/10.1016/j.scitotenv.2019.03.207

Cedergreen N, Spliid NH, Streibig JC (2004) Species-specific sensitivity of aquatic macrophytes towards two herbicide. Ecotoxicol Environ Saf 58:314–323. https://doi.org/10.1016/j.ecoenv.2004.04.002

Cedergreen N, Andersen L, Olesen CF et al (2005) Does the effect of herbicide pulse exposure on aquatic plants depend on K_{ow} or mode of action? Aquat Toxicol 71:261–271. https://doi.org/10.1016/j.aquatox.2004.11.010

Chalifour A, LeBlanc A, Sleno L et al (2016) Sensitivity of *Scenedesmus obliquus* and *Microcystis aeruginosa* to atrazine: effects of acclimation and mixed cultures, and their removal ability. Ecotoxicology 25:1822–1831. https://doi.org/10.1007/s10646-016-1728-5

Chefetz B, Bilkis YI, Polubesova T (2004) Sorption–desorption behavior of triazine and phenylurea herbicides in Kishon river sediments. Water Res 38:4383–4394. https://doi.org/10.1016/j.watres.2004.08.023

Chesworth JC, Donkin ME, Brown MT (2004) The interactive effects of the antifouling herbicides Irgarol 1051 and Diuron on the seagrass *Zostera marina* (L.). Aquat Toxicol 66:293–305. https://doi.org/10.1016/j.aquatox.2003.10.002

Chon HS, Ohandja DG, Voulvoulis N (2012) The role of sediments as a source of metals in river catchments. Chemosphere 88:1250–1256. https://doi.org/10.1016/j.chemosphere.2012.03.104

Clausen L, Larsen F, Albrechtsen HJ (2004) Sorption of the herbicide dichlobenil and the metabolite 2,6-dichlorobenzamide on soils and aquifer sediments. Environ Sci Technol 38:4510–4518. https://doi.org/10.1021/es035263i

Coors A, Kuckelkorn J, Hammers-Wirtz M, Strauss T (2006) Application of in-situ bioassays with macrophytes in aquatic mesocosm studies. Ecotoxicology 15:583–591. https://doi.org/10.1007/s10646-006-0095-z

Coupe RH, Blomquist JD (2004) Water–soluble pesticides in finished water of community water supplies. J Am Water Works Ass 96:56–68. https://doi.org/10.1002/j.1551-8833.2004.tb10723.x

Cronk JK, Fennesy MS (2001) Wetland plants: biology and ecology. Lewis Publishers, Boca Raton

Crum SJH, Van Kammen-Polman AMM, Leistra M (1999) Sorption of nine pesticides to three aquatic macrophytes. Arch Environ Con Toxicol 37:310–316. https://doi.org/10.1007/s002449900519

Cui S, Hough R, Yates K et al (2020) Effects of season and sediment-water exchange processes on the partitioning of pesticides in the catchment environment: implications for pesticides monitoring. Sci Total Environ 698:134228. https://doi.org/10.1016/j.scitotenv.2019.134228

Dalton RL, Boutin C, Pick FR (2015) Nutrients override atrazine effects on riparian and aquatic plant community structure in a north American agricultural catchment. Freshw Biol 60:1292–1307. https://doi.org/10.1111/fwb.12563

Davies J, Honegger JL, Tencalla FG et al (2003) Herbicide risk assessment for non-target aquatic plants: sulfosulfuron – a case study. Pest Manag Sci 59:231–237. https://doi.org/10.1002/ps.625

De Baat ML, Bas DA, Van Beusekom SAM et al (2018) Nationwide screening of surface water toxicity to algae. Sci Total Environ 645:780–787. https://doi.org/10.1016/j.scitotenv.2018.07.214

De Baat ML, Kraak MHS, van der Oost R et al (2019) Effect-based nationwide surface water quality assessment to identify ecotoxicological risks. Water Res 159:434–443. https://doi.org/10.1016/j.watres.2019.05.040

de Carvalho RF, Bromilow RH, Greenwood R (2007a) Uptake and translocation of non-ionised pesticides in the emergent aquatic plant parrot feather *Myriophyllum aquaticum*. Pest Manag Sci 63:798–802. https://doi.org/10.1002/ps.1394

de Carvalho RF, Bromilow RH, Greenwood R (2007b) Uptake of pesticides from water by curly waterweed *Lagarosiphon major* and lesser duckweed *Lemna minor*. Pest Manag Sci 63:789–797. https://doi.org/10.1002/ps.1389

De Deckere E, De Cooman W, Leloup V et al (2011) Development of sediment quality guidelines for freshwater ecosystems. J Soils Sed 11:504–517. https://doi.org/10.1007/s11368-010-0328-x

De Jong FMW, Brock TCM, Foekema EM, Leeuwangh P (2008) Guidance for summarizing and evaluating aquatic micro- and mesocosm studies. RIVM report 601506009, Bilthoven, The Netherlands, 59 pp

De Zwart D, Posthuma L (2005) Complex mixture toxicity for single and multiple species: proposed methodologies. Environ Toxicol Chem 24:2665–2676. https://doi.org/10.1897/04-639r.1

Debenest T, Silvestre J, Coste M, Pinelli E (2010) Effects of pesticides on freshwater diatoms. Rev Environ Contam Toxicol 203:87–103. https://doi.org/10.1007/978-1-4419-1352-4_2

Delle Site A (2001) Factors affecting sorption of organic compounds in natural sorbent/ water systems and sorption coefficients for selected pollutants. A review. Phys Chem Ref Data 30:187–439. https://doi.org/10.1063/1.1347984

DeLorenzo ME, Scott GI, Ross PE (2001) Toxicity of pesticides to aquatic microorganisms: a review. Environ Toxicol Chem 20:84–98. https://doi.org/10.1002/etc.5620200108

Devault DA, Pascaline H (2013) Herbicide impact on seagrass communities. In: Price AJ, Kelton JA (eds) Herbicides – current research and case studies in use, InTechOpen, pp 353–375. https://doi.org/10.5772/55973

Devault DA, Gérino M, Laplanche C et al (2009) Herbicide accumulation and evolution in reservoir sediments. Sci Total Environ 407:2659–2665. https://doi.org/10.1016/j.scitotenv.2008.12.064

Devine MD, Bestman HD, Vanden Born WH (1987) Uptake and accumulation of the herbicides chlorsulfuron and clopyralid in excised pea root tissue. Plant Physiol 85:82–86. https://doi.org/10.1104/pp.85.1.82

Dhir B, Sharmila P, Pardha Saradhi P (2009) Potential of aquatic macrophytes for removing contaminants from the environment. Crit Rev Environ Sci Technol 39:754–781. https://doi.org/10.1080/10643380801977776

Diepens NJ, Arts GH, Focks A, Koelmans AA (2014a) Uptake, translocation, and elimination in sediment-rooted macrophytes: a model-supported analysis of whole sediment test data. Environ Sci Technol 48:12344–12353. https://doi.org/10.1021/es503121x

Diepens NJ, Arts GHP, Brock TCM et al (2014b) Sediment toxicity testing of organic chemicals in the context of prospective risk assessment: a review. Crit Rev Environ Sci Technol 44:255–302. https://doi.org/10.1080/01496395.2012.718945

EFSA PPR (2018) Scientific Opinion on the state of the art of Toxicokinetic/Toxicodynamic (TKTD) effect models for regulatory risk assessment of pesticides for aquatic organisms. EFSA Journal 16(8):5377

EFSA PPR (European Food Safety Authority Panel on Plant Protection Products and their Residues) (2013) Guidance on tiered risk assessment for plant protection products for aquatic organisms in edge-of-field surface waters. EFSA J 11:3290. https://doi.org/10.2903/j.efsa.2013.3290

EFSA PPR (European Food Safety Authority Panel on Plant Protection Products and their Residues) (2015) Scientific opinion on the effect assessment for pesticides on sediment organisms in edge-of-field surface water. EFSA J 13:4176. https://doi.org/10.2903/j.efsa.2015.4176

Eggleton J, Thomas KV (2004) A review of factors affecting the release and bioavailability of contaminants during sediment disturbance events. Environ Int 30:973–980. https://doi.org/10.1016/j.envint.2004.03.001

Eklund BT, Kautsky L (2003) Review on toxicity testing with marine macroalgae and the need for method standardization–exemplified with copper and phenol. Mar Pollut Bull 46:171–181. https://doi.org/10.1016/S0025-326X(02)00225-4

Ensminger MP, Budd R, Kelley KC, Goh KS (2013) Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008-2011. Environ Monit Assess 185:3697–3710. https://doi.org/10.1007/s10661-012-2821-8

Fahl GM, Kreft L, Altenburger R et al (1995) pH–dependent sorption, bioconcentration and algal toxicity of sulfonylurea herbicides. Aquat Toxicol 31:175–187. https://doi.org/10.1016/0166-445X(94)00067-Z

Fang W, Peng Y, Muir D et al (2019) A critical review of synthetic chemicals in surface waters of the US, the EU and China. Environ Int 131:104994. https://doi.org/10.1016/j.envint.2019.104994

Faure M, San Miguel A, Ravanel P, Raveton M (2012) Concentration responses to organochlorines in *Phragmites australis*. Environ Pollut 164:188–194. https://doi.org/10.1016/j.envpol.2012.01.040

Faust M, Altenburger R, Boedeker W, Grimme LH (1993) Additive effects of herbicide combinations on aquatic non-target organisms. Sci Total Environ 134(Suppl 2):941–952. https://doi.org/10.1016/S0048-9697(05)80101-9

Feiler U, Kirchesch I, Heininger P (2004) A new plant bioassay for aquatic sediments. J Soil Sediment 4:261266. https://doi.org/10.1007/BF02991122

Feiler U, Ratte M, Arts G et al (2014) Inter-laboratory trial of a standardized sediment contact test with the aquatic plant *Myriophyllum aquaticum* (ISO 16191). Environ Toxicol Chem 33:662–670. https://doi.org/10.1002/etc.2483

Fernandez RT, Whitwell T, Riley MB, Bernard CR (1999) Evaluating semiaquatic herbaceous perennials for use in herbicide phytoremediation. J Am Soc Hort Sci 124:539–544. https://doi.org/10.21273/JASHS.124.5.539

Fernández D, Vermeirssen ELM, Bandow N, Muñoz K, Schäfer RB (2014) Calibration and field application of passive sampling for episodic exposure to polar organic pesticides in streams. Environ Pollut 194:196–202. https://doi.org/10.1016/j.envpol.2014.08.001

Feurtet-Mazel A, Grollier T, Grouselle M et al (1996) Experimental study of bioaccumulation and effects of the herbicide isoproturon on freshwater rooted macrophytes (*Elodea densa* and

Ludwigia natans). Chemosphere 32:1499–1512. https://doi.org/10.1016/0045-6535(96)00058-6

Förstner U (2004) Sediments – resource of waste. J Soil Sediment 4:3. https://doi.org/10.1007/BF02990821

Gao Y, Fang J, Zhang J et al (2011) The impact of the herbicide atrazine on growth and photosynthesis of seagrass, *Zostera marina* (L.), seedlings. Mar Pollut Bull 62:1628–1631. https://doi.org/10.1016/j.marpolbul.2011.06.014

Gao Y, Fang J, Du M et al (2017) Response of the eelgrass (*Zostera marina* L.) to the combined effects of high temperatures and the herbicide, atrazine. Aquat Bot 142:41–47. https://doi.org/10.1016/j.aquabot.2017.06.005

Ge X, d'Avignon DA, Ackerman JJH, Sammons RD (2014) *In vivo* P-nuclear magnetic resonance studies of glyphosate uptake, vacuolar sequestration, and tonoplast pump activity in glyphosate-resistant horseweed. Plant Physiol 166:1255–1268. https://doi.org/10.1104/pp.114.247197

Ghattas A-K, Fischer F, Wick A, Ternes TA (2017) Anaerobic biodegradation of (emerging) organic contaminants in the aquatic environment. Water Res 116:268–295. https://doi.org/10.1016/j.watres.2017.02.001

Giddings JM, Brock TCM, Heger W, Heimbach F, Maund SJ, Norman S, Ratte H-T, Schäfers C, Streloke M (2002) Community-level aquatic system studies-interpretation criteria (CLASSIC). SETAC, Pensacola, p 44

Gomes MP, Juneau P (2017) Temperature and light modulation of herbicide toxicity on algal and cyanobacterial physiology. Front Environ Sci 5:50. https://doi.org/10.3389/fenvs.2017.00050

González-Barreiro O, Rioboo C, Herrero C, Cid A (2006) Removal of triazine herbicides from freshwater systems using photosynthetic microorganisms. Environ Pollut 144:266–271. https://doi.org/10.1016/j.envpol.2005.12.014

Graymore M, Stagnitti F, Allinson G (2001) Impacts of atrazine in aquatic ecosystems. Environ Int 26:483–495. https://doi.org/10.1016/S0160-4120(01)00031-9

Guida M, Inglese M, Meriç S (2008) A multi-battery toxicity investigation on fungicides. Desalination 226:262–270. https://doi.org/10.1016/j.desal.2007.04.096

Guilizzoni P (1991) The role of heavy metals and toxic materials in the physiological ecology of submersed macrophytes. Aquat Bot 41:87–109. https://doi.org/10.1016/0304-3770(91)90040-C

Hampel M, Moreno-Garrido I, Sobrino C et al (2001) Acute toxicity of LAS homologues in marine microalgae: esterase activity and inhibition growth as endpoints of toxicity. Ecotoxicol Environ Safe 48:287–292. https://doi.org/10.1006/eesa.2000.2028

Hanson ML, Sanderson H, Solomon KR (2003) Variation, replication, and power analysis of *Myriophyllum* spp. microcosm toxicity data. Environ Toxicol Chem 22:1318–1329. https://doi.org/10.1002/etc.5620220619

Hasenbein S, Peralta J, Lawler SP, Connon RE (2017) Environmentally relevant concentrations of herbicides impact non-target species at multiple sublethal endpoints. Sci Total Environ 607-608:733–743. https://doi.org/10.1016/j.scitotenv.2017.06.270

Haynes D, Müller J, Carter S (2000) Pesticide and herbicide residues in sediments and seagrasses from the great barrier reef world heritage area and Queensland coast. Mar Pollut Bull 41:279–287. https://doi.org/10.1016/S0025-326X(00)00097-7

Heine S, Schmitt W, Schäffer A et al (2015) Mechanistic modelling of toxicokinetic processes within *Myriophyllum spicatum*. Chemosphere 120:292–298. https://doi.org/10.1016/j.chemosphere.2014.07.065

Hermosin MC, Calderon MJ, Real M, Cornejo J (2013) Impact of herbicides used in olive groves on waters of the Guadalquivir river basin (southern Spain). Agric Ecosyst Environ 164:229–243. https://doi.org/10.1016/j.agee.2012.09.021

Hershner C, Havens KJ (2008) Managing invasive aquatic plants in a changing system: strategic consideration of ecosystem services. Conserv Biol 22:544–550. https://doi.org/10.1111/j.1523-1739.2008.00957.x

Hill IR, Heimbach F, Leeuwangh P, Matthiessen P (1994) Freshwater field tests for Hazard assessment of chemicals. Chemical Rubber Company Press, Boca Raton

Hinman ML, Klaine SJ (1992) Uptake and translocation of selected organic pesticides by the rooted aquatic plant *Hydrilla verticillata* Royle. Environ Sci Technol 26:609–613. https://doi.org/10.1021/es00027a026

Hsu FC, Kleier DA (1996) Phloem mobility of xenobiotics VIII. A short review. J Exp Bot 47:1265–1271. https://doi.org/10.1093/jxb/47.Special_Issue.1265

Hussner A, Stiers I, Verhofstad MJJM et al (2017) Management and control methods of invasive alien freshwater aquatic plants: a review. Aquat Bot 136:112–137. https://doi.org/10.1016/j.aquabot.2016.08.002

ISO (The International Organization for Standardization) (2005) Water quality – determination of the toxic effect of water constituents and waste water on duckweed (*Lemna minor*) – Duckweed growth inhibition test. ISO Water quality, 20079

ISO (The International Organization for Standardization) (2010) Water quality – growth inhibition test with the marine and brackish water macroalga Ceramium tenuicorne. ISO Water quality, 10710

ISO (The International Organization for Standardization) (2012) Water quality – fresh water algal growth inhibition test with unicellular green algae. ISO Water quality, 8692

ISO (The International Organization for Standardization) (2013) Water quality – determination of the toxic effect of sediment on the growth behaviour of Myriophyllum aquaticum. ISO Water quality, 16191

ISO (The International Organization for Standardization) (2016) Water quality – marine algal growth inhibition test with Skeletonema sp and Phaeodactylum tricornutum ISO Water quality, 10253

ISO (The International Organization for Standardization) (2017) Water quality – determination of the growth inhibition effects of waste waters, natural waters and chemicals on the duckweed *Spirodela polyrhiza* – Method using a stock culture independent microbiotest. ISO Water quality, 20227

Jones TW, Winchell L (1984) Uptake and photosynthetic inhibition by atrazine and its degradation products on four species of submerged vascular plants 1. J Environ Qual 13:243–247. https://doi.org/10.2134/jeq1984.00472425001300020014x

Jones L, Ronan J, McHugh B et al (2015) Emerging priority substances in the aquatic environment: a role for passive sampling in supporting WFD monitoring and compliance. Anal Methods 7:7976–7984. https://doi.org/10.1039/c5ay01059d

Kanissery R, Gairhe B, McAvoy C, Sims G (2019) Herbicide bioavailability determinant processes in the soil. J Bioremed Biodegr 10:458. https://doi.org/10.4172/2155-6199.1000458

Kemp WM, Boynton WR, Cunningham JJ et al (1985) Effects of atrazine and linuron on photosynthesis and growth of the macrophytes, *Potamogeton perfoliatus* L. and *Myriophyllum spicatum* L. in an estuarine environment. Mar Environ Res 16:255–280. https://doi.org/10.1016/0141-1136(85)90023-6

Kettenring KM, Adams CR (2011) Lessons learned from invasive plant control experiments: a systematic review and meta-analysis. J Appl Ecol 48:970–979. https://doi.org/10.1111/j.1365-2664.2011.01979.x

Klaus J, Zehe E, Elsner M et al (2014) Controls of event-based pesticide leaching in natural soils: a systematic study based on replicated field scale irrigation experiments. J Hydrol 512:528–539. https://doi.org/10.1016/j.jhydrol.2014.03.020

Knauer K (2016) Pesticides in surface waters: a comparison with regulatory acceptable concentrations (RACs) determined in the authorization process and consideration for regulation. Environ Sci Eur 28:13. https://doi.org/10.1186/s12302-016-0083-8

Knauer K, Vervliet-Scheebaum M, Dark RJ, Maund SJ (2006) Methods for assessing the toxicity of herbicides to submersed aquatic plants. Pest Manag Sci 62:715–722. https://doi.org/10.1002/ps.1226

Knauer K, Mohr S, Feiler U (2008) Comparing growth development of *Myriophyllum* spp. in laboratory and field experiments for ecotoxicological testing. Environ Sci Pollut Res 15:322–331. https://doi.org/10.1007/s11356-008-0008-1

Knauer K, Homazava N, Junghans M, Werner I (2017) The influence of particles on bioavailability and toxicity of pesticides in surface water. Integr Environ Assess Manag 2017:585–600. https://doi.org/10.1002/ieam.1867

Knauert S, Singer H, Hollender J, Knauer K (2010) Phytotoxicity of atrazine, isoproturon, and diuron to submersed macrophytes in outdoor mesocosms. Environ Pollut 158:167–174. https://doi.org/10.1016/j.envpol.2009.07.023

Knuteson SL, Whitwell T, Klaine SJ (2002) Influence of plant age and size on simazine toxicity and uptake. J Environ Qual 31:2096–2103. https://doi.org/10.2134/jeq2002.2096

Kookana RS, Baskaran SNR, Naidu R (1998) Pesticide fate and behaviour in Australian soils in relation to contamination and management of soil and water: a review. Aust J Soil Res 36:715–764. https://doi.org/10.1071/S97109

Kottuparambil S, Lee S, Han T (2013) Single and interactive effects of the antifouling booster herbicides diuron and Irgarol 1051 on photosynthesis in the marine cyanobacterium, *Arthrospira maxima*. Toxicol Environ Health Sci 5:71–81. https://doi.org/10.1007/s13530-013-0157-6

Kronvang B, Laubel A, Larsen SE, Friberg N (2003) Pesticides and heavy metals in Danish streambed sediment. Hydrobiologia 494:93–101. https://doi.org/10.1023/A:1025441610434

Kumar KS, Han T (2011) Toxicity of single and combined herbicides on PSII maximum efficiency of an aquatic higher plant, *Lemna* sp. Toxicol Environ Health Sci 3:97–105. https://doi.org/10.1007/s13530-011-0084-3

Lake EC, Minteer CR (2018) A review of the integration of classical biological control with other techniques to manage invasive weeds in natural areas and rangelands. BioControl 63:71–86. https://doi.org/10.1007/s10526-017-9853-5

Lamoureux EM, Brownawell BJ (1999) Chemical and biological availability of sediment-sorbed hydrophobic organic contaminants. Environ Toxicol Chem 18:1733–1741. https://doi.org/10.1002/etc.5620180818

Landrum PF, Fisher SW (1998) Influence of lipids on the bioaccumulation and trophic transfer of organic contaminants in aquatic organisms. In: Arts MT, Wainman BC (eds) Lipids in freshwater ecosystems. Springer, New York, pp 203–234. https://doi.org/10.1007/978-1-4612-0547-0_10

Landrum PF, Harkey GA, Kukkonen J (1996) Evaluation of organic contaminant exposure in aquatic organisms: the significance of bioconcentration and bioaccumulation. In: Newman MC, Jagoe CH (eds) Ecotoxicology – a hierarchical treatment. Lewis Publishers, Ann Arbor, pp 85–127

Leu C, Singer H, Stamm C, Müller SR, Schwarzenbach RP (2004) Variability of herbicide losses from 13 fields to surface water within a small catchment after a controlled herbicide application. Environ Sci Technol 38:3835–3841. https://doi.org/10.1021/es0499593

Leusch FDL, Khan SJ, Laingam S et al (2014) Assessment of the application of bioanalytical tools as surrogate measure of chemical contaminants in recycled water. Water Res 49:300–315. https://doi.org/10.1016/j.watres.2013.11.030

Lewis MA, Weber DE, Stanley RS, Moore JC (2001) The relevance of rooting vascular plants as indicators of estuarine sediment quality. Arch Environ Con Toxicol 40:25–34. https://doi.org/10.1007/s002440010145

Lockhart WL, Billeck BN, Baron CL (1989) Bioassays with a floating aquatic plant (*Lemna minor*) for effects of sprayed and dissolved glyphosate. Hydrobiologia 188:353–359. https://doi.org/10.1007/BF00027800

Loos R, Gawlik BM, Locoro G et al (2009) EU-wide survey of polar organic persistent pollutants in European river waters. Environ Pollut 157:561–568. https://doi.org/10.1016/j.envpol.2008.09.020

Lopez B, Ollivier P, Togola A et al (2015) Screening of French groundwater for regulated and emerging contaminants. Sci Total Environ 518-519:562–573. https://doi.org/10.1016/j.scitotenv.2015.01.110

Lorenz S, Rasmussen JJ, Süß A et al (2017) Specifics and challenges of assessing exposure and effects of pesticides in small water bodies. Hydrobiologia 793:213–224. https://doi.org/10.1007/s10750-016-2973-6

Lovett-Doust J, Schmidt M, Lovett-Doust L (1994) Biological assessment of aquatic pollution: a review, with emphasis on plants as biomonitors. Biol Rev 69:147–186. https://doi.org/10.1111/j.1469-185X.1994.tb01504.x

Macinnis-Ng CMO, Ralph PJ (2004) In situ impact of multiple pulses of metal and herbicide on the seagrass, *Zostera capricorni*. Aquat Toxicol 67:227–237. https://doi.org/10.1016/j.aquatox.2004.01.012

Magnusson M, Heimann K, Quayle P, Negri AP (2010) Additive toxicity of herbicide mixtures and comparative sensitivity of tropical benthic microalgae. Mar Pollut Bull 60:1978–1987. https://doi.org/10.1016/j.marpolbul.2010.07.031

Magnusson M, Heimann K, Ridd M, Negri AP (2013) Pesticide contamination and phytotoxicity of sediment interstitial water to tropical benthic microalgae. Water Res 47:5211–5221. https://doi.org/10.1016/j.watres.2013.06.003

Malaj E, von der Ohe PC, Grote M et al (2014) Large-scale risk assessment of organic chemicals. Proc Natl Acad Sci 111:9549–9554. https://doi.org/10.1073/pnas.1321082111

Maltby L, Arnold D, Arts G et al (2009) Aquatic Macrophyte risk assessment for pesticides. Society of Environmental Toxicology and Chemistry Press & Chemical Rubber Company Press, Boca Raton, pp 1–162

Masiá A, Campo J, Vázquez-Roig P et al (2013) Screening of currently used pesticides in water, sediments and biota of the Guadalquivir River basin (Spain). J Hazard Mater 263:95–104. https://doi.org/10.1016/j.jhazmat.2013.09.035

Massei R, Busch W, Wolschke H et al (2018) Screening of pesticide and biocide patterns as risk drivers in sediments of major European river mouths: ubiquitous or river basin-specific contamination? Environ Sci Technol 524:2251–2260. https://doi.org/10.1021/acs.est.7b04355

Mercurio P, Mueller JF, Eaglesham G et al (2016) Degradation of herbicides in the tropical marine environment: influence of light and sediment. PLoS One 11:e0165890. https://doi.org/10.1371/journal.pone.0165890

Moore MT, Locke MA (2012) Phytotoxicity of atrazine, s-metolachlor, and permethrin to *Typha latifolia* (Linneaus) germination and seedling growth. Bull Environ Contam Toxicol 89:292–295. https://doi.org/10.1007/s00128-012-0682-z

Moore MT, Huggett DB, Huddleston GM, Rodgers JH, Cooper CM (1999) Herbicide effects on *Typha latifolia* (Linneaus) germination and root and shoot development. Chemosphere 38:3637–3647. https://doi.org/10.1016/S0045-6535(98)00561-X

Moschet C, Wittmer I, Simovic J et al (2014) How a complete pesticide screening changes the assessment of surface water quality. Environ Sci Technol 48:5423–5432. https://doi.org/10.1021/es500371t

Moser A, Wemyss D, Scheidegger R et al (2018) Modelling biocide and herbicide concentrations in catchments of the Rhine basin. Hydrol Earth Syst Sci 22:4229–4249. https://doi.org/10.5194/hess-22-4229-2018

Muller S, Huggett D, Rodgers J Jr (2001) Effects of copper sulfate on *Typha latifolia* seed germination and early seedling growth in aqueous and sediment exposures. Arch Environ Contam Toxicol 40:192–197. https://doi.org/10.1007/s002440010163

Müller R, Shinn C, Waldvogel AM et al (2019) Long-term effects of the fungicide pyrimethanil on aquatic primary producers in macrophyte-dominated outdoor mesocosms in two European ecoregions. Sci Total Environ 665:982–994. https://doi.org/10.1016/j.scitotenv.2019.02.050

Munz N, Melo L, Reyes M et al (2017) Pesticides drive risk of micropollutants in wastewater impacted streams during low flow conditions. Water Res 110:366–377. https://doi.org/10.1016/j.watres.2016.11.001

Mynampati KC, Lee YJ, Wijdeveld A et al (2015) RhizoFlowCell system reveals early effects of micropollutants on aquatic plant rhizosphere. Environ Pollut 207:205–210. https://doi.org/10.1016/j.envpol.2015.08.047

Neale PA, Munz NA, Aït-Aïssa S et al (2017) Integrating chemical analysis and bioanalysis to evaluate the contribution of wastewater effluent on the micropollutant burden in small streams. Sci Total Environ 576:785–795. https://doi.org/10.1016/j.scitotenv.2016.10.141

Netherland MD (2014) Chemical control of aquatic weeds. In: Gettys L, Haller W, Petty D (eds) Biological control of aquatic plants: a best management practices handbook, 3rd edn. Aquatic Ecosystem Restoration Foundation, Michigan, pp 71–88

OECD (Organization for Economic Cooperation, Development and Growth) (2006a) OECD terrestrial plant test: seedling emergence and seedling growth test. OECD guidelines for the testing of chemicals, 208

OECD (Organization for Economic Cooperation, Development and Growth) (2006b) OECD Lemna growth inhibition test. OECD guidelines for the testing of chemicals, 221

OECD (Organization for Economic Cooperation, Development and Growth) (2006c) Guidance document on simulated freshwater lentic field tests (outdoor microcosms and mesocosms). Series on testing and assessment, no 53, ENV/JM/MONO(2006)17, OECD Environment Directorate, Paris, 37 pp

OECD (Organization for Economic Cooperation, Development and Growth) (2011) OECD freshwater alga and cyanobacteria, Growth inhibition test. OECD guidelines for the testing of chemicals, 201

OECD (Organization for Economic Cooperation, Development and Growth) (2014a) OECD sediment-free Myriophyllum spicatum toxicity test. OECD guidelines for the testing of chemicals, 238

OECD (Organization for Economic Cooperation, Development and Growth) (2014b) OECD water-sediment Myriophyllum spicatum toxicity test. OECD guidelines for the testing of chemicals, 239

Olette R, Couderchet M, Biagianti S, Eullaffroy P (2008) Toxicity and removal of pesticides by selected aquatic plants. Chemosphere 70:1414–1421. https://doi.org/10.1016/j.chemosphere.2007.09.016

Pandey P, Caudill J, Lesmeister S et al (2019) Assessing glyphosate and fluridone concentrations in water column and sediment leachate. Front Environ Sci 7:22. https://doi.org/10.3389/fenvs.2019.00022

Plant and Soil Sciences eLibrary (2019) https://passel.unl.edu

Pérez DJ, Okada E, Menone ML, Costa JL (2017) Can an aquatic macrophyte bioaccumulate glyphosate? Development of a new method of glyphosate extraction in *Ludwigia peploides* and watershed scale validation. Chemosphere 185:975–982. https://doi.org/10.1016/j.chemosphere.2017.07.093

Pipe AE, Cullimore DR (1984) Influence of five phenylurea herbicides on the diatom *Hantzschia* in a sandy loam soil. Bull Environ Contam Toxicol 33:439–443. https://doi.org/10.1007/BF01625567

Rabodonirina S, Net S, Ouddane B et al (2015) Distribution of persistent organic pollutants (PAHs, Me–PAHs, PCBs) in dissolved, particulate and sedimentary phases in freshwater systems. Environ Pollut 206:38–48. https://doi.org/10.1016/j.envpol.2015.06.023

Ralph PJ, Smith RA, Macinnis-Ng CMO, Seery CR (2007) Use of fluorescence-based ecotoxicological bioassays in monitoring toxicants and pollution in aquatic systems: review. Toxicol Environ Chem 89:589–607. https://doi.org/10.1080/02772240701561593

Ramezani M, Oliver DP, Kookana RS, Gill G, Preston C (2008) Abiotic degradation (photodegradation and hydrolysis) of imidazolinone herbicides. J Environ Sci Health B 43:105–112. https://doi.org/10.1080/03601230701794968

Rämö RA, Van den Brink PJ, Ruepert C, Castillo LE, Gunnarsson JS (2018) Environmental risk assessment of pesticides in the river Madre de Dios, Costa Rica using PERPEST, SSD, and msPAF models. Environ Sci Pollut Res 25:13254–13269. https://doi.org/10.1007/s11356-016-7375-9

Rasmussen JJ, Wiberg-Larsen P, Baattrup-Pedersen A et al (2015) The legacy of pesticide pollution: an overlooked factor in current risk assessments of freshwater systems. Water Res 84:25–32. https://doi.org/10.1016/j.watres.2015.07.021

Ratte M, Ratte H (2014) Myriophyllum toxicity test: result of a ring test using M. aquaticum and M. spicatum grown in a water-sediment system. OECD Environment, Health and Safety Publications (EHS), series on testing and assessment, no. 206, OECD Publishing, Paris

Reilly TJ, Smalling KL, Orlando JL, Kuivila KM (2012) Occurrence of boscalid and other selected fungicides in surface water and groundwater in three targeted use areas in the United States. Chemosphere 89:228–234. https://doi.org/10.1016/j.chemosphere.2012.04.023

Remucal CK (2014) The role of indirect photochemical degradation in the environmental fate of pesticides: a review. Environ Sci Process Impacts 16:628–653. https://doi.org/10.1039/C3EM00549F

Rice PJ, Anderson TA, Coats JR (2004) Effect of sediment on the fate of metolachlor and atrazine in surface water. Environ Toxicol Chem 23:1145–1155. https://doi.org/10.1897/03-110

Roessink I, Belgers JDM, Crum SJH et al (2006) Impact of triphenyltin acetate in microcosms simulating floodplain lakes. II. Comparison of species sensitivity distributions between laboratory and semi-field. Ecotoxicology 15:411–424. https://doi.org/10.1007/s10646-006-0063-7

Scarlett A, Donkin P, Fileman TW, Morris RJ (1999) Occurrence of the antifouling herbicide, irgarol 1051, within coastal-water seagrasses from Queensland, Australia. Mar Pollut Bull 38:687–691. https://doi.org/10.1016/S0025-326X(99)00003-X

Schneiders GE, Koeppe MK, Naidu MV et al (1993) Fate of rimsulfuron in the environment. J Agric Food Chem 41:2404–2410. https://doi.org/10.1021/jf00036a036

Schreiner VC, Szöcs E, Bhowmik AK et al (2016) Pesticide mixtures in streams of several European countries and the USA. Sci Total Environ 573:680–689. https://doi.org/10.1016/j.scitotenv.2016.08.163

Schroer AFW, Belgers JDM, Brock TCM et al (2004) Comparison of laboratory single species and field population-level effects of the pyrethroid insecticide λ-cyhalothrin on freshwater invertebrates. Arch Environ Contam Toxicol 46:324–335. https://doi.org/10.1007/s00244-003-2315-3

Semple KT, Doick KJ, Jones KC et al (2004) Peer reviewed: defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. Environ Sci Technol 38:228A–231A. https://doi.org/10.1021/es040548w

Semple KT, Riding MJ, McAllister LE et al (2013) Impact of black carbon on the bioaccessibility of organic contaminants in soil. J Hazard Mater 261:808–816. https://doi.org/10.1016/j.jhazmat.2013.03.032

Sherwani SI, Arif IA, Khan HA (2015) Modes of action of different classes of herbicides. In: Price A, Kelton J, Sarunaite L (eds) Herbicides, physiology of action, and safety. IntechOpen, p 23. https://doi.org/10.5772/61779

Singh B, Singh K (2016) Microbial degradation of herbicides. Crit Rev Microbiol 42:245–261. https://doi.org/10.3109/1040841X.2014.929564

Sjollema SB, Vavourakis CD, Van der Geest HG et al (2014) Seasonal variability in irradiance affects herbicide toxicity to the marine flagellate *Dunaliella tertiolecta*. Front Mar Sci 1:13. https://doi.org/10.3389/fmars.2014.00013

Snel JFH, Vos JH, Gylstra R, Brock TCM (1998) Inhibition of photosystem II (PSII) electron transport as a convenient endpoint to assess stress of the herbicide linuron on freshwater plants. Aquat Ecol 32:113–123. https://doi.org/10.1023/A:1009971930626

Stehle S, Schulz R (2015) Insecticide contamination of global surface waters. Proc Natl Acad Sci 112:5750–5755. https://doi.org/10.1073/pnas.1500232112

Storck FR, Sacher F, Brauch HJ (2015) Hazardous and emerging substances in drinking water resources in the Danube river basin. In: Liska I (ed) The Danube river basin. Springer, Heidelberg. https://doi.org/10.1007/978-3-662-47739-7

Tang J, Hoagland KD, Siegfried BD (1998) Uptake and bioconcentration of atrazine by selected freshwater algae. Environ Toxicol Chem 17:1085–1090. https://doi.org/10.1897/1551-5028(1998)017%3C1085:UABOAB%3E2.3.CO;2

Tang T, Stamm C, Van Griensven A et al (2017) Hysteresis and parent-metabolite analyses unravel characteristic pesticide transport mechanisms in a mixed land use catchment. Water Res 124:663–672. https://doi.org/10.1016/j.watres.2017.08.016

Thompson PA, Couture P (1991) Short- and long-term changes in growth and biochemical composition of *Selenastrum capricornutum* populations exposed to cadmium. Aquat Toxicol 21:135–143. https://doi.org/10.1016/0166-445X(91)90068-K

Thorngren JL, Harwood AD, Murphy TM et al (2017) Fate and risk of atrazine and sulfentrazone to nontarget species at an agriculture site. Environ Toxicol Chem 36:1301–1310. https://doi.org/10.1002/etc.3664

Traas TP, Van de Meent D, Posthuma L, Hamers T, Kater BJ et al (2002) The potentially affected fraction as a measure of ecological risk. In: Posthuma L, Suter GW II, Traas TP (eds) Species sensitivity distributions in ecotoxicology. Lewis Publishers, Boca Raton, pp 315–344

Tuckey DM, Orcutt DM, Hipkins PLL (2002) Inherent and growth stage-related differences in growth and lipid and sterol composition of algal species sensitive and tolerant to sterol-inhibiting fungicides. Environ Toxicol Chem 21:1715–1723. https://doi.org/10.1002/etc.5620210825

Turgut C (2005) Uptake and modeling of pesticides by roots and shoots of parrotfeather (*Myriophyllum aquaticum*). Environ Sci Pollut Res 12:342–346. https://doi.org/10.1065/espr2005.05.256

Turgut C, Fomin A (2002) Sensitivity of the rooted macrophyte *Myriophyllum aquaticum* (Vell.) Verdcourt to seventeen pesticides determined on the basis of EC_{50}. B Environ Contam Toxicol 69:601–608. https://doi.org/10.1007/s00128-002-0103-9

USEPA (United States Environmental Protection Agency) (2012a) Algal toxicity. USEPA ecological effects test guidelines, 850.4500

USEPA (United States Environmental Protection Agency) (2012b) Aquatic plants field study. USEPA ecological effects test guidelines, 850.4450

USEPA (United States Environmental Protection Agency) (2012c) Aquatic plant toxicity test using Lemna spp. USEPA ecological effects test guidelines, 850.4400

USEPA (United States Environmental Protection Agency) (2012d) Cyanobacteria (Anabaena flos-aquae) toxicity. USEPA ecological effects test guidelines, 850.4550

USEPA (United States Environmental Protection Agency) (2012e) Seedling emergence and seedling growth. USEPA ecological effects test guidelines, 850.4100

USEPA (United States Environmental Protection Agency) (2016) Species sensitivity distribution generator. https://www.epa.gov/caddis-vol4/caddis-volume-4-data-analysisdownload-software

Van den Brink PJ, Blake N, Brock TC, Maltby L (2006) Predictive value of species sensitivity distributions for effects of herbicides in freshwater ecosystems. Hum Ecol Risk Assess 12:645–674. https://doi.org/10.1080/10807030500430559

Van Wijngaarden R, Arts GH (2018) Is the tier-1 effect assessment for herbicides protective for aquatic algae and vascular plant communities? Environ Toxicol Chem 37:175–183. https://doi.org/10.1002/etc.3936

Vijver MG, van 't Zelfde M, Tamis WLM et al (2008) Spatial and temporal analysis of pesticides concentrations in surface water: pesticides atlas. J Environ Sci Health B 43:665–674. https://doi.org/10.1080/03601230802388728

Voice TC, Weber WJ Jr (1983) Sorption of hydrophobic compounds by sediments, soils and suspended solids – I. Theory and background. Water Res 17:1433–1441. https://doi.org/10.1016/0043-1354(83)90275-0

Vonk JA, Benigni R, Hewitt M et al (2009) The use of mechanisms and modes of toxic action in integrated testing strategies: the report and recommendations of a workshop held as part of the European Union OSIRIS integrated project. ATLA-Altern Lab Anim 37:557–571. https://doi.org/10.1177/026119290903700512

Vrana B, Allan IJ, Greenwood R et al (2005) Passive sampling techniques for monitoring pollutants in water. TrAC Trends Anal Chem 24:845–868. https://doi.org/10.1016/j.trac.2005.06.006

Wang P, Liu X, Wu X et al (2018) Evaluation of biochars in reducing the bioavailability of flubendiamide in water/sediment using passive sampling with polyoxymethylene. J Hazard Mater 344:1000–1006. https://doi.org/10.1016/j.jhazmat.2017.12.003

Weiner JA, DeLorenzo ME, Fulton MH (2004) Relationship between uptake capacity and differential toxicity of the herbicide atrazine in selected microalgal species. Aquat Toxicol 68:121–128. https://doi.org/10.1016/j.aquatox.2004.03.004

Whatley MH, Van Loon EE, Van Dam H et al (2014) Macrophyte loss drives decadal change in benthic invertebrates in peatland drainage ditches. Freshw Biol 59:114–126. https://doi.org/10.1111/fwb.12252

Wilkinson AD, Collier CJ, Flores F et al (2015) A miniature bioassay for testing the acute phytotoxicity of photosystem II herbicides on seagrass. PLoS One 10(2):e0117541. https://doi.org/10.1371/journal.pone.0117541

Wilson PC, Wilson SB (2010) Toxicity of the herbicides bromacil and simazine to the aquatic macrophyte, *Vallisneria americana* Michx. Environ Toxicol Chem 29:201–211. https://doi.org/10.1002/etc.22

Wilson PC, Wilson SB (2011) Characterization of selected organo-nitrogen herbicides in South Florida canals: exposure and risk assessments. Sci Total Environ 412-413:119–126. https://doi.org/10.1016/j.scitotenv.2011.09.058

Wittmer IK, Bader H-P, Scheidegger R et al (2010) Significance of urban and agricultural land use for biocide and pesticide dynamics in surface waters. Water Res 44:2850–2862. https://doi.org/10.1016/j.watres.2010.01.030

Wood RJ, Mitrovic SM, Lim RP, Kefford BJ (2016) How benthic diatoms within natural communities respond to eight common herbicides with different modes of action. Sci Total Environ 557-558:636–643. https://doi.org/10.1016/j.scitotenv.2016.03.142

Wu F, Gao Y, Zuo Z et al (2020) Different decreasing rates of chemical threshold concentrations can be explained by their toxicokinetic and toxicodynamic characteristics. Sci Total Environ 708:135234. https://doi.org/10.1016/j.scitotenv.2019.135234

Zhang W (2018) Global pesticide use: Profile, trend, cost/benefit and more. P Int Acad Ecol Environ Sci 8(1):1–27

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https://doi.org/10.1007/978-3-030-67852-4