

Behaviour and fate of metals in urban wastewater treatment plants: a review

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Abstract The concerns on metals in urban wastewater treatment plants (WWTPs) are mainly related to its contents in discharges to environment, namely in the final effluent and in the sludge produced. In the near future, more restrictive limits will be imposed to final effluents, due to the recent guidelines of the European Water Framework Directive (EUWFD). Concerning the sludge, at least seven metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn) have been regulated in different countries, four of which were classified by EUWFD as priority substances and two of which were also classified as hazardous substances. Although WWTPs are not designed to remove metals, the study of metals behaviour in these systems is a crucial issue to develop predictive models that can help more effectively the regulation of pre-treatment requirements and contribute to optimize the systems to get more acceptable metal concentrations in its discharges. Relevant data have been published in the literature in recent decades concerning the occurrence/fate/behaviour of metals in WWTPs. However, the information is dispersed and not standardized in terms of parameters for comparing results. This work provides a critical review on this issue through a careful systematization, in tables and graphs, of the results reported in the literature, which allows its comparison and so its analysis, in order to conclude about the state of the art in

this field. A summary of the main consensus, divergences and constraints found, as well as some recommendations, is presented as conclusions, aiming to contribute to a more concerted action of future research.

Keywords Metals removal mechanisms · Metals mass balances · Metals behaviour models · Priority pollutants · Sewage sludge metals content · Urban wastewater metals sources

Introduction

Metals and its compounds are of great concern, even at trace levels, primarily due to their potential toxicity to all aspects of the environment. The risks of their bioaccumulation in the food chains pose one of the major environmental and health problems of our modern society (Mudho and Kumar 2013). Being natural components of the Earth's crust, most metals present a background concentration. Thus, the anthropogenic emissions, which promote the increase in natural concentrations and its transport to different environmental compartments, are the ones of major concern. Trace quantities of many metals are found in sewage from various sources. Among them, arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) are classified as potentially toxic elements, which mean that depending on the concentration and time of exposure, they can pose problems of acute or chronic human health effects, carcinogenicity, phytotoxicity and bioaccumulation (EC 2001a, b).

Municipal wastewater treatment plants (WWTPs) are not designed for metals removal. Despite the fact that for a long time, it has been reported that metals were significantly removed from the final effluents, its removal is in most of the

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cases the result of the metals partitioning to the solid phase of the treatment systems. The sludge, originated from the treatment of wastewater, retains a significant part of some of the metals entering the WWTPs. Since the implementation of the US Clean-Water Act (CWA) in the USA and of the Urban Wastewater Treatment European Directive (UWTEd) in the European Union (EU) (EC 1991), the removal of metals in WWTPs could no longer be considered only in terms of the final effluent quality. In fact, the two end products in a WWTP are the effluent and the sludge, and so, according to the article 14 of the UWTEd, WWTPs have also to consider the quality of the sludge produced and minimize its adverse effects in the environment. Moreover, the regulation of industrial wastewater discharges into municipal sewers was defined as a crucial issue in order to control the quality of the sludge produced and so article 11 set out provisions for this purpose.

Once the sludge has been treated in the WWTPs, it can be disposed of in different ways. The most common procedures are landfilling, land application as a fertilizer and incineration. Land application of treated sewage sludge has been adopted worldwide as an economically and environmentally sustainable option for sludge management, as it promotes a desirable nutrient recycling and helps to improve soils productivity. Within the EU countries, about 37 % of the total annual production of treated sewage sludge is used in agriculture, and in the USA the corresponding figure is 60 % (Olofsson et al. 2012; NRC 2002). Moreover, land application of treated sewage sludge is likely to increase in importance due to the global depletion of phosphorus resources and the need of sustainable management strategies (Mattsson et al. 2012; Olofsson et al. 2012). However, metals that contaminate sewage sludge may prohibit the recycling of valuable nutrients (Ayari et al. 2010). The use of sludge in agriculture is regulated in the EU by the Sewage Sludge Directive, which establishes maximum residue limits for six metals in sludge (Annex 1B) (EC 1986), and in the USA by the federal Part 503 rule (40 CFR Part 503), which sets ceiling concentrations for ten metals in sludge (NRC 2002; US EPA 1995). Repeated applications of sludge gradually increase the metal contents in soil. Depending on sludge application rate and on its metal contents, there is a maximum permissible level for each of the regulated metals in the soil. Therefore, besides the concentrations of metals in the sludge itself, legislation also considers restrictions concerning the total amount of metals that can be added to soils where sludge is applied. Within the EU, the revision of the Sewage Sludge Directive is envisaged and there is already a proposal for more restrictive limits concerning the maximum allowable metal concentrations on sludge (EC 2000a). In the Member States, the legislation implemented at national level, in order to transpose the requirements of the Sewage Sludge

Directive, differs significantly with respect to the limits of metals concentrations in sludge and extremely stringent limits have been set in some cases. Swedish, Dutch and Danish limit values are the most protective in the world, while higher acceptable limits are set in the USA. Table 1 shows an overview of the different ranges of threshold values currently in place in this area.

Despite the different approaches concerning limits, metals are an unwanted content in a potential product. From this perspective, in recent decades, major concerns regarding the metals issue in the WWTPs were primarily focused on the quality of generated sludge and in the possibilities of its improvement, mainly within a strategy of controlling the industrial discharges into urban wastewater systems (UWSs), laid down by the above legislation. Metals in the sewage sludge have received a great scientific attention in recent years, in order to get information about their bioavailability and ecotoxicity, through a large number of studies concerning metal speciation by sequential chemical extraction schemes (Lasheen and Ammar 2009; Chen et al. 2008; Mantis et al. 2005; Fuentes et al. 2004; Merrington et al. 2003; Álvarez et al. 2002; Scancar et al. 2000), and about possible technologies for its removal (Stylianou et al. 2007; Babel and Dacera 2006; Youshizaki and Tomida 2000).

In the EU countries, from 2000, the implementation of the European Water Framework Directive (EUWFD) (EC 2000b) and its most recent upgrade, the Directive 2013/39/EU (EC 2013), have brought new challenges to the issue of metals removal in the WWTPs (Ruel et al. 2012). The last upgrade of the EUWFD (EC 2013, Annex I) lists forty-five priority pollutants, whose emissions to the environment must cease (priority hazardous substances) or be reduced in order to meet the Environmental Quality Standards (EQS) (EC 2013, Annex II) and so achieve a good status for all surface water and groundwater in the near future. Four metals were classified as priority substances, Cd, Hg, Ni and Pb, the top two also classified as hazardous. Other metals as As, Cu, Cr and Zn are also frequently included in the additional list of substances that potentially may become priority substances in the future (Ruel et al. 2008). Within this new scenario, the expectations are of more stringent criteria and more control requirements to be apply at point source discharges, particularly at WWTPs, which are important secondary sources of anthropogenic substances. Effluents from WWTPs must result in compliance with the surface water EQS, which may involve new requirements for existing WWTPs in the form of advanced wastewater treatment technologies such as ion-exchange, adsorption and membrane filtration (Fu and Wang 2011; Høiby et al. 2008; Bailey et al. 1999). Therefore, there was a new focus in most of the research conducted in the last decade concerning the issue of metals in WWTPs, with a significant amount of published scientific literature within a broader range of

Table 1 Limit values for metals in sludge for agricultural use (mg/kg dry matter)

	EU directive 86/278/EEC ^a	EU working document sludge 3rd draft (proposed) ^b	EU countries with more stringent limits than EU provisions ^c	EU countries with far more stringent limits than EU provisions ^d	USA 40 CFR Part 503
References	EC (1986)	EC (2000a)	EC (2001c), Salado et al. (2008)	EC (2001c), Salado et al. (2008), Olofsson et al. (2012)	US EPA (1995), NRC (2002)
As	–	–	20–150	25	75
Cd	20–40	10	2–10	0.8–2	85
Cr	–	1000	70–1000	75–100	3000 ^e
Cu	1000–1750	1000	70–1000	75–600	4300
Hg	16–25	10	2–10	0.75–2.5	57
Ni	300–400	300	25–200	30–50	420
Pb	750–1200	750	45–900	100–120	840
Zn	2500–4000	2500	200–3000	300–800	7500

^a Countries such as Bulgaria, Cyprus, Estonia, Greece, Luxembourg and Spain set limit values within the same ranges; Ireland, Italy and Portugal set limit values corresponding to the lowest value of the ranges. With the exception of Ireland and Italy, all of these countries have also set limit values for Cr, in most cases in the same order as proposed in the Working Document Sludge, 3rd Draft (EC 2001c; Salado et al. 2008)

^b Proposed concentrations for future revise of the Directive 86/278/EEC

^c Countries such as Austria, Belgium, Finland, France, Germany, Hungary, Poland and Slovenia set limits within the specified ranges; limit values for As only apply in Austria (Bungerland) (20) and Belgium (Flanders) (150)

^d Netherlands and Sweden set limits within the specified ranges for all metals; Denmark set limits within the specified ranges for all metals except for Cu (1000) and Zn (4000); limit value for As only applies in Denmark

^e Chromium was deleted from the regulation in 1995, and EPA is re-examining this limit

issues beyond the exclusive concerns about the quality of the sludge. Some early studies were revisited, and further studies have emerged, which can be grouped according to the following four *subjects/objectives*:

- *Identification and quantification of the sources of metals entering the WWTPs*/to assess the main sources of metals to WWTPs and appropriate strategies to limit its release into the UWS;
- *Removal performance of metals and sludge quality in WWTPs*/to ascertain the ability of treatment systems to achieve the limits imposed by the present and future legal framework;
- *Removal mechanisms, partitioning and mass balances for metals in WWTPs*/to establish the main mechanisms of metals removal and quantify the apportioning of metals, in order to conceive conceptual models of its behaviour;
- *Modelling of metals behaviour in WWTPs*/to establish models of metals behaviour during the liquid and solid phases of treatment, which may be useful in monitoring and optimizing the systems and in supporting regulatory actions and decisions by UWS operators.

Evolving from the above subjects list, the aim of the present work is to critically review the fate and behaviour of metals in WWTPs, through a systematization of results reported in relevant literature in this area. A summary of the main consensus, divergences, constraints and

recommendations is presented as conclusions, aiming to contribute to a more concerted action of future research.

Sources of metals entering the WWTPs

Wastewater is a complex mixture of natural organic and inorganic material mixed with man-made substances. It contains everything discharged to the sewer, including material washed from roads and roofs. It is this complex mixture that ends up at the WWTP for purification. So, a significant part of the anthropogenic emissions of metals ends up in wastewater (suspended, dissolved or complexed) (Sörme et al. 2003). UWSs are the sum of several elements that are managed separately to finally discharge into surface water. The current tendency, promoted by the EUWFD, is to treat the UWS as a single area of operations, where hydraulic infrastructures, WWTPs and point source discharges have to be managed from an integrated point of view (Murillo et al. 2011). There are two basic types of sewerage systems, combined and separate. Combined sewerage is common in most European cities, and both surface runoff from paved areas and sewage are collected together for subsequent treatment (Gray 2005). The WWTP is the central unit of the UWS, receiving the polluted wastewater coming from the urban area, originated from several sources as *industrial sites, households/domestic* (faeces and urine, food, amalgam, detergents, pipes and taps, drinking water, artist paint),



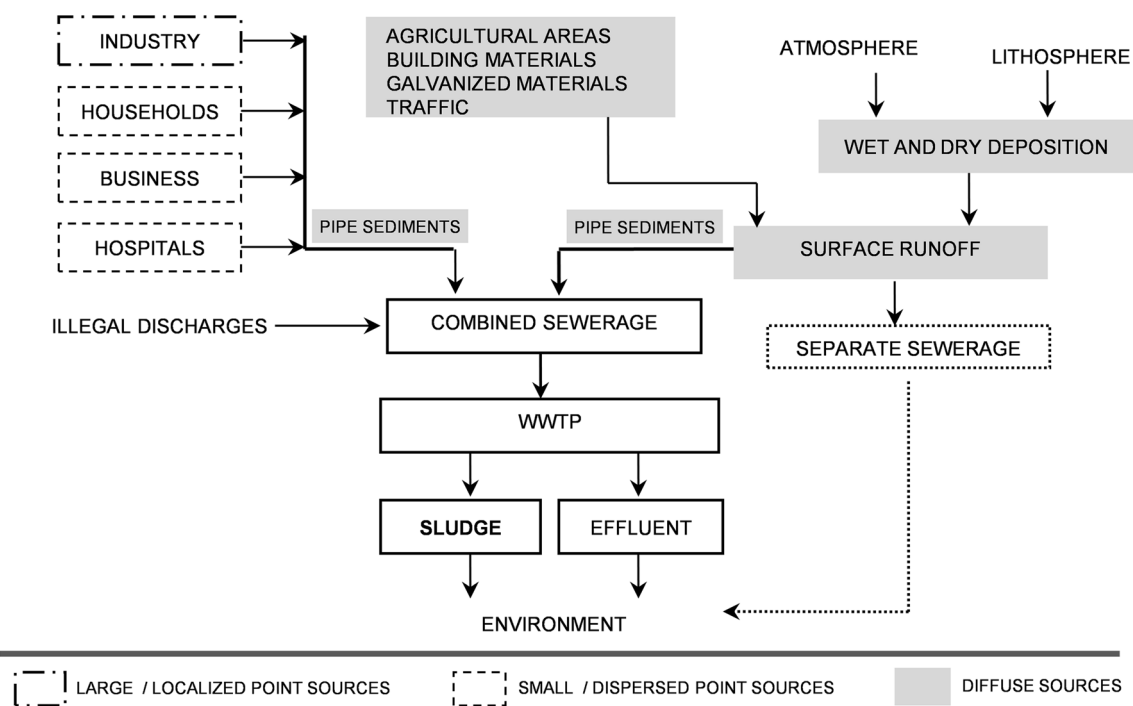


Fig. 1 Different sources for metals entering the WWTPs

business/commercial (car washes, dentists, large enterprises), *hospitals* (diagnostic agents, disinfectants, pharmaceuticals), *pipe sediments* and *surface runoff* from *building materials* (roofs and fronts), *galvanized materials*, *traffic* (brake linings, tires, asphalt wear, gasoline/oil leakages) and *agricultural areas*. As a significant part of the urban soil surfaces is impermeable, metals via *atmospheric deposition* will also be transported with storm water to WWTPs in combined sewage pipes, or directly to water recipients (Emmanuel et al. 2005; Nabizadeh et al. 2005; Sörme and Lagerkvist 2002; Bergbäck et al. 2001; EC 2001a). Apparently, there is not a general consensus in the literature regarding the classification of these sources, as point or diffuse sources, probably because it depends on the referential that is being considered. Our view is that given the collecting system as a reference, there are two main groups of *point sources* into the WWTP influent—*large/localized* and *small/dispersed*, and a group of *diffuse sources*, which are all the inflows carried with storm water to the collecting system, including the releases from the sediments accumulated in pipes. Large point sources, such as industrial sites and hospitals, are more easily identifiable and quantifiable and so susceptible to end of pipe treatments, which does not happen with other sources, for which the strategy to minimize its pollution must pass by upstream precautionary measures. However, discharges from small/dispersed sources, as households or business, can be identified in the collection system and be sampled by area in order to distinguish different sources as was done in some studies (Mattsson et al. 2012; Rule et al. 2006). UWSs are also

vulnerable to illegal pollutant discharges; therefore, these have also to be considered as potential sources. A schematic diagram of the different sources for metals entering the WWTPs is presented in Fig. 1.

Impact of discharge regulation for large point sources

The sources of metals to WWTPs were early mostly connected to industrial activities. In recent years, due to the stringent limits in legislation, pre-treatments were generally imposed to industrial effluents and clean technologies have increased. Also, conditions for the connection of hospital wastewater systems into the UWS have been fixed in most countries (Emmanuel et al. 2005). Therefore, the levels of metals emitted by large point sources have been declining in many countries. According to some recent studies, time-trend analyses of metals in sewage sludge reflect this decrease. Data from three WWTPs in Stockholm allowed to conclude that metal contents (Cd, Cr, Cu, Hg, Ni, Pb and Zn) in sewage sludge significantly decreased in the late 1970s and the early 1980s, but since then the contents have stabilized (Sörme and Lagerkvist 2002). Olofsson et al. (2012) performed a time-trend analysis of various contaminants in sludge, based on samples collected from 2004 to 2010 at nine WWTPs distributed across Sweden, and concluded that sewage sludge could be a suitable matrix for tracking changes in chemical use in society. The median concentrations

obtained for different classes of sludge contaminants showed very large differences, with metals being the most abundant. Many of the contaminants, including some metals, followed the trends of quantities used in the society, generally decreasing due to regulatory actions. However, the levels of some priority contaminants, as is the case of Cd, appeared to be rather constant, although they are also expected to decline in the future, due to stricter regulations being imposed. In a study concerning historical data from Rya WWTP in Sweden, Mattsson et al. (2012) observed a significant decrease in metal concentrations into the influent wastewater and a consequent improvement in sludge quality, due to the drastic reduction in industrial emissions as well as to the bans on the use of Cd, Pb and Hg in most applications. An improvement of storm water quality was also recorded, due to the less deposition of metals and less corrosion of buildings and other structures, because of the improved air quality. With the exception of Cu, where no major change has occurred, the concentration of the remaining six regulated metals in sludge has decreased to between one-tenth and one-third of the concentrations in the 1970s.

Undoubtedly, national and international environmental legislation and regulations have been proven to be powerful tools in order to minimize the release of hazardous substances into the environment and so into the wastewaters. At present, most chemical restrictions apply across Europe under the *Registration, Evaluation, Authorization and restriction of Chemical substances* (REACH) regulation (EC 2007), which entered into force on 1 June 2007 and will be applied in the Member States. The use of Cd, Hg, Pb and hexavalent Cr in new electrical and electronic equipment has been prohibited since 2006 in the EU market by the EU directives on the Restriction of the use of certain Hazardous Substances (RoHS) (EC 2002, 2011). However, these regulations and legislations only cover a part of the problem of urban metal flows, noting that the progress of their effective implementation should be quite distinct in the different countries.

Increased relevance of other sources

In fact, industrial sources have been declining, but the relevance of other sources has increased due to the consumption of various metal-containing goods (Olofsson et al. 2013). Some goods applications may correspond to significant emissions, e.g. the traffic sector (Cu, Zn, Cr, Ni, Pb), the tap water system (Cu) and roofs/fronts or other metal surfaces (Cu, Zn) (Bergbäck et al. 2001), although quantitative information on metals in urban runoff arising from anthropogenic activities is difficult to evaluate due to the lack of information on its background levels in the environment. Background concentrations are related to natural geochemical and biochemical sources and include amounts in soils, dusts and waters,

derived from historical pollution (EC 2001a). Historical and present emissions may be responsible for high metal concentrations found in sediments (particularly Cd, Hg and Pb, but also Cu and Zn), groundwater (Cu, Hg) and soils (Hg, Cu, Pb) (Bergbäck et al. 2001). The actual contribution from different goods to sewage and storm water seems to be relatively unknown, with few studies providing a comparison of the significance of various sources (Rule et al. 2006), although some important studies have been undertaken. Table 2 presents the source emissions estimated on some recent studies reported in the literature. More often, sources are quantified according to three main classes, households/domestic, business/commercial and urban runoff/storm water, while these sources are studied in more detail in a few studies that quantify the different sources within each class.

In general, published data in this field indicate a high degree of uncertainty regarding the inputs of some metals entering the WWTPs. It should also be noted that there are significant differences between the conditions from which data are obtained in the different studies (sampling, duration, location, measurement targets, etc.).

According to EC (2001a), data collected from a review on the assessment of metals entering UWS in three European countries (France, Norway and UK) allowed to conclude that domestic inputs were the largest sources of Cu, Zn and Pb, whereas commercial sources represent the major inputs of Hg and Cr.

Sörme and Lagerkvist (2002) investigated the sources of metals in sewage and storm water influents to Henriksdal WWTP in Stockholm and concluded that it was possible to track the sources of Cu, Zn, Ni and Hg (110, 100, 70 and 70 % found, respectively). The largest sources for these metals have been identified, tap water and roofs for Cu, galvanized materials and car washes for Zn, drinking water and chemicals used in the WWTP for Ni and amalgam in teeth for Hg. For Cd, Pb and Cr, where sources were more poorly understood (60, 50 and 20 % found, respectively), the larger contributors for all were car washes. However, the comparison of these estimated contributions with previously done measurements showed that measured contribution from households was higher than that estimated for all metals, except Hg, leading to the conclusion that the sources of sewage water from households are still poorly understood or that known sources were underestimated. In the case of storm water, the estimated contributions were rather well in agreement with measured contributions, although with large uncertainties for both estimations and measurements. Hg and Pb releases from existing pipe sediments in the plumbing system are given as a likely explanation for the missing amount of these metals.

Mattsson et al. (2012), in a study concerning the Gothenburg region in Sweden, noted that due to the decrease in industrial activity, aforementioned, and to an

Table 2 Emission of metals from different sources entering the UWS (% of total load to WWTP)

	Source	Cd	Cr	Cu	Hg	Ni	Pb	Zn
EU countries ^a EC (2001a)	<i>Household/domestic</i>	20–40	2–20	30–75	4 ^b	10–50	26–80	28–50
	<i>Business/commercial</i>	29–61	35–60	3–21	58 ^b	27–34	2–24	5–35
	<i>Urban runoff/storm water</i>	3–41	2–22	4–6	1 ^b	9–16	29–33	10–16
Sweden, Stockholm Henriksdal WWTP Sörme and Lagerkvist (2002)	<i>Sewage water</i>	55	17	91	66–69	39	40	61
	<i>Household/domestic</i>	20	2	59	44–47	16	1	30
	<i>Drainage water</i>	3	2	2	1	10	1	4
	<i>Pipe sediments^c</i>	(–)	(–)	(–)	(+)	(–)	(+)	(–)
	<i>Business/commercial</i>	32	13	30	21	13	38	27
	<i>Urban runoff/storm water</i>	5	1	18–22	(–)	1	13–15	36–37
	<i>Buildings^c</i>	1	(–)	13–17	(–)	(–)	(–)	24
	<i>Traffic^c</i>	1	<1	5	(–)	<1	9–11	10–11
	<i>Atmos. deposition^c</i>	4	1	<1	(–)	1	4	2
	<i>Pipe sediments^c</i>	(–)	(–)	(–)	(+)	(–)	(+)	(–)
	<i>WWTP chemicals</i>		5			31		2
Sweden, Gothenburg ^d Rya WWTP Mattsson et al. (2012)	<i>Household/domestic 1988</i>	25	21	29	40	23	15	38
	<i>Household/domestic 2006/07</i>	35	34	54	43	32	41	54

^a Ranges of values for three countries, France, Norway and UK (ADEM 1995, SFT report 97/98 and WRc, 1994 cited by EC 2001a)

^b Data for France only (ADEM 1995 cited by EC 2001a)

^c (–) Indicates that the source is insignificant compared to other sources in the study; (+) indicates that the source probably is significant, but the amount has not been estimated

^d Data from two residential areas served by the Rya WWTP (700 inhabitants, detached houses; 2400 inhabitants, apartments)

increase in the number of inhabitants connected to the Rya WWTP (16 %), the relative contribution of metal loads from households increased by 10–25 % between 1988 and 2006/07, being particularly highlighted the relevance of artist paints as a source of Cd (10 % of the Cd to Swedish WWTPs) and of pipe sediments in sewers connected to dentists and hospitals as a source of Hg.

Although the emissions are not available in terms of percentage of the total load received by the WWTP, and so not displayed in Table 2, an important study on this field was recently performed by Rule et al. (2006), which determined the concentrations of metals listed in the EUWFD in the wastewater from an urban catchment in the UK, including samples from dispersed point sources in different urban areas (light industrial estate, new housing estate, old housing estate, town centre north and town centre south) and samples from runoff in two sites that were collected throughout the duration of rain events. Concentrations in the wastewater samples from domestic and commercial sources were found at similar levels for all the metals, with both Cr and Hg less than or near to the limit of detection for most samples, while average concentrations in the light industrial estate samples were higher than in domestic or commercial samples for four of

the seven metals (Cr, Cu, Pb and Zn). In domestic wastewater samples, the most significant differences were observed for Cd and Cu, both of which were found in the new housing estate at concentrations approximately double those in the older housing estate, attributable, in the case of Cu, to leaching from the newer plumbing systems. For the commercial wastewater samples, metals were generally found at similar levels in samples from the north and south sides of the town centre, with the exceptions of Hg and Zn, both of which were higher in the north town centre. This difference was attributed to discharges from dental practices via the sewer sampled at the north town centre, in the case of Hg, although no particular justification could be found for Zn. In urban runoff samples, concentrations for all metals were generally higher in the light industrial estate samples than in the household samples, being particularly highlighted that the first rain event sampled at the light industrial estate came after a long antecedent dry period, and so the intensity of the rain event leads to high suspended solids loadings in the sample, with associated high concentrations of metals.

Despite the similarities and differences in the conclusions that were found, all the above studies point to the conclusion of a general change in the main sources of

metals to the WWTPs. The major share of metals originates from small dispersed point sources and diffuse sources, due to consumption of various products, which means that a focus on large point sources is no longer sufficient. So, long-term strategies to reduce metals emissions to WWTPs must involve the reduction in dispersed and diffuse emissions, meaning the inflow of metals in society, and a better overview of the urban erosion processes. The analysis of the extent to which an UWS has the capacity to influence the dispersed and diffuse emissions into the WWTP allows us to conclude that it is in general very limited. The management of collective pollution problems is complicated to regulate and also demands cooperation between different actors (Sörme et al. 2003). Regulation in the commercialization and use of hazardous substances as metals is undoubtedly a crucial reduction strategy for the future, but, in the meantime, WWTPs have an important role as a barrier between the urban metal flows and the environment. Therefore, it is essential to know the ability of treatment systems to achieve the concentration limits imposed or planned by the actual legal framework and to assess the possibilities of optimizing its performance in what concerns the removal of metals, as have been suggested by many studies outlined below.

Removal performance of metals and sludge quality in WWTPs

WWTPs are designed for the physical, chemical and biological removal of readily biodegradable organic materials, which correspond to the so-called conventional parameters of wastewater, namely biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), nutrients (nitrogen and phosphorus) and bacterial pathogens. The treatment system is a combination of unit operations and processes, designed to produce an effluent of specified quality (liquid-phase treatment) and to process the sludge arising from the treatment of wastewater to a suitable condition for disposal (solid-phase treatment).

Treatment systems in WWTPs

In the liquid-phase treatment, unit operations and processes are usually classified into sequential treatment stages (preliminary, primary, secondary, tertiary), according to the conventional parameters that are removed (Metcalf & Eddy Inc 2003). Depending on the quality required for the final effluent, not all the stages will be considered, but secondary treatment is mandatory to all urban effluents discharged to inland waters (Gray 2005).

In the so-called conventional WWTPs, secondary treatment consists of an aerobic biological reactor (BR)

followed by a sedimentation tank to separate the microbial biomass from the treated effluent. The BR may be a fixed-film process (e.g. percolating filters, rotating biological contactors), but most usually is an activated sludge process (ASP) in which a dense microbial biomass is kept in suspension mixed with the wastewater (mixed liquor), and where the required concentration of biomass is maintained by the recirculation of some of the settled activated sludge in the secondary settler. After treatment, the clarified water is released into superficial waters or eventually reused. In the solid phase, sludge treatment usually follows the sequence of thickening, stabilization and/or chemical conditioning and dewatering, being the respective supernatant streams returned to the liquid phase of treatment. The mean flow of wet sludge produced at a conventional WWTP will be in the order of 1–2 % of the influent wastewater flow (Gray 2005). A typical layout of a conventional WWTP is depicted in Fig. 2.

ASP and modifications

ASP is arguably the most common biological process adopted in WWTPs worldwide (Pomiès et al. 2013; Choubert et al. 2011b; Murillo et al. 2011; Gray 2005; Álvarez et al. 2002), although the characteristics of the reactors may vary in which concerns the hydraulic regime and the operating conditions, the latter mainly determined by the rate of recirculation of activated sludge (RAS). Operating conditions establish the loading rate, i.e. the substrate/biomass ratio (F/M , kg BOD/kg MLVSS) and the solids retention time (SRT, days), which determine the predominant removal mechanisms of organic matter in the reactor (adsorption/agglomeration into microbial flocs, assimilation/conversion to new microbial cell material and mineralization/complete oxidation) and therefore are crucial issues to consider when analysing any ASP. ASP more often operates in continuous mode, although a renewed interest in batch operation has emerged in recent decades, with the introduction of the sequencing batch reactors (SBRs), in which reaction/aeration and settlement take place in the same tank according to a cyclic sequence previously defined. More recently, there is an increasing interest in replacing the secondary settler unit with either an internal or external membrane filtration unit to separate the solids from the final effluent (Judd 2006; Berthold and Krauth 1998; Côté et al. 1998; Engelhardt et al. 1998). These membrane bioreactors (MBRs) offer several advantages, but its higher operation costs, due to energy consumption and membrane replacement, remain a significant drawback for its wider application in municipal wastewater treatment (Meng et al. 2009; Judd 2008).



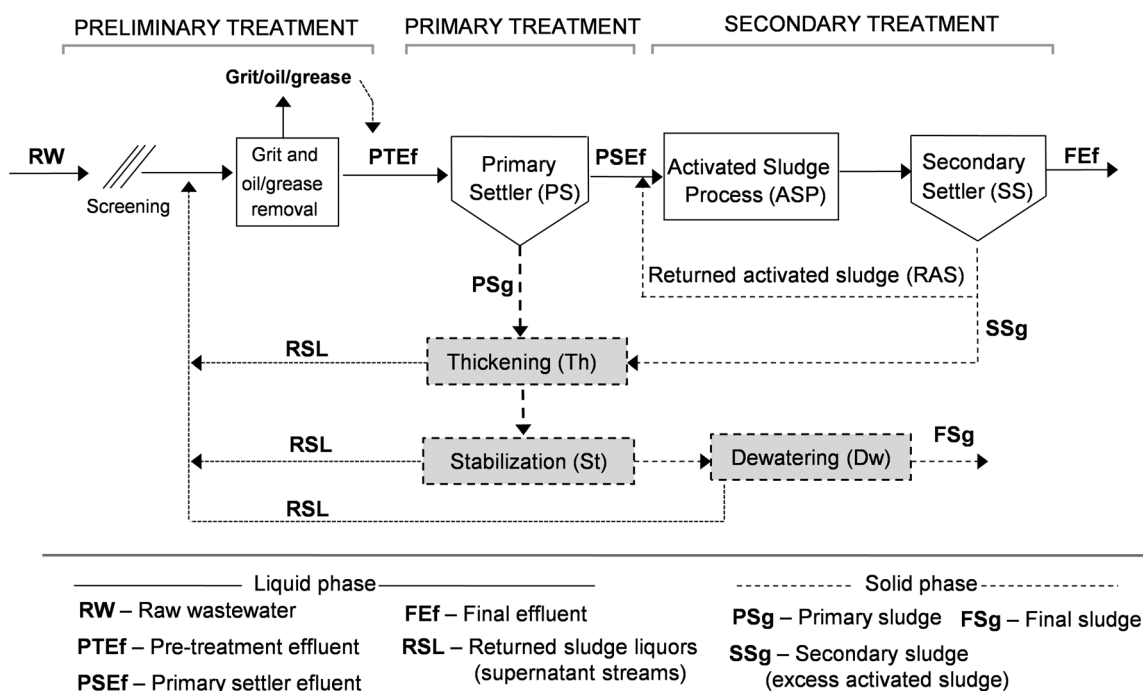


Fig. 2 Typical layout of a conventional WWTP

Sludge treatment options

Options for sludge stabilization may vary between biological, chemical or thermal processes, all with the aim of preventing the utilization of the volatile and organic fraction of the sludge during storage. Biological stabilization processes are the most widely practiced, and anaerobic digesters are the most common method for medium- to large-sized treatment plants (Gray 2005). Sludge can also be stabilized by continuing oxidation of waste activated sludge over a prolonged period in the ASP reactor (extended aeration, low load, high SRT), option that is often adopted for small-sized WWTPs, which not only reduces sludge production and simplifies the subsequent solid-phase line (liming and dewatering), but also may have the additional advantage of making the primary settling operation dispensable.

Thus, all the above aspects have to be taken into account when trying to perform a comparative analysis on removal performance of any contaminant in different full-scale WWTPs, in this case for metals, since the fate of contaminants after reaching the WWTP, during wastewater treatment, should depend not only on the nature of the compounds but also on the present operating conditions. The literature review on this point showed a great lack of uniformity in the way WWTPs are described, with missing information about fundamental aspects of the studied WWTPs as are the WWTP capacity, the loading rate of the BR (L_R), the SRT in the BR and the treatment line for solid phase.

Metals removal efficiencies in the liquid phase of treatment

In recent decades, numerous studies concerning the issue of metals in WWTPs have focused on the levels of metals in the influent raw wastewater, the final effluent, and the final sludge, in order to assess the ability of the treatment systems to achieve the concentration limits imposed, or planned, by the actual framework. A fewer number of studies focused on the fate and behaviour in terms of removal efficiency, mass balances and partitioning of metals. Unfortunately, most of the studies in this field only provide partial information, only focused on final effluents or final sludge, with disseminated data in a manner which is not easily available for practical use, as was well detailed by Ruel et al. (2008).

Much data have been published in scientific literature and considered in official reports concerning metals removal in the final effluent and the quality of sludge produced in the WWTPs in different countries (e.g. Salado et al. 2008; EC 2001a). However, although it is generally accepted that most of the metals entering the WWTP will end up in the sludge and that only a small amount is released via the final effluent, relevant data about their removal efficiencies and fate in treatment systems remain contradictory. In order to illustrate this context and to allow identifying the main agreements/disagreements, a set of studies was selected for review in the present work, based on their relevance in terms of timeliness or citation frequency in the literature. The data collected are presented in Tables 3 and 4.

Table 3 Wastewater treatment plants descriptive data

WWTP	Capacity (population equivalent)	WWTP sources ⁽¹⁾	Treatment system	WWTP _{TRH} ⁽⁴⁾	$L_R^{(5)}$	SRT ⁽⁶⁾	$T^{(7)}$
			Liquid phase ⁽²⁾	Solid phase ⁽³⁾	Liquid phase	Days	°C
Italy							
5 WWTPs	400,000	D_f, I_f (70 %), U_r	Scr/Gr/PS/ASP/SS	$Th/AnD/Dw$	–	–	–
Carletti et al. (2008)							
WWTP A	70,000	D_f, U_r	Scr/Gr/ASP/SS	$Th/AnD/Dw$	–	–	–
WWTP B	100,000	D_f, U_r	Scr/Gr/MBR	$Th/AnD/Dw$	–	–	–
WWTP C	440,000	D_f, I_f (37 %), U_r	Scr/Gr/ASP/SS	$Th/AnD/Dw$	–	–	–
WWTP D	80,000	D_f, I_f (6 %), U_r	Scr/Gr/PS/ASP/SS	$Th/AnD/Dw$	–	–	–
WWTP E	6,500,000	D_f, I_f, U_r	Scr/Gr/PS/ASP/SS/TT(FeCl ₃)	$Th/AnD/Dw$	≈ 6 h (2 h in ASP)	–	–
Seine_Aval WWTP, Paris, France	1,000,000	D_f, I_f, U_r	Scr/Gr/PS/ASP/SS/Df	$Th/AnD/Dw_{bf}$	≈ 24 h	–	–
Buzier et al. (2006)	–	D_f, I_f, U_r	Scr/Gr/PS/ASP _{ML} (_{rns} ep)/SS	$Th/Mix/AnD/Dw_c$	–	–	–
Thessaloniki, Greece, Karvelas et al. (2003)	–	D_f, I_f, U_r	Scr/Gr/PS/ASP/SS	$Th^{(8)}/AnD/Dw$	–	–	–
Gdansk, Poland, Chipasa (2003)	900,000	D_f, I_f, U_r	Scr/Gr/PS/ASP/SS ⁽⁹⁾	$Th/AnD/Dw$	–	15	–
Whitlingham WWTP, Norwich, UK							
Goldstone et al. (1990a, b, c)	680,000	D_f, I_f, U_r	Scr/Gr/PS/ASP/SS ⁽⁹⁾	$Th/AnD/Dw$	–	15	–
Sweden	330,000	D_f, I_f, U_r	Scr/Gr/PS/ASP/SS ⁽¹⁰⁾	$Th/AnD/Dw$	–	30	–
7 WWTPs	116,000	D_f, I_f, U_r	Scr/Gr/PS/ASP/SS ⁽⁹⁾	$Th/AnD/Dw$	–	18	–
Olofsson et al. (2013)	110,000	D_f, I_f, U_r	Scr/Gr/PS/ASP/SS ⁽⁹⁾	$Th/AnD/Dw$	–	29	–
	60,000	D_f, I_f, U_r	Scr/Gr/ASP/SS ⁽⁹⁾	$Th/AnD/Dw$	–	17	–
	13,000	D_f, I_f, U_r	Scr/Gr/ASP _{LL,est} /SS ⁽⁹⁾	Th/SDw	–	18	–
France	2900	Rural area	Scr/Gr/ASP _{LL,est} /SS	Th/Dw	0.07	25	9
9 WWTPs							
Choubert et al. (2011a, b)							
WWTP 1	13,000	Rural area	Scr/Gr/ASP _{LL,est} /SS	Th/Dw	0.1	16	13
WWTP 2	36,000	D_f, I_f, U_r	Scr/Gr/ASP _{LL,est} /SS	Th/Dw	0.04	27	15
WWTP 3	250,000	D_f, I_f, U_r	Scr/Gr/PS/ASP _{LL,est} /SS	Th/Dw	0.08	13	20
WWTP 4	500,000	D_f, I_f, U_r	Scr/Gr/ASP _{LL,est} /SS	Th/Dw	0.05	26	23
WWTP 5	110,000	D_f, I_f, U_r	Scr/Gr/ASP _{LL,est} /SS	Th/Dw	0.06	18	20
WWTP 6	950,000	D_f, I_f, U_r	Scr/Gr/PS/ASP _{ML} /SS + BF _N	–	–	–	20
WWTP 7							

Table 3 continued

WWTP	Capacity(population equivalent)	WWTP sources ⁽¹⁾	Treatment system	WWTP ⁽⁴⁾ _{TRH}	L _R ⁽⁵⁾	SRT ⁽⁶⁾	T ⁽⁷⁾
WWTP 8	1000	Rural area	Scr/Gr/RBC + RBF	5.3 h (RBC?)	5 ⁽¹¹⁾	na ⁽¹²⁾	–
WWTP 9	24,000	D _f , I _f , U _r	Scr/Gr/MBR	–	0.06	17	20
5 ASP _{LL}	–	–	Scr/Gr/ASP _{LL} /SS	–	–	–	–
11 WWTPs							
5 Low-loaded ASP (ASP _{LL})							
6 Biofilm Processes (BioFP)							
Choubert et al. (2011b)							
BioFP A	80,000	–	PS _c /BF (1 stage)	–	–	na ⁽¹²⁾	–
BioFP B	26,000	–	PS _c /BF (2 stages)	–	–	na ⁽¹²⁾	–
BioFP C	17,000	–	PS _c /MBBR (2 stages)	–	–	na ⁽¹²⁾	–
BioFP D	300	–	PS/SP/vertical RBF (2 stages)	–	3 ⁽¹¹⁾	na ⁽¹²⁾	–
BioFP E	1000	–	RBC/vertical RBF (2 stages)	–	5 ⁽¹¹⁾	na ⁽¹²⁾	–
BioFP F	100	–	Horiz RBF/vertical RBF (2 stages)	–	100 ⁽¹¹⁾	na ⁽¹²⁾	–
Seville, Spain							
5 WWTPs	–	D _f , I _f , U _r	Scr/Gr/PS/ASP _{ML} /SS	Th/AnD/Dw _{bf}	–	–	–
Álvarez et al. (2002)							
Domzale, Slovenia	–	D _f , I _f ⁽¹³⁾ , U _r	–	–	–	–	–
Scancar et al. (2000)							

⁽¹⁾ D_f—domestic flow; I_r—industrial flow; U_r—urban runoff; ⁽²⁾ *italic*—presumed in view of what is usually adopted in WWTPs) Ser—screening; Gr—grit removal; PS—primary settler; PS_c—primary settler with chemical addition; ASP—activated sludge process (loading rate not specified, presumably medium/high load); ASP_{LL,cat}—low-load/extended aeration; ASP_{ML}—medium load; ASP_{ML(RNep)}—ASP configured to enhance biological nutrient removal); SS—secondary settler; DF—disinfection; RBC—rotating biological contactor; RBF—reed bed filter; MBR—membrane bioreactor; MBBR—moving bed bioreactor; BF—biofilter; BF_N—biofilter for N removal; SP—stabilization pond; TT—tertiary treatment; ⁽³⁾ Th—thickening; AnD—anaerobic digestion; SI—stabilization; Mix—mixture of primary and secondary sludge; Dw—dewatering (Dw_{bf}—belt filter presses; Dw_c—centrifuges); ⁽⁴⁾ WWTP_{TRH}—residence time of wastewater in the WWTP; ⁽⁵⁾ L_R—loading rate (F/M) (kg BOD/kg MLVSS); ⁽⁶⁾ SRT—solids retention time in ASP (sludge age); ⁽⁷⁾ T—temperature in biological reactor; ⁽⁸⁾ only applies to secondary sludge, primary sludge is directly purged to the anaerobic digester; ⁽⁹⁾ chemical addition before ASP; flocculation of phosphorus with ferrous sulphate (Olofsson et al. 2010); ⁽¹⁰⁾ chemical addition after ASP; ⁽¹¹⁾ g BOD₅/m²/d; ⁽¹²⁾ na—not applicable; ⁽¹³⁾ industrial sources are mainly metal works

Table 4 Sampling campaigns, sample types, total metal concentrations in liquid and solid phases and liquid-phase removal efficiencies in various WWTPs

WWTP	Sampling Campaigns	Sample ⁽¹⁾	Sample type ⁽²⁾	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	SS/d.w. ⁽³⁾	
Italy 5 WWTPs Carletti et al., 2008	18 months sampling frequency? number of samples?	WWTP A (70% Ind)	Liquid phase, Mean (µg/L) ± Var.Coeff.									mg/L	
			RW	Cs (24h)	8.8	0.4	26.2 ± 68%	32.2 ± 19%	3.8 ± 49%	17 ± 75%	6.5 ± 29%	254 ± 42%	101
		WWTP B	FEF		2.7	0.25	8.6	20.8	2.0	11.7	2.5	223	
			T Mean Removal (%)	69	38	67	35	47	31	62	12		
		Solid phase, Mean (mg/kg d.w.) ± Var.Coeff.											
		SSg		3	1.0 ± 7.5%	560 ± 9%	192 ± 12%	3 ± 52%	35 ± 8%	46 ± 6%	840 ± 4%		
		Liquid phase, Mean (µg/L) ± Var.Coeff.											
		RW	Cs (24h)	4.0	nd	8.1 ± 11%	9.9 ± 56%	1.5 ± 58%	3.5 ± 31%	8.0	348 ± 31%	129	
		FEF		2.0	nd	6.9	13.5	0.6	3.9	9.5	82.8		
		T Mean Removal (%)	50	–	15	–36	60	–11	76				
Solid phase, Mean (mg/kg d.w.) ± Var.Coeff.													
SSg		7	1.0 ± 57%	46 ± 56%	165 ± 18%	5 ± 96%	31 ± 40%	72 ± 30%	1408 ± 74%				
FSg		nd	1.0	40	196	nd	36	56	8900				
(4) Sg accordance													
Liquid phase, Mean (µg/L) ± Var.Coeff.													
RW	Cs (24h)	nd	8.7 ± 13%	56.4 ± 24%	9.8 ± 44%	0.7 ± 8%	16.6 ± 23%	8.6	1233 ± 20%	262			
FEF		nd	< 0.25	2.7	5.59	0.7	2.41	4.4	63				
T Mean Removal (%)	–	≥ 97	95	43	0	85	49	95					
Solid phase, Mean (mg/kg d.w.) ± Var.Coeff.													
SSg		nd	1.0	17	264	nd	34	78	716				
FSg		12	1.6	30	317	5.1	25.5	64.5	946				
(4) Sg accordance													
Liquid phase, Mean (µg/L) ± Var.Coeff.													
RW	Cs (24h)	2.7 ± 68%	27.8 ± 62%	56.4 ± 37%	38.0 ± 61%	1.8 ± 40%	61.7 ± 4%	2.0 ± 60%	2411 ± 29%	247			
FEF		1.6	0.1	14.0	15.2	1.35	7.15	16.4	325				
T Mean Removal (%)	41	100	75	60	25	88	–720	87					
Solid phase, Mean (mg/kg d.w.) ± Var.Coeff.													
SSg		15 ± 42%	3.0 ± 50%	118 ± 56%	239 ± 61%	35.9	35 ± 67%	135 ± 50%	2341 ± 98%				
FSg		40.4	6.8	310.2	38.9	3.2	201.2	3.1	8385				
(4) Sg accordance													
Liquid phase, Mean (µg/L) ± Var.Coeff.													
RW	Cs (24h)	6.0 ± 33%	0.6 ± 34%	59.2 ± 99%	60.9 ± 39%	nd	21.6 ± 60%	10.5 ± 27%	227 ± 37%	327			
FEF		4.9	< 0.25	19.8	15.6	nd	1.93	4.95	164				
T Mean Removal (%)	18	≥ 58	67	74	–	91	53	28					
Solid phase, Mean (mg/kg d.w.) ± Var.Coeff.													
SSg		4 ± 35%	1.0 ± 49%	525	348 ± 8%	2 ± 81%	107 ± 45%	61 ± 18%	433 ± 27%				

Table 4 continued

WWTP	Sampling Campaigns	Sample ⁽¹⁾	Sample type ⁽²⁾	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	SS/d.w. ⁽³⁾		
Paris, France Seine_Aval WWTP Buzier <i>et al.</i> , 2006	6 days	<i>Liquid phase, Median (µg/L)</i>												
		RW	Cs (24h),fp	nd	0.6	9	60–65	nd	10–12.5	17.5–20	nd	nd		
		PSEF	Cs (24h),fp	nd	0.4	3.5–4	35–40	nd	7.5–10	5	nd	nd		
			P Mean Removal (%)	–	33	58	40	–	22	73	–	–	–	
		Ef _{RT}	Cs (24h),fp	nd	0.3	3–4	15–20	nd	7.5–10	3–4	nd	nd		
		FEF	Cs (24h),fp	nd	< 0.2	2–3	5–10	nd	11–12.5	< 1	nd	nd		
	T Mean Removal (%)	–	≥ 67	72	88	–	–	–	–	–	–			
Greece Thessaloniki WWTP Karvelas <i>et al.</i> , 2003	2 x 5 days N=9	<i>Liquid phase, Mean ± SD (µg/L)</i>												
		RW	Cs (24h),fp	nd	3.3 ± 1.1	40 ± 12	79 ± 35	nd	770 ± 200	39 ± 9.4	470 ± 140	690 ± 160		
		PSEF	Cs (24h),fp	nd	2.3 ± 0.9	25 ± 12	58 ± 37	nd	600 ± 270	31 ± 12	380 ± 50	340 ± 129		
			P Mean Removal (%)	–	30	38	27	–	22	21	19	–	–	
		FEF	Cs (24h),fp	nd	1.5 ± 0.7	20 ± 4	33 ± 6	nd	430 ± 97	27 ± 3.6	270 ± 53	12 ± 9.3		
			T Mean Removal (%)	–	55	50	58	–	44	31	43	–	–	
	FEFD limits ⁽⁵⁾ (µg/L)	–	500	4000	2000	–	4000	1000	10 000	–	–			
Poland Gdansk WWTP Chipasa, 2003	2 years, 1/month	<i>Solid phase, Mean ± SD (mg/kg d.w.)</i>												
		PSg	Gs-c	nd	1 ± 0.4	17 ± 6	100 ± 21	nd	37 ± 12	28 ± 8	350 ± 3	2.3 ± 0.4		
		SSg	Gs-c	nd	1 ± 0.4	32 ± 13	91 ± 17	nd	31 ± 16	16 ± 3	440 ± 59	0.7 ± 0.1		
		FSG	Gs-t _{AN} (21 d)	nd	10 ± 4	370 ± 100	1200 ± 220	nd	300 ± 76	330 ± 84	4500 ± 450	22 ± 0.5		
			(⁽⁴⁾) Sg accordance	(+)	(+)	(+)	(+)	(+)	(+)	(+)	(+)	(+)	NA	
			FEFD limits ⁽⁵⁾ (µg/L)	–	500	4000	2000	–	4000	1000	10 000	–	–	
Whitlingham WWTP Norwich, UK Goldstone and Lester, 1990a, 1990b, 1990c	8/10 days (2 days to As)	<i>Liquid phase, Mean (µg/L)</i>												
		RW	CgS(8/d)	11–12.5	1.5–2.0	35	250–300	2.5	40	600	275–300			
		RW+RSLAN	CgS(=4/d)	12.5–13	2.75–3.0	65–70	650–700	4.0–4.25	50–55	600–650	500–525			
		PSEF	CgS(8/d)	2.5–4	0.75–1.0	20–25	175–200	0.5–0.75	25–30	175–200	150–175			
			P Mean Removal (RSD) (%)	72	41 (23)	55 (41)	39 (20)	62 (19)	43 (28)	50 (29)	64 (23)			
		PSEF+RAS	CgS(=8/d)	4.5–5	1.25–1.5	75–80	800–825	2.5	35	500–525	300			
	FEF	1/d	2–2.5	0.25–0.5	10	50–75	0.25	20–25	25	100–125	61			
	T Mean Removal (%)	81	79	71	77	90	44	96	–	–	–			
	<i>Solid phase, Mean (RSD) (mg/kg d.w.)</i>													
	PSg	1/d	nd	41.4	719.7	6415.6	39.6	441.7	2425.1	6293.4	nd			
	SSg	nd	nd	(40.8)	(22.3)	(29.6)	(40.4)	(21.5)	(41.3)	(33.6)	nd			



Table 4 continued

WWTP	Sampling Campaigns	Sample ⁽¹⁾	Sample type ⁽²⁾	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	SS/d.w. ⁽³⁾
Solid phase, Mean (mg/kg d.w.)												
1 Stockholm		FSg		4.2	1.2	19.9	387	1.4	22.4	26.5	501	
2 Gothenburg		FSg		3.9	1.1	24.3	433	0.7	17.1	29.5	548	
3 Eslöv		FSg		3.8	1.2	18.6	336	0.4	9.9	14	329	
4 Urmeå		FSg		4.3	1.1	15.3	132	0.9	16.6	17.9	569	
5 Borås		FSg		3.2	0.8	28.7	337	1.1	9.5	22	430	
6 Alingsås		FSg		4.6	0.8	42.4	298	0.7	9.9	27.5	389	
7 Floda		FSg		2.4	0.6	48.1	159	0.5	14.6	11.7	252	
⁽⁴⁾ Sg accordance (+) (+) (+) (+) (+) (+) (+) (+) (+)												
Liquid phase, Range between the first and the third quartile (µg/L)												
France 9 WWTPs	2-3 days (consecutive) N=21	RW	Cs (24h),fp	3-10	≤3	10-100	10-100	nd	10-100	10-100	100-1600	
Choubert et al., 2011a	(2-3/WWTP)	FEF	Cs (24h),fp	-	-	-	-	nd	-	-	-	
T Mean Removal (%) 20 40-75 ≥75 ≥75												
Liquid phase, Mean (µg/L)												
France 11 WWTPs	2-3 days (consecutive)	5 ASP_{LL}	T Mean Removal (%)	<30	30-70	>70	>70	>70	30-70	>70	30-70	
Choubert et al., 2011b		6 BiofP A-F	T Mean Removal (%)	<30	30-70	>70	>70	>70	30-70	>70	30-70	
dry weight (% w/w)												
Spain 5 WWTPs - Seville		PSg	Range of concentration (mg/kg d.w.)	-	1.89-6.03	36.1-239	131-256	-	14.3-21.7	72.5-222	633-997	2.6-11.6
Alvarez et al., 2002		SSg		-	1.68-4.44	23.2-245	145-278	-	9.8-18.2	47.2-142	519-883	1.5-4.3
		FSg		-	3.37-9.20	54.4-439	204-326	-	23.2-36.5	179-223	930-1636	17.5-35.7
⁽⁴⁾ Sg accordance (+) (+) (+) (+) (+) (+) (+) (+) (+)												
Solid phase, Mean ± SD (mg/kg d.w.)												
Domzale, Slovenia Scancar et al., 2000	2 Years N=18	FSg		-	2.8 ± 0.8	856 ± 259	433 ± 126	-	621 ± 187	128 ± 23	2032 ± 393	
⁽⁴⁾ Sg accordance (+) (+) (+) (+) (+) (+) (+) (+) (+)												

Italic—estimated values from the data available in the respective literature references. nd—not determined/not available in the reference; P Mean Removal—removal efficiency of primary settler. T Mean Removal—removal efficiency of the overall treatment

⁽¹⁾ RW—raw wastewater; PSEf—primary sedimentation effluent; FEF—final effluent; Ef_{FTT}—effluent before tertiary treatment; PSg—primary sludge (sludge purged from the primary sedimentation tank); SSg—secondary sludge (sludge purged from the secondary sedimentation tank); FSg—final sludge; MSg—mixture of primary and secondary sludge; DSG—digested sludge not dewatered; RSLAn—returned sludge liquor from the anaerobic digester; RAS—returned activated sludge. ⁽²⁾ Cs—composite samples; fp—flow proportioned; CgS—composite grab sample (in brackets = number of samples contributing to the grab sample/day); Gs—grab samples (Gs-c—collected concurrently with wastewater samples; Gs-t_{An} (retention time)—collected considering the retention time of the anaerobic digester). ⁽³⁾ SS—suspended solids. ⁽⁴⁾ Sludge metal content in accordance (+) or not (NA) with the limits set out in the respective country (see Table 1). ⁽⁵⁾ FEF D limits—final effluent constraints in the concerned country

Table 3 refers to descriptive data on the WWTPs considered in the studies, although it should be noted that in some cases, the information presented was not objectively explicit in the respective references but, as is noted at the end of table, was easy to presume from the knowledge of what is commonly stipulated. Examples are the consideration of pre-treatment operations, such as screening and grit removal, before any ASP, and the non consideration of primary settling before low-loaded/extended aeration ASPs (ASP_{LL/ea}).

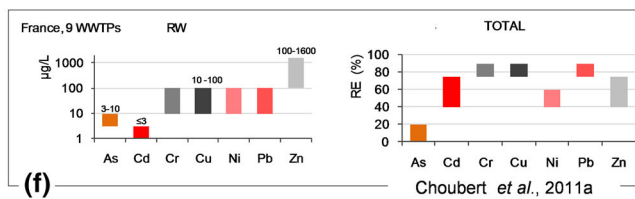
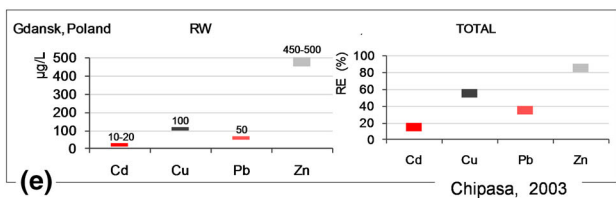
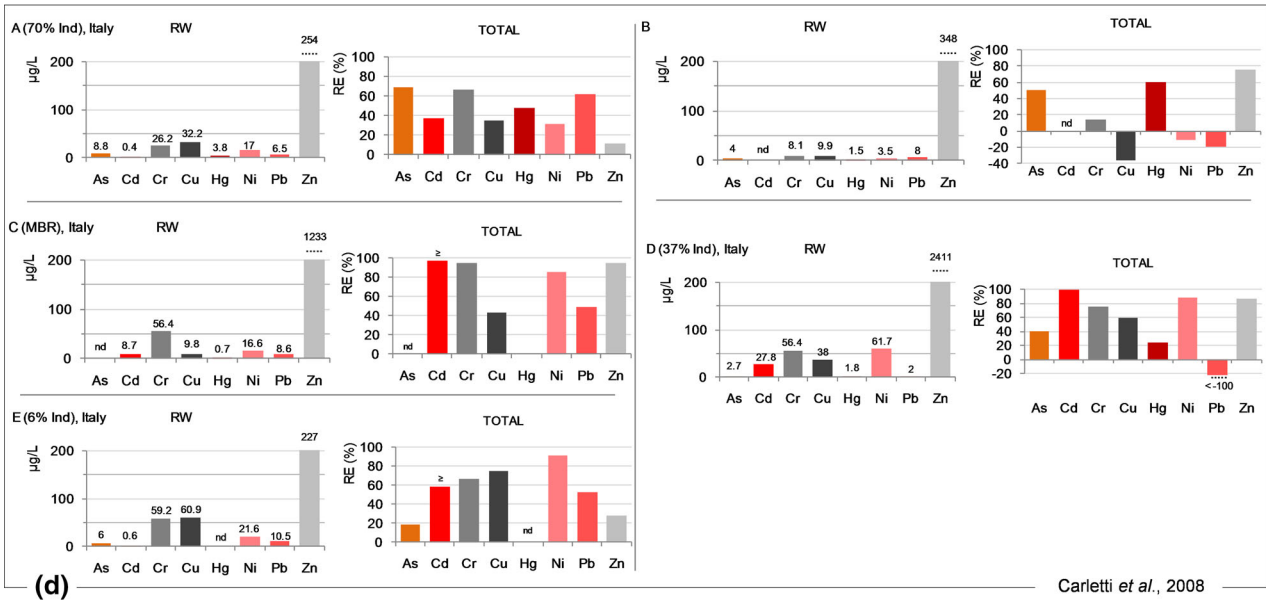
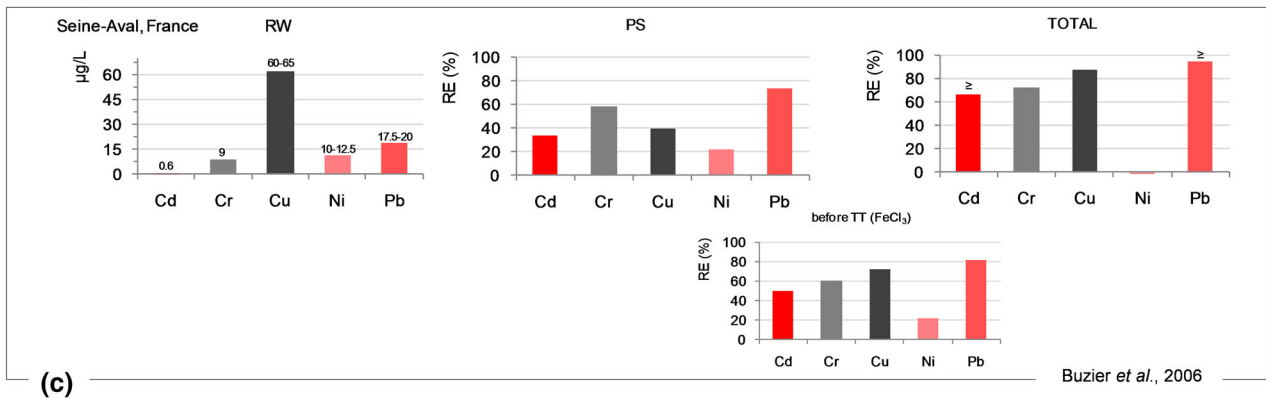
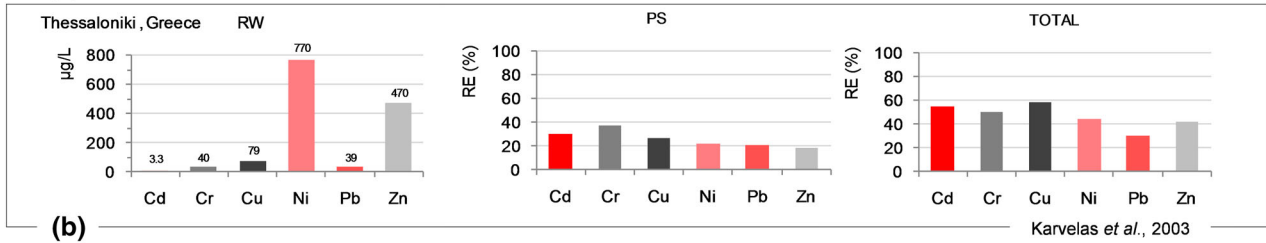
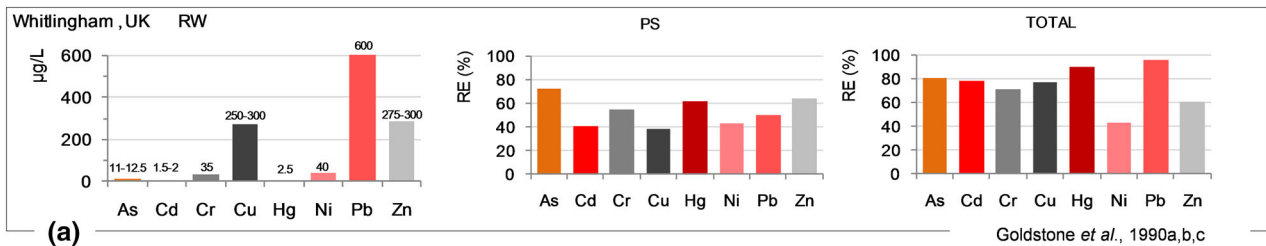
Table 4 refers to the characterization of study conditions and to the observed results, according to the information provided by each study. In some cases, data presented correspond to approximations estimated by careful interpretation of the graphs in the peer-reviewed articles, a value or a range of values depending on what the scale of the graphics allows. As is noted at the end of the table, also a significant number of removal efficiencies were estimated within this work, based on reported concentrations for raw wastewater (RW) and final effluent (FEf). Studies conditions refer to the reported sampling description (campaigns duration, sampled points, sampling frequency, sample type), which is a crucial issue when comparing this kind of data, and therefore should be taken into account in the following considerations.

The concentrations of metals in the influents to different WWTPs as well as the removal efficiencies during the liquid phase of treatment are graphed in Fig. 3.

The comparison between the observed results for different WWTPs in Fig. 3 shows that the mean metal concentrations found in RW are dispersed in a broad range, even within the same country. This may be related to the relative importance of the contribution of different sources, although this is not particularly quantified in most of the studies (Table 3). Carletti et al. (2008) monitored five large WWTPs in Italy, with different industrial contributions in its influents (Fig. 3d), and found notable differences for some metals (e.g. Cr, Ni, Zn) even between plants without relevant industrial contribution. Choubert et al. (2011a) within an extensive study dealing with the fate of xenobiotics through full-scale WWTPs in France (AMPERES project), in samples collected from nine WWTPs (described in Table 3), found that metal contents in the influent were highly variable between the WWTPs and also within each WWTP. The comparison between rural and urban wastewaters confirmed that urban areas with higher industrial contribution released more metals. For Cd, Pb, Cu and Zn, some urban wastewaters showed mean values and concentration ranges similar to rural wastewaters, but the mean concentrations were higher for Cr and Ni in all urban wastewaters. A higher concentration range in rural influents was only observed for As, attributed to a geochemical source in the area of one of the WWTPs. Given the data of the nine WWTPs, four concentration classes were defined as shown in Fig. 3f. Results obtained by

Fig. 3 Total metal contents in the influents (RW) and removal efficiencies (RE) during the liquid phase of treatment in different WWTPs: primary settling (PS); overall treatment (TOTAL); before tertiary treatment with FeCl₃ [before TT(FeCl₃)]; *nd*—not determined/not available in the reference

Buzier et al. (2006), also in France, for five metals (Cd, Cr, Cu, Ni and Pb) monitored along the liquid phase of Seine-Aval WWTP (Fig. 3c) are in accordance with those ranges. Chipasa (2003) in a 2-year investigation on the occurrence of Cd, Cu, Pb and Zn in the Gdansk WWTP in Poland (Fig. 3e) observed high variations in the influent metal contents along the months, particularly pronounced for Cu and Zn. Data obtained in the influents of Thessaloniki (Karvelas et al. 2003) and Whitlingham (Goldstone et al. 1990a, b, c) are distinguished from all the others, due to the much higher contents of Ni (Thessaloniki), Pb and Cu (Whitlingham) (Fig. 3a, b). Concerning the total metals removal in the WWTPs, Fig. 3 reveals the significant contradiction between observed results. The most concordant removals were obtained for Ni, within the range of about 40–60 %. In Seine-Aval, to be comparable, we should consider the removals obtained before tertiary treatment, as all other are secondary effluents. The tertiary flocculation with FeCl₃ significantly improved metals removal from the liquid phase with the exception of Ni, due to its content in the reagent composition. This kind of chemical addition is common in WWTPs, in order to remove phosphorus, but, within the studies here considered, was only also referred by Olofsson et al. (2013). None justification was found for the increased concentrations of Cu, Ni and Pb in the WWTP B in Italy, which may be related to various reasons including some malfunction in the operation of the solid phase. Chipasa (2003) concluded that metals removals were directly proportional to metal influent concentrations, with low removals of Cd and Pb when their influent concentrations were about 20 and 50 µg/l, respectively. This conclusion does not seem to be in agreement with the results obtained by other that present significant removals for Cd with influent concentrations near or below that value (Choubert et al. 2011a; Buzier et al. 2006; Karvelas et al. 2003; Goldstone et al. 1990a). However, the biological process is quite different in the Gdansk WWTP, with an ASP configured to enhance biological nutrient removal, which may influence the mechanisms associated with the metals removal. Anyway, metals removals shown in Fig. 3 do not allow to conclude any direct proportionality with the influent total concentrations. Moreover, removals for As and Hg, when considered, are significantly different, although the influent concentrations are similar. Many reasons may be behind contradictory results in Fig. 3, from actual differences in metals removal determined by operating conditions until differences in the



analytical techniques used to measure the metal concentrations (FAAS, GFAAS, ICP-MS). Although not graphed in Fig. 3, Table 4 also includes results observed by Choubert et al. (2011b), also under the AMPERES project, in an assessment concerning on-site metal mass balances over nineteen municipal WWTPs. Concentration ranges greater than 0.1 µg/L in RW and FEf were measured for all the metals except Hg, which was always below that concentration. The objective was to assess the removal efficiencies of primary, secondary and tertiary levels in different treatment lines, with various capacities and various types of secondary biological treatment (ASP with different operating conditions—loading rate, solids retention time, temperature, with or without primary settling; biofilm processes; stabilization ponds; membrane bioreactor). The comparison between five low-loaded activated sludge plants and six plants with various biofilm processes (described in Table 3) allowed to conclude that there were no significant differences in the metals removal efficiencies (Table 4).

Relative abundance of metals in the successive treatment steps

Given the characteristics of the treatment systems and depending on the contaminants involved, removal efficiencies in the liquid phase will result in its transfer to the solid phase of treatment, via the settleable fraction of the RW at the primary sedimentation stage (PSg) and of the settleable solids produced in the BR at the secondary stage (SSg) (Fig. 2). Most of the above studies usually express and compare the obtained results also in terms of relative abundance of metals in the outputs of the different treatment steps of liquid and solid phases. Thus, for easy comparison, these results were here translated as percentage of the total metals considered for each study and are summarized in Figs. 4 and 5. Figure 6 refers to other studies, also included in Tables 3 and 4, which only consider the solid phase of treatment.

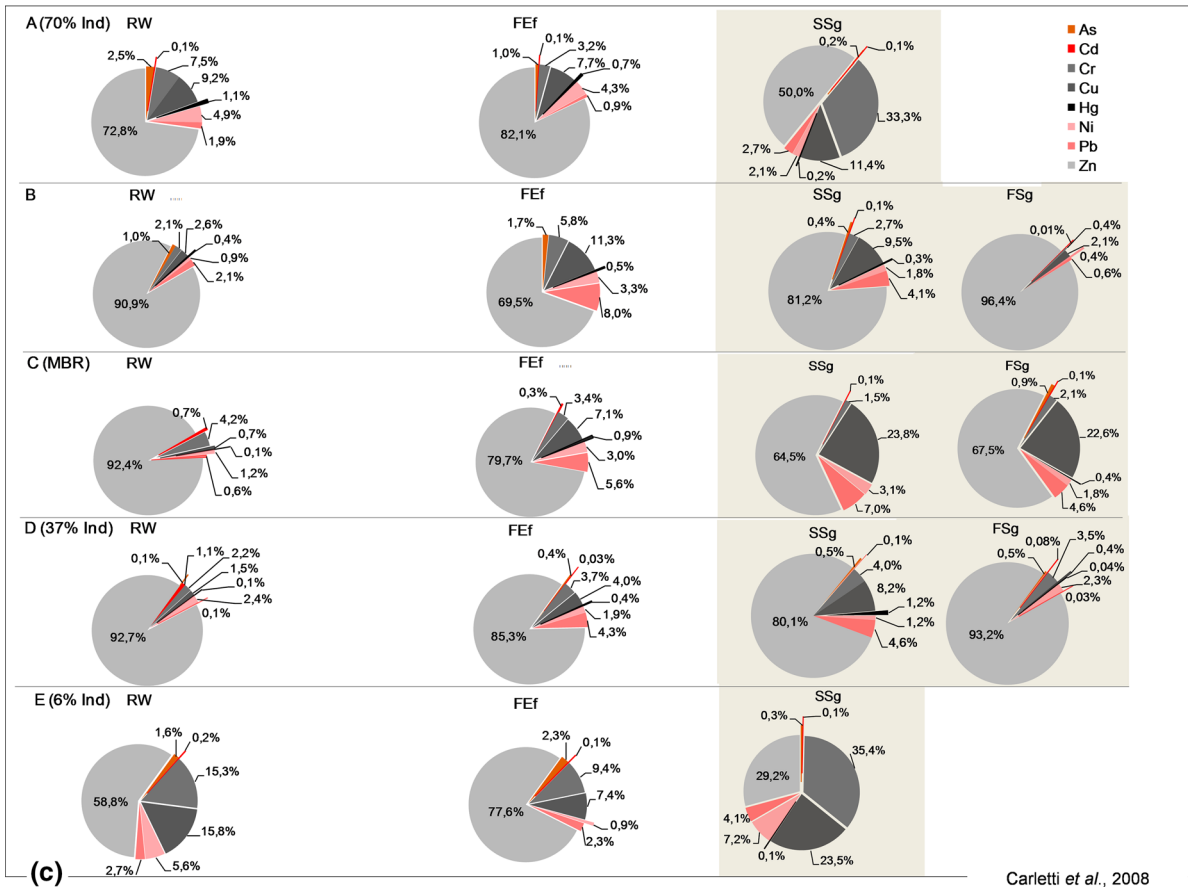
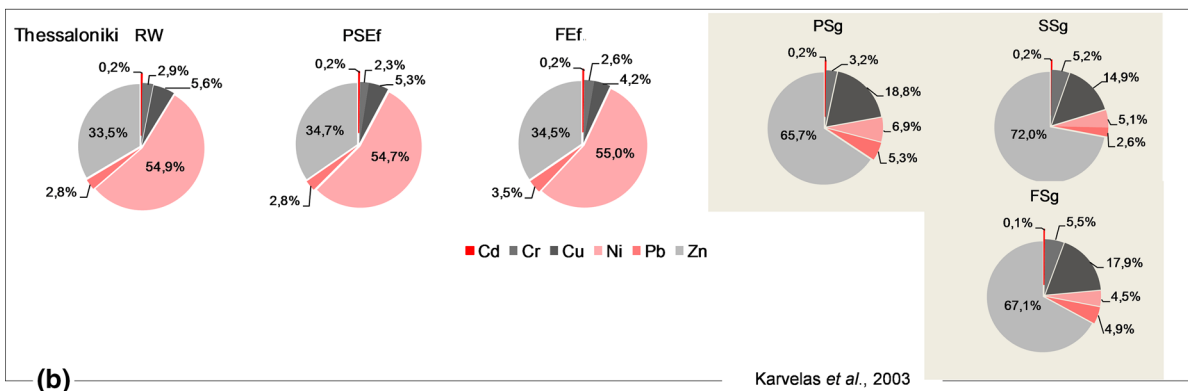
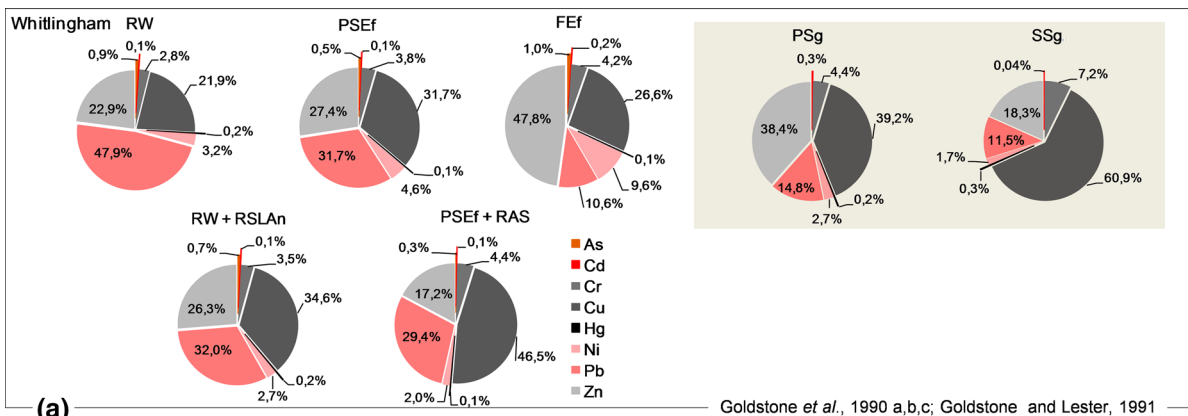
A comparative analysis of the data shown in Fig. 4 allows to admit some differences between metals behaviour in different WWTPs. In Thessaloniki WWTP (b), during liquid phase the relative abundance of metals remains fairly similar to what is observed in the RW, looking like as most of the metals were equally affected by the successive steps of the treatment. However, in the solid phase, Ni contribution decreases significantly, and the percentage of Cu and Zn increases. The behaviour pattern is quite different in the Whitlingham WWTP (a), in which occurs a significant decrease in Pb contribution, about three times lower in the FEf than in RW, while the contribution of Zn and Ni increases, two and three times higher than in RW, respectively. The returned supernatant from the anaerobic digester

Fig. 4 Relative abundance (%) of total metals in the influent (RW), primary sedimentation effluent (PSEf), final effluent (FEf), influent + returned sludge liquor from anaerobic digestion (RW + RSLAn), primary sedimentation effluent + returned activated sludge (PSEf + RAS); primary sludge (PSg), secondary sludge (SSg) and final sludge (FSg) of different WWTPs. **a** UK; **b** Greece; **c** Italy; figure legends also indicate the metals that were determined for each reference

(RSLAn) and the returned activated sludge (RAS) to the BR seem to introduce significant differences in the relative abundance of some metals in the RW and PSEf, respectively. Pb relative abundance remarkably decreases in RW + RSLAn, Cu increases in RW + RSLAn and in PSEf + RAS, and Zn decreases in PSEf + RAS. In the solid phase, the relative importance of Ni is too small, as is the case in Thessaloniki, but the contribution of Pb is less than a half in RW, while Cu significantly increases in its contribution, particularly in the SSg. The relative abundance of metals in PSg and SSg is quite different which is not observed in Thessaloniki. For the five WWTPs in Italy (c), the results are quite variable, some being more similar to Thessaloniki, other more similar to Whitlingham and other totally different, as is the case of WWTP E which presents a lower contribution of Ni in the FEf than in the SSg. In Seine-Aval WWTP (Fig. 5), where Zn was not studied and data are only available for the liquid phase, a significant increase in the per cent contribution of Ni and a decrease in Pb were observed in the FEf, in accordance with what was observed in Whitlingham.

Final sludge quality

The final sludges (FSg) in Fig. 4 can also be compared with Fig. 6, which presents the relative abundances in the final sludges of some other WWTPs, also characterized in Tables 3 and 4. As noted in Table 3, almost all the Swedish WWTPs include chemical addition before ASP, FeSO₄ for phosphorus removal, and similarly to what happens in Umeå, which is more fully described by Olofsson et al. (2010), all probably include the addition of a polymer before dewatering. In fact, at this point it must be noted that the addition of polyelectrolyte before dewatering is a common practice in WWTPs, in order to improve the operation efficiency, although this reference was only found in these Swedish studies. Thus, this is one more type of missing information in WWTP descriptions that can interfere with the interpretation of data. In the screening of metals in FSg from seven WWTPs, Olofsson et al. (2013) found constant relative contents, of about 50 % for Zn and 40 % for Cu, which clearly dominate, in the order of 1–3 % for Ni, 2–4 % for Pb, 2–10 % for Cr and below 0.6 % for As, Cd and Hg (Fig. 6a). Accordingly, all other studies found similar percentages for these last three



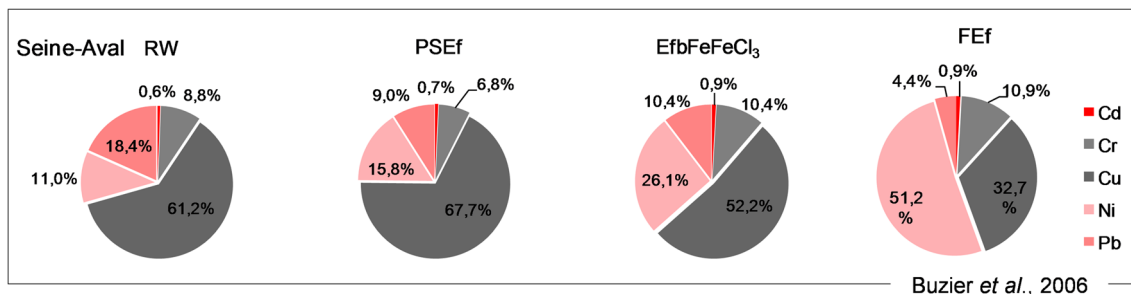
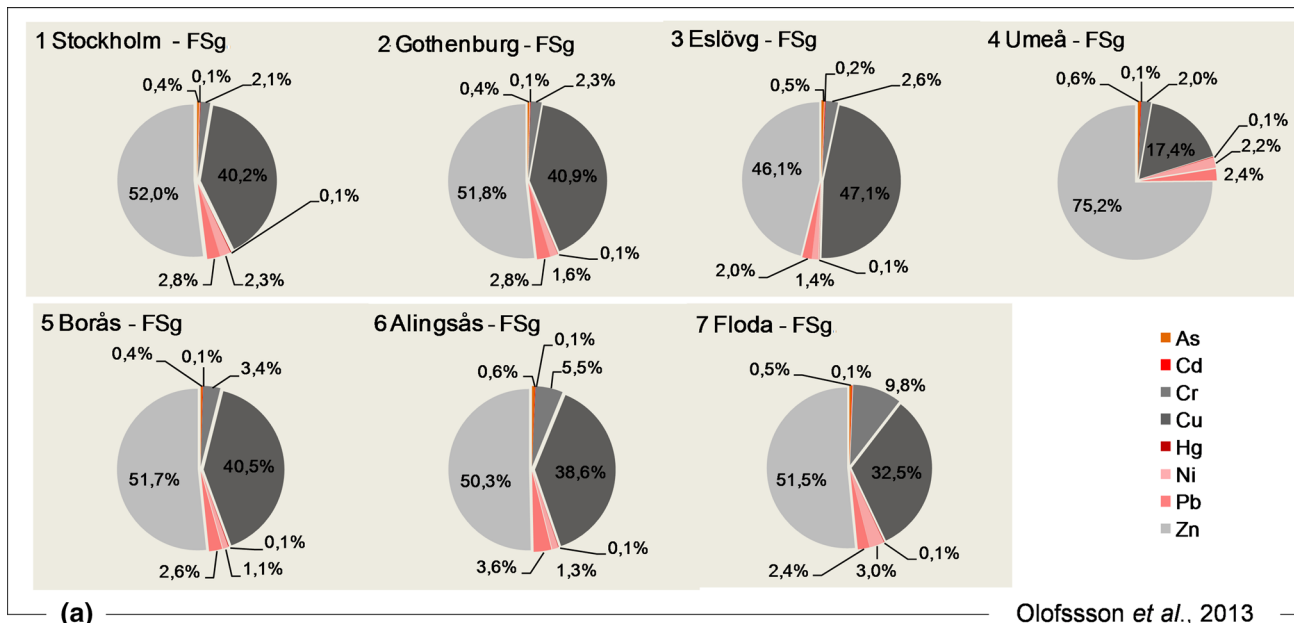
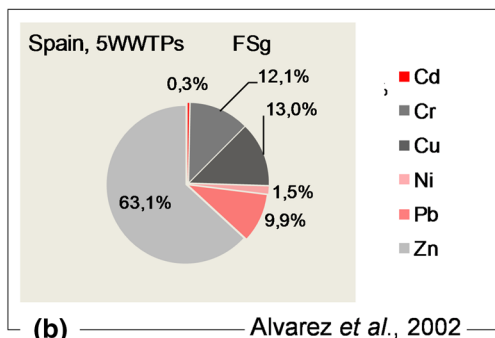


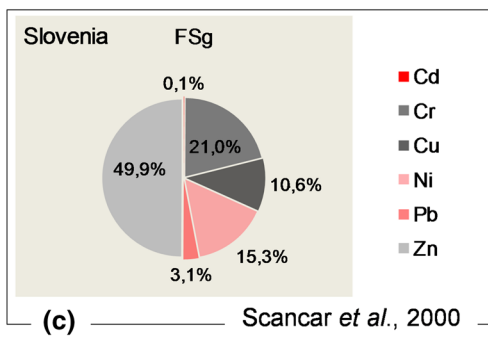
Fig. 5 Relative abundance (%) of total metals in the influent (RW), primary sedimentation effluent (PSEf), secondary effluent before tertiary treatment with FeCl₃ (EfbFeFeCl₃) and final effluent (FEf) in Seine-Aval WWTP; legend also indicates the metals that were determined



(a) Olofsson et al., 2013



(b) Alvarez et al., 2002

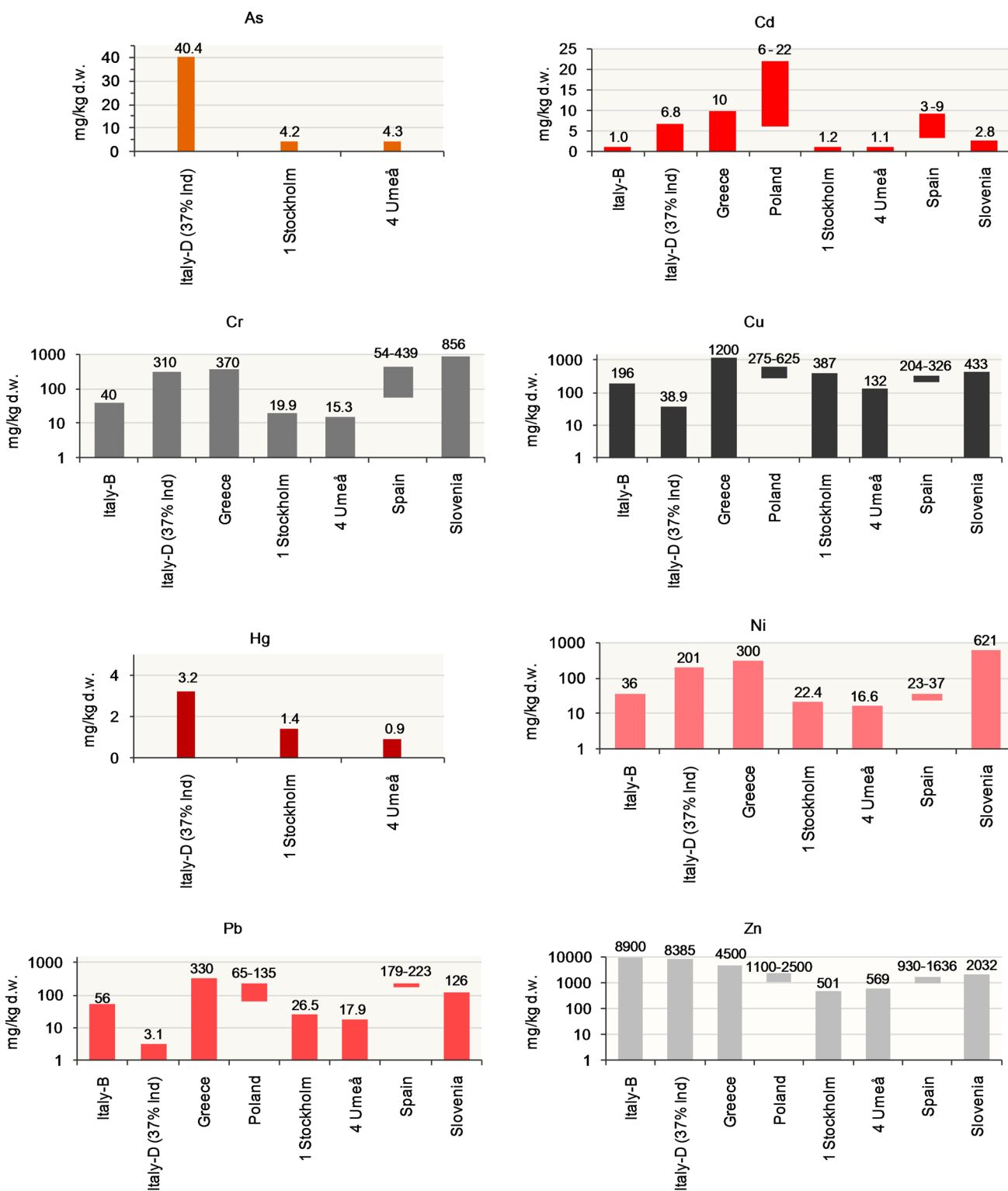


(c) Scancar et al., 2000

Fig. 6 Relative abundance (%) of total metals in the final sludge (FSg) of different WWTPs

metals, when they were considered. The relative abundances of metals observed in FSg of five WWTPs in Spain (Álvarez et al. 2002) are very similar to those found in some of the Italian WWTPs (Fig. 6b, Fig. 4c). Contrary to what happens for all other WWTPs considered in this work, results obtained in Domzale WWTP in Slovenia (Scancar et al. 2000) show a significant relative abundance

of Ni in FSg (Fig. 6c). Figure 7 graphically depicts metals concentrations in the FSg of some of the WWTPs that here have been considered, which not only allows to compare the orders of magnitude obtained in the different countries, but also allows to estimate concentration factors for metals in sludge relatively to concentrations recorded in the RW (Fig. 3) for each WWTP.



Carletti *et al.*, 2006; Karvelas *et al.*, 2003; Chipasa., 2003; Olofsson *et al.*, 2013; Alvarez *et al.*, 2002; Scancar *et al.*, 2000;

Fig. 7 Metal contents in the final sludge (FSg) of WWTPs in different countries

With few exceptions, metal contents in the FSg of all WWTPs in Fig. 7 are in accordance with the limits in force in the respective countries (Table 1). However, when

compared to the more restrictive limits set in Sweden (Table 1), it turns out that other countries are far to reach them, for most of the metals. Thus, optimization of sludge

treatment to reduce metals content in sludge will probably represent one of the major challenges of the next years. Concerning the liquid phase, noteworthy are the findings highlighted by Ruel et al. (2012), under the AMPERES project above mentioned, which concluded that even after tertiary treatments, three priority metals, Ni, Pb and Cd, were still present in the FEF at concentrations higher than 0.1 µg/L.

Removal mechanisms, partitioning and mass balances for metals in WWTPs

Removal mechanisms in WWTPs

The three main mechanisms that generally determine the fate of micropollutants in WWTPs are sorption, biological conversion (biodegradation) and volatilization (Pomiès et al. 2013; Ruel et al. 2008). Sorption and volatilization consist in a transfer of the micropollutant, based on equilibrium mechanisms, between two compartments, dissolved-solid and dissolved-gas compartments, respectively, whereas biodegradation implies an elimination of the micropollutant from the dissolved or solid compartment (Pomiès et al. 2013). So, among these three mechanisms, sorption is the only that is usually considered for metals removal (Pomiès et al. 2013; Cloutier et al. 2009; Wang et al. 2006), which is of course a simplification and certainly not applicable to some metals (As, Hg) that may form volatile compounds when in contact with organic matter. Parker et al. (1994) concluded that partitioning due to precipitation is another mechanism that must be considered, particularly for metals with low solubility. However, the authors point out that some simplifications in metals behaviour are usually needed, in order to conceive useful models. Metals enter the WWTPs in a variety of forms (soluble, organically complexed, precipitated and physically sorbed to organic matter) and during treatment the forms distribution for a given metal may be modified due to degradation of organic ligands, biomass uptake and changes in pH. Also, the operating conditions may change temporarily and from plant to plant. Wang et al. (2006) concluded that metal uptake by primary sludge is significantly affected by pH and developed a mathematical model to describe metals partitioning as a function of pH. The influence of the ASP operating parameters on the removal of metals has been studied since long (Rossin et al. 1982). Parameters as the SRT may have an important role on the interpretation of metals removal. Clara et al. (2005) concluded that the SRT can be a critical parameter concerning the removal of some organic micropollutants in ASP. The same may be true for metals, once SRT is related to the bacterial growth phase that predominates in the BR and

therefore to the condition of the suspended solids in there, which may influence the sorption/desorption mechanisms for metals. This must be taken into account when comparing metal removals between WWTPs with no comparable SRT. Unfortunately, as was already mentioned, there is a lack of supporting information about this and other operating conditions in reported data on metals removals in WWTPs.

Metals partitioning

The fate and behaviour, in terms of metal partitioning and mass balance, have been studied in recent decades, in order to contribute to the improvement of the WWTP performance and to provide data that could support the development of models in this field. Metal removal efficiencies in WWTPs are mainly related to metal partitioning between the liquid and solid phases, although only a few studies from the above described (Tables 3 and 4) have also considered this issue. The obtained percentages of total metals present in the dissolved phase of samples (f_{diss}), collected through the treatment lines, are plotted in Fig. 8.

The distribution of metals between the dissolved and particulate phases in Fig. 8 may be interpreted in terms of sorption of the metals ($100-f_{\text{diss}}$) (%) along the liquid phase of treatment in the WWTPs and related to the correspondent removal efficiencies in Fig. 3. Data from Whitlingham (Fig. 8d) (Goldstone et al. 1990a, b, c) are not comparable to the others, once in this WWTP the dissolved samples were obtained through 0.2 µm filters. However, for this WWTP, some interesting points may be noted, concerning the impact of the supernatant streams in the liquid phase. The f_{diss} significantly decreases for some metals (Cd, Cr, Cu and Zn) in RW + RSLAn samples, with respect to RW, which indicates the relevance of the particulate phase for these metals in the RSLAn. Concerning the impact of the RAS stream into the BR, the f_{diss} decreases for more than a half for Cd, Cr, Cu, Hg, Pb and Zn, meaning that they are found predominantly sorbed to suspended solids (MLSS) in the RAS, while for Ni the decrease is much less significant and an increase is observed for As, showing the importance of the soluble phase of RAS to these metals. Choubert et al. (2011a) related the removal efficiencies (Fig. 3) to the metals partitioning in the RW and attributed the greatest removals to the higher sorption. Cd, Cr, Cu, Pb and Zn were mostly adsorbed to the particulate phase in the influents (average $f_{\text{diss}} \leq 25$ %), while Ni and As were intermediately adsorbed (average $f_{\text{diss}} = 57-71$ %). This seems to be in accordance with what was obtained in Seine-Aval (Buzier et al. 2006). However, in Thessaloniki (Karvelas et al. 2003) where all f_{diss} were less than or equal to 25 % in RW, Pb and Zn were poorly removed (<50 %). In fact, the literature concerning the sorption behaviour of



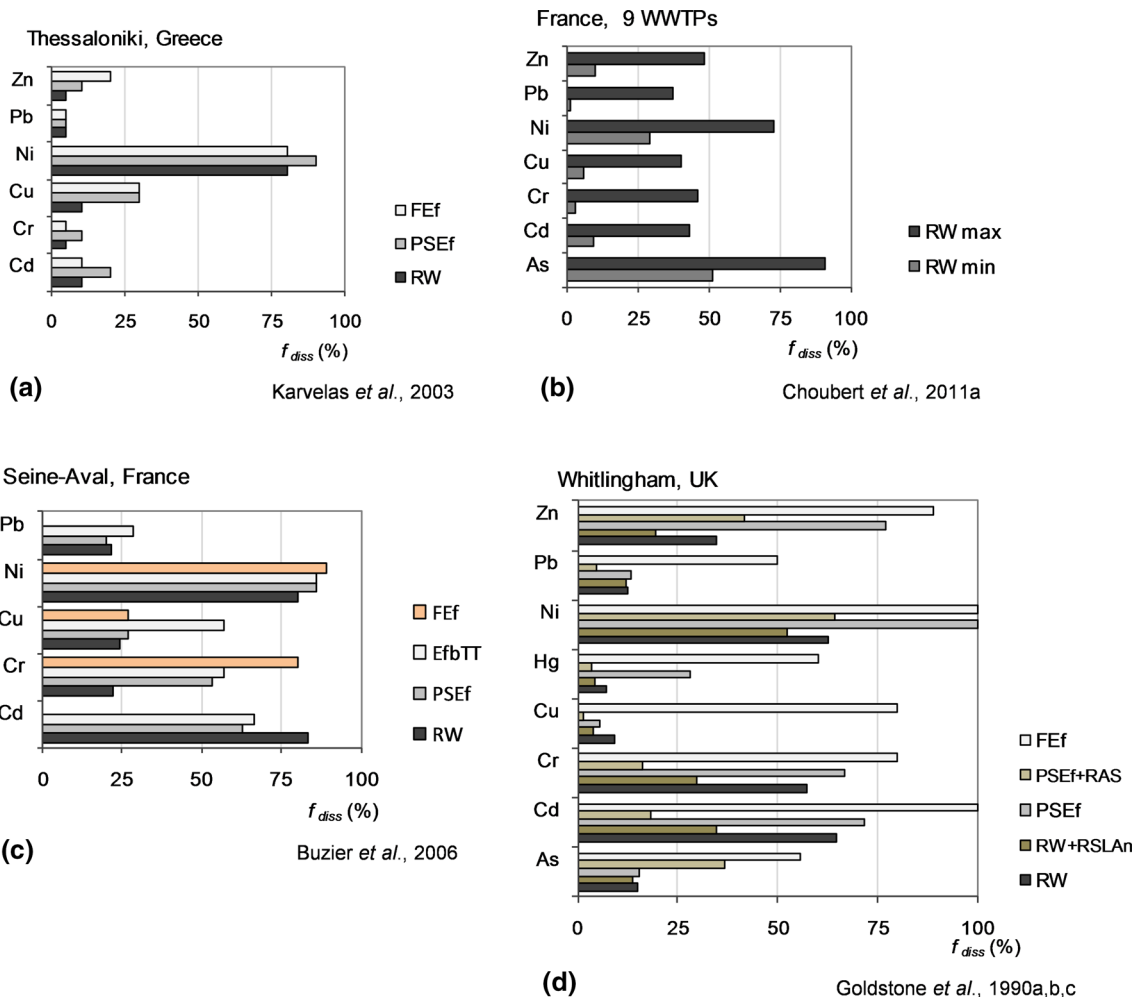


Fig. 8 Metal partitioning. $f_{diss}(\%) = \frac{C_{dissolved}(\frac{\mu g}{L})}{C_{total}(\frac{\mu g}{L})} \times 100$, through the liquid phase of different WWTPs. Porosity of the filters used to obtain the dissolved phase of samples was of 0.45 μm in (a), (b) and (c) and

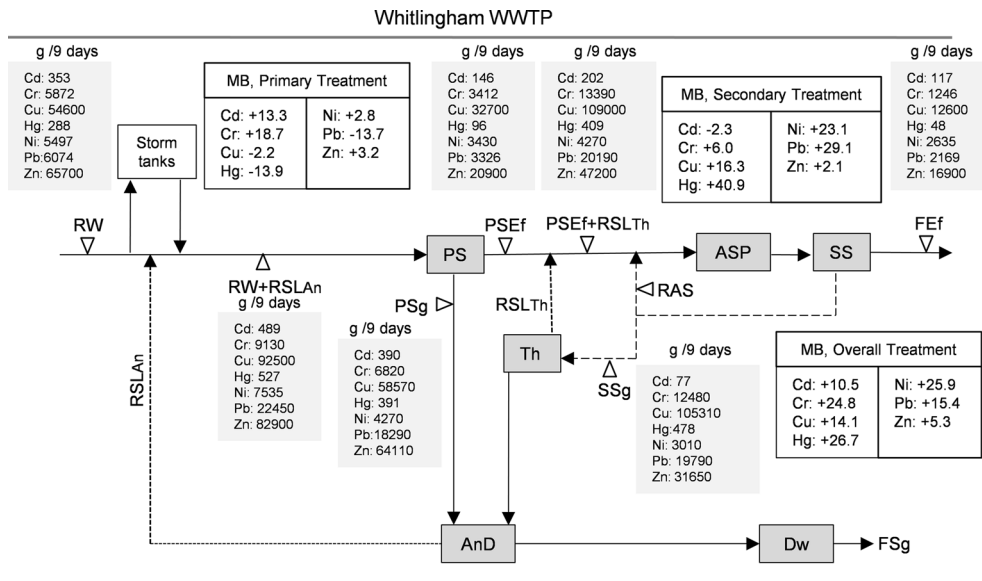
of 0.2 μm in (d). Raw wastewater (RW), primary sedimentation effluent (PSEf), final effluent (FEf), secondary effluent before tertiary treatment with $FeCl_3$ (Efb $FeCl_3$), influent + returned sludge liquor from anaerobic digestion (RW + RSLAn), primary sedimentation effluent + returned activated sludge (PSEf + RAS)

metals in these systems also seems to remain contradictory. Olofsson et al. (2010) investigated the behaviour and fate of metals (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) in the Umeå WWTP and concluded that Cu, Ni and Zn appeared in the FEF in approximately the same concentrations as those that they entered in the RW therefore were mainly present in the dissolved phase of the treatment system, whereas other metals were mainly associated with the particulate phase. Ruel et al. (2008) report that metals are generally poorly adsorbed in the treatment systems, with the exception of Cd, Pb and Zn. In a study conducted in a pilot-scale plant, over two decades ago, concerning the removal mechanisms of Cd, Cu and Ni in ASP, Stephenson et al. (1987) concluded that Cd and Cu were predominantly insoluble and presented high removal efficiencies, while Ni was mostly soluble and therefore was poorly removed. Carletti et al. (2008) conducted a simultaneous sampling, with an

automatic sampler equipped with an ultra-filtration membrane, to collect the dissolved phase in the RW of the five Italian WWTPs above mentioned (Tables 3 and 4; Figs. 3 and 4) and concluded that Hg, Cu and Pb tended to be present in a soluble form in WWTPs with higher industrial contribution, while in the other WWTPs all metals were mainly associated with the suspended phase.

Mass balances

The use of mass balances (MB) to account for the apportioning of contaminants through WWTPs plays a fundamental role in order to conceive models of contaminants behaviour and to allow their validation. However, there are a few published MB of metals through full-scale WWTPs. Goldstone and Lester (1991), in a review on this issue, in 1991, concluded that there were a limited number and that



Δ sampling points

Mass balances (MB) using total masses (g) of metals passing through sampling points during nine days, except or lead (8 days), expressed as % difference in relation to RW $[(M_{IN} - M_{OUT}) / M_{IN}] \times 100$:

Primary Treatment: $M_{IN}(g) = M_{RW+RSLAn}(g)$; $M_{OUT}(g) = M_{PSg}(g) + M_{PSEf}(g)$

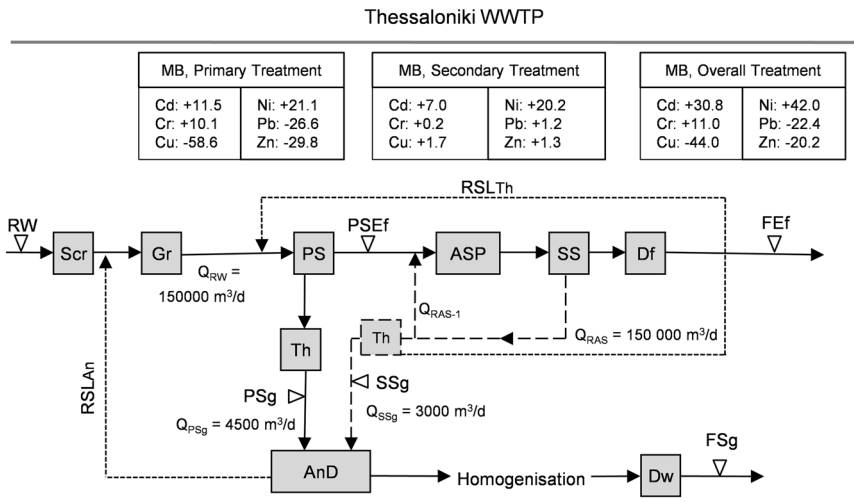
Secondary Treatment: $M_{IN}(g) = M_{PSEf+RSLTh}(g)$; $M_{OUT}(g) = M_{SSg}(g) + M_{FEf}(g)$

Overall Treatment: $M_{IN}(g) = M_{RW}(g)$;

$M_{OUT}(g) = M_{FEf}(g) + [M_{SSg}(g) - (M_{PSEf+RSLTh}(g) - M_{PSEf}(g))] + [M_{PSg}(g) - (M_{RW+RSLAn}(g) - M_{RW}(g))]$

(a)

Goldstone and Lester, 1991



Δ sampling points

Mass balances (MB) using daily masses (g/d) of metals passing through sampling points, expressed as %difference in relation to RW $[(M_{IN} - M_{OUT}) / M_{IN}] \times 100$:

Primary Treatment: $M_{IN}(g/d) = M_{RW}(g/m^3) \times Q_{RW}(m^3/d)$;

$M_{OUT}(g/d) = M_{PSEf}(g/m^3) \times (Q_{RW} - Q_{PSg})(m^3/d) + M_{PSg}(g/g) \times Q_{PSg}(m^3/d) \times SSolids_{PSg}(g/m^3)$

Secondary Treatment:

$M_{IN}(g/d) = M_{PSEf}(g/m^3) \times (Q_{RW} - Q_{PSg})(m^3/d) + M_{RAS}(g/g) \times (Q_{RAS} - Q_{SSg})(m^3/d) \times SSolids_{SSg}(g/m^3)$

$M_{OUT}(g/d) = M_{FEf}(g/m^3) \times (Q_{RW} - Q_{PSg})(m^3/d) + M_{RAS}(g/g) \times Q_{RAS}(m^3/d) \times SSolids_{SSg}(g/m^3)$

Overall Treatment:

$M_{IN}(g/d) = M_{RW}(g/m^3) \times Q_{RW}(m^3/d)$

$M_{OUT}(g/d) = M_{FEf}(g/m^3) \times (Q_{RW} - Q_{PSg})(m^3/d) + M_{PSg}(g/g) \times Q_{PSg}(m^3/d) \times SSolids_{PSg}(g/m^3) +$

$M_{RAS}(g/g) \times Q_{SSg}(m^3/d) \times SSolids_{SSg}(g/m^3)$

(b)

Karvelas et al., 2003

Fig. 9 Mass balances of metals in Whitlingham and Thessaloniki WWTPs. AnD—anaerobic digester, ASP—activated sludge process, Df—disinfection, Dw—dewatering, Gr—grit removal, Q—flow rate, FEf—final effluent, FSg—final sludge, RAS—returned activated sludge, RW—raw wastewater, RSLAn—returned sludge liquor from the anaerobic digester, RSLTh—returned sludge liquor from sludge thickening, PS—primary settler, PSEf—primary settler effluent, PSg—primary sludge, Scr—screening, SSg—secondary sludge, SSolids—suspended solids, SS—secondary settler, Th—thickening

the methodology and method of reporting were highly variable between authors. Problems associated with the collecting of representative samples, particularly during the solid phase of treatment, were identified as a source of fairly high errors and the inexistence of a standard way of reporting MB in WWTPs was related to the sampling logistics. According to the literature review, it seems that this is still true today, although we may say there are standard ways to develop mass balances in WWTPs, particularly in which concerns the solid phase (Metcalf & Eddy Inc 2003). The problem seems indeed to be related to the difficulty of getting representative samples and also, in some cases, to the underestimation of the returns from the solid phase back to the liquid phase of treatment. Most of the metals MB through WWTPs reported in literature do not close and, on the contrary, show significant gains or losses, which are not consistent between different studies (Olofsson et al. 2010; Karvelas et al. 2003; Goldstone and Lester 1991). This is illustrated by metals MB to the above-described WWTPs of Whitlingham and Thessaloniki that are presented in Fig. 9. In order to allow an easier analysis by other, the way how M_{IN} and M_{OUT} were obtained in each case is also indicated in the respective figures. Metals MB in Fig. 9b were obtained within this work, according to equations in Fig. 9. Data obtained by Goldstone and Lester (1991) (Fig. 9a) allow the understanding about the fundamental importance of convenient consideration of all the returns to liquid phase of treatment, although are not frequently considered as is shown by MB in Thessaloniki (Fig. 9b).

Frequently, authors refer to the gains or losses obtained in metals MB as errors, but our view is that given the characteristics of the biological process in these systems, the issue may not be to achieve MB of near 0 % $[(M_{IN} - M_{OUT})/M_{IN} \times 100]$ or 100 % $[(M_{OUT}/M_{IN}) \times 100]$ depending on the authors. The recirculation into the BR may cause temporary metal accumulations, higher or lower depending on many factors such as the concentration of suspended solids (biomass) in the RAS and in the BR, the recirculation rate (meaning higher or lower SRT) and the metal sorption/desorption behaviour in face of present operating conditions. Also, the sludge (SSg) returned to the BR is essentially liquid (moisture content >90 %), and therefore the accumulation in the BR may happen for metals

mainly associated with particulate phase or with soluble phase. Thus, what seems to be more relevant concerning MB in WWTPs, in order to gain a clear insight into the behaviour of metals in these systems, is to get consistent data on the observed gains or losses in comparable WWTPs, i.e. with similar capacities and similar operating conditions. Moreover, the most frequent consideration of the simultaneous analysis of other parameters of organic matter such as SS, COD and TOC, the last two also in total and dissolved samples, in order to study correlations as was done in some studies (Katsoyiannis and Samara 2007; Karvelas et al. 2003; Huang and Wang 2001), may help to clarify the mechanisms involved in metals removals. The consideration of the mechanism of sorption into SS may not be enough, as some recent studies on other micropollutants have shown that colloidal fraction of organic matter (measured as DOC) may interfere with its solubility (Piósz et al. 2013; Pomiès et al. 2013).

The monitoring of full-scale WWTPs in order to get data that allows us to understand the fate and behaviour of metals is costly and, in some cases, difficult to perform. However, it is conceivable that a fewer number of campaigns, but more comprehensive and concerted on some of the aspects referred into the literature, may contribute to clarify some of the disagreements above described and help to improve the development of more robust models in this field.

Modelling of metals behaviour in WWTPs

Modelling and simulation of WWTPs are complex when compared to the modelling of well-defined systems. The nonlinear dynamics and properties of the biological processes are still not very well understood, and calibration of the models may be particularly hard, requiring many expensive experiments to accurately determine model parameters (Vanhooren et al. 2003). However, even with difficulties and limitations, modelling and simulation of wastewater treatment can be very useful to summarize and increase the understanding of complex interactions in biological processes and to predict the dynamic response of the system to various disturbances. Currently, there are several models that can be used to predict conventional pollutants behaviour in WWTPs (BOD, COD, SS and nutrients), most of which were based on the Activated Sludge Models (ASM) conceived by a research group of International Water Association (IWA) (Metcalf & Eddy Inc 2003; Henze et al. 2002). Some dedicated simulators have been marketed (e.g. GPS-X, SIMBA, WEST) and are widely used around the world to support the design, optimization and operation of WWTPs. But, due to the limitations that were previously identified in this work, most of these models do not consider the predicting of specific micropollutants, particularly



metals, although some research has been developed in this area, with a limited number of models reported. Based on scientific literature and expert knowledge, Pomiès et al. (2013), in a recent comprehensive review on the removal of micropollutants in biological wastewater treatment, identified two main references concerning metals modelling in WWTPs, both of them patented and marketed: Toxchem model (Parker et al. 1994) and WEST model (Cloutier et al. 2009; Vanhooren et al. 2003). Both models consider similar mass balance equations, but the first is defined as a static model, meaning that it only simulates permanent regime, while WEST is a dynamic model, meaning that it is more adapted to account to the temporal variations of micropollutant concentrations in WWTPs. The authors also note that Hg has never been considered for modelling in scientific papers.

The WEST software, based on the ASM models above mentioned, allows the modelling of a WWTP and the simulation of the dynamic behaviour of pollutants through the treatment lines. Cloutier et al. (2009), based on this software, developed a model to describe the fate of metals, in simultaneous with common pollutants, in a conventional WWTP. For this purpose, an adjustment was made in ASM1 model, in order to include six new processes related to the six studied metals (Cd, Cr, Cu, Ni, Pb and Zn). Among the aforementioned three mechanisms of micropollutant removal in WWTPs, sorption onto SS was the only mechanism considered in metals removal. Sorption rates (k) were obtained from data (f_{diss} , %) of the above-mentioned study for Whitlingham WWTP (Goldstone et al. 1990a, b) and partition coefficients ($k_{\text{sorption}}/k_{\text{desorption}}$) from Allison and Allison (2005). Model assessment was also made with data from the referred study. It was concluded that the model was able to describe the metals concentration dynamic inside the WWTP, although the results showed a significant sensitivity of the model towards the significant variations in the influent metal concentrations.

Parker et al. (1994) developed a comprehensive model to predict the fate of seven metals (Al, Cd, Cr, Cu, Ni, Pb and Zn) in WWTPs, based on a prior version of Toxchem model. The authors proposed that the metals are partitioned between the liquid and solid phases according to two mechanisms, sorption and precipitation. A set of simplifications in the unit operations and processes was assumed in order to simplify the model. The model includes two empirical parameters, the sorption partitioning coefficient, K_p , and the solubility limit, C_{SOL} , which is found by using a fitting parameter k . Due to the difference in the type of solids present, and in the inorganic ligands that complex the metal ions in the successive steps of the treatment system (grit removal, PS, ASP and SS), these empirical factors were established for two kind of matrixes. Two separate batch experiments were conducted in order to

obtain the solubility limits and sorption coefficients for the two matrixes (effluent from grit removal and mixed liquor) with a spike solution containing the seven metals. A statistical evaluation of the model performance, with data obtained from three full-scale WWTPs, was performed to appraise the validity of the experimentally determined solubility and sorption coefficients and to determine whether the coefficients were transferable from plant to plant. The authors concluded that the model was correct, since the behaviour of metals with significant different physical properties was well predicted. However, in discussion on these results, Khudenko (1996), without underestimating the relevance of the study, notes that some fundamental factors were not considered in the model (e.g. pH, operating conditions), which are time variable and cannot be accounted for in a bulk matrix approach. The author concludes by stressing the need of a model for predicting the fate of metals in WWTPs that conveniently correlates the metals concentrations with physical–chemical characteristics of wastewater, and considers the dynamic of the treatment systems, based on data collection from full-scale WWTPs. According to Ruel et al. (2008), the fate and behaviour of micropollutants in WWTPs could be better predicted by coupling the main mechanisms responsible for its removal with operational conditions characteristic of the different WWTPs (e.g. hydraulic and sludge retention times, air-flow in biological tanks, sludge concentration) through an appropriate model, such general fate models already described in the literature. The comparison of theoretical and measured fate of the substances will be extremely relevant with an increase in the quantity and the quality of data obtained at full-scale WWTPs.

Conclusion

The concerns on metals in WWTPs discharges are mainly related to its contents in sludge, which can prevent sludge application in land and so the recycling of valuable nutrients, and to the more restrictive limits provided to final effluents due to the recent guidelines introduced by EUWFD. At least, seven metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn) are regulated on sludge in the different countries, four of which were classified as priority substances by the EUWFD (Cd, Hg, Ni and Pb) and two of which were also classified as hazardous substances.

The classification of the sources of metals entering the WWTPs does not seem to be uniform in the literature. In this review, three types of sources were proposed: *large/point sources*, *small/dispersed point sources* and *diffuse sources*. At present, there is general consensus on a significant change in the relevance of the different sources of metals to WWTPs,

with a major share of metals originated from small/dispersed point sources (households, business) and diffuse sources (surface runoff from roofs and fronts, galvanized materials, traffic, agricultural areas within urban area), due to the restrictions in the emissions of other sources (industry, hospitals) imposed by legislation and regulatory actions. However, the actual contribution from different goods to UWS seems to be relatively unknown, with a few studies providing a comparison of the significance of various sources. Some main sources have been identified for some metals, e.g. tap water and roofs for Cu, galvanized materials and car washes for Zn, drinking water for Ni and dental practices for Hg, but in general, published data in this field indicate a high degree of uncertainty regarding the inputs of some metals entering the WWTPs. Long-term strategies have been adopted to reduce metals emissions from these sources in the future, mainly via regulation in the commercialization and use of some products, but, in the meantime, WWTPs may have an important role as a barrier between the urban metal flows and the environment.

Relevant data have been published in scientific literature in recent decades, concerning removal efficiencies, sludge quality, main mechanisms of metals removal and mass balances in WWTPs, but results obtained are contradictory and do not allow to conclude typical behaviour patterns for most of the metals. The most consensual data were obtained for Ni, with overall removal efficiencies in the range of 40–60 % and similar sorption rates in all samples ($f_{\text{diss}} > 50\%$) of most studies, meaning that it is mainly present in the dissolved phase of the treatment systems. Regarding Cu and Zn, results are remarkably contradictory, some pointing them to be predominantly present in dissolved phase, while others indicate that they have high sorption rates. Cr, Cd and Pb are generally considered mostly associated with particulate phase, although consistent overall removals were not always observed. Hg and As have been little studied to allow any generalized conclusion on its behaviour during treatment. Metal concentrations found in the influents of different WWTPs are dispersed in a broad range, even within the same country, and the results do not suggest any direct proportionality between these contents and the observed removal efficiencies. Thus, some metal concentrations found in the FEF of different WWTPs are highly variable: 2–5 µg/L for As, 0.1–2 µg/L for Cd, 2–20 µg/L for Cr, 5–75 µg/L for Cu, 0.25–2 µg/L for Hg, 2–97 µg/L for Ni, 1–27 µg/L for Pb and 63–325 µg/L for Zn. Also, in the final sludges, the order of magnitude for the concentrations found may be very different: 4–40 mg/kg d.w. for As; 1–22 mg/kg d.w. for Cd, 15.3–856 mg/kg d.w. for Cr, 38.9–1200 mg/kg d.w. for Cu, 0.9–3.2 mg/kg d.w. for Hg, 16.6–621 mg/kg d.w. for Ni, 3.1–330 mg/kg d.w. for Pb and 501–8900 mg/kg d.w. for Zn. With few exceptions,

metal contents in the final sludge are in accordance with the limits in force in respective countries. However, when compared to the more restrictive limits already set by some countries, it turns out that most countries are far to reach them, for most of the metals. Thus, optimization of sludge treatment to reduce metals content in sludge will probably represent one of the major challenges of the next years.

Different operating conditions in WWTPs may be the cause of some of the contradictions aforementioned, but it is not possible to draw such conclusions due to a lack of supporting information in the reported data. Most of the studies only provide partial information, only focused on final effluents or final sludge and do not refer some fundamental operating conditions of the WWTPs, such as the F/M ratio, MLSS and SRT in the ASP reactor, the options adopted in the treatment of sludge and the chemical additions during treatment (e.g. FeCl₃, FeSO₄ for phosphorus removal, polymers before sludge dewatering). This missing information prevent the interpretation and comparison of data for other purposes than those of the involved studies, which is a waste of effort, and therefore it is recommended to create protocols in order to define the descriptive data to include in future researches at full-scale WWTPs. Other information such as clear definition of the sampling points in the liquid phase of treatment, the entry points of the returns from the solid phase, the entry of RAS into BR, sampling frequency, type of sampling (grab or composite samples, flow proportional or not), pH of the samples, pore size of filters used in SS determination and on soluble fraction of samples to metals analyses, limits of quantification and detection for analytical methods used to measure the metal concentrations must also be mandatory in order to allow an effective comparison of the results.

The use of mass balances (MB) to account for the apportioning of contaminants through WWTPs plays a fundamental role in order to conceive models of contaminants behaviour and to allow their validation. However, only a few published MB of metals through full-scale WWTPs were found, and the methodology and method of reporting are highly variable between authors mainly due to the underestimation of the returns from the solid phase back to the liquid phase of treatment, which is a crucial issue in these systems. Thus, not only the MB do not close as gain and losses are not consistent between studies. Given the characteristics of these systems, it is to admit that the issue may not be to achieve closures, but to get consistent data on the observed gains or losses between comparable WWTPs, in order to typify behaviour patterns for each metal in the treatment systems.

Among the three main mechanisms that generally determine the fate of contaminants in WWTPs (sorption, biodegradation and volatilization), sorption is consensually

the only one considered for metals removal. However, this may correspond to oversimplification because some studies indicate that during treatment, the forms distribution for a given metal may be modified due to degradation of organic ligands, biomass uptake and changes in pH. Also, operating conditions, as MLSS and SRT, may influence the sorption/desorption mechanisms for metals in WWTPs. So, more comprehensive studies are required to thoroughly understand the behaviour of metals in WWTPs. The consideration of the simultaneous analysis of other parameters of organic matter such as SS, COD and TOC is particularly recommended, the last two also in total and dissolved samples, in order to study correlations as was done in some studies, which may help to clarify the mechanisms involved in metals removals.

Two main references were found in the literature concerning metals modelling in WWTPs, one on the development of a specific model to predict the fate of metals, based on a prior version of Toxchem model (static model), and another, using the WEST software, involving the development of an adjustment to ASM1 model in order to describe the fate of metals (dynamic model). Both models consider similar mass balance equations and the prediction of six metals (Cd, Cr, Cu, Ni, Pb and Zn), but in Toxchem two mechanisms are considered for metals partitioning, sorption to SS and metals precipitation, while in WEST only sorption to SS is considered. In Toxchem, partition coefficients and solubility limits were obtained from batch experiments and validated with data obtained from three full-scale WWTPs. In the WEST application, sorption rates were estimated based on data from a full-scale WWTP, which was also used to validate the model, and partition coefficients were adopted from specific literature. In both cases, validation of the models allowed to conclude acceptable predictions, but only applicable to the specific conditions of the studied WWTPs. Therefore, models need more validation and improvement by considering data collected from more full-scale WWTPs with similar and different operating conditions.

The monitoring of full-scale WWTPs in order to get data that allow us to understand the fate and behaviour of metals is costly and, in some cases, difficult to perform. However, it is conceivable that even with a fewer number of campaigns, more comprehensive and more concerted studies concerning the aforementioned aspects may contribute to clarify metals removal mechanisms and help to improve the development of more robust models in this field.

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References

- Allison JD, Allison TL (2005) Partition coefficients for metals in surface water, soil and waste. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC
- Álvarez EA, Mochón MC, Sánchez JC, Rodríguez MT (2002) Heavy metal extractable forms in sludge from wastewater treatment plants. *Chemosphere* 47:765–775
- Ayadi F, Hamdi H, Jedidi N, Gharbi N, Kossai R (2010) Heavy metal distribution in soil and plant in municipal solid waste compost amended plots. *Int J Environ Sci Technol* 7(3):465–472
- Babel S, Dacera D (2006) Heavy metal removal from contaminated sludge for land application: a review. *Waste Manag* 26:988–1004
- Bailey SE, Olin TJ, Bricka RM, Adrian DD (1999) A review of potentially low-cost sorbents for heavy metals. *Water Res* 11:2469–2479
- Bergbäck B, Johansson K, Mohlander U (2001) Urban metal flows—a case study of Stockholm. *Water Air Soil Pollut Focus* 1:3–24
- Berthold G, Krauth K (1998) Replacement of secondary clarification by membrane separation—results with plate and hollow fibre modules. *Water Sci Technol* 38(4–5):383–393
- Buzier R, Tusseau-Vuillemin MH, Meriadec CM, Rousselot O, Mouchel JM (2006) Trace metal speciation and fluxes within a major French wastewater treatment plant: impact of the successive treatment stages. *Chemosphere* 65:2419–2426
- Carletti G, Fatone F, Bolzonella D, Cecchi F (2008) Occurrence and fate of heavy metals in large wastewater treatment plants treating municipal and industrial wastewaters. *Water Sci Technol* 57(9):1329–1336
- Chen M, Li X, Yang Q, Zeng G, Zhang Y (2008) Total concentrations and speciation of heavy metals in municipal sludge from Changsha, Zhuzhou and Xiangtan in middle-south region of China. *J Hazard Mater* 160:324–329
- Chipasa K (2003) Accumulation and fate of selected heavy metals in a biological wastewater treatment system. *Waste Manag* 23:135–143
- Choubert JM, Pomiés M, Martin Ruel S, Coquery M (2011a) Influent concentrations and removal performances of metals through municipal wastewater treatment processes. *Water Sci Technol* 63(9):1967–1973
- Choubert JM, Martin Ruel S, Esperanza M, Budzinski H, Miège C, Lagarrigue C, Coquery M (2011b) Limiting the emissions of micro-pollutants: what efficiency can we expect from wastewater treatment plants? *Water Sci Technol* 63(1):57–65
- Clara M, Kreuzinger N, Strenn B, Gans O, Kroiss H (2005) The solids retention time—a suitable parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants. *Water Res* 39:97–106
- Cloutier F, Jalby G, Lessard P, Vanrolleghem PA (2009) Modélisation dynamique du comportement des métaux lourds dans des stations d'épuration. *Rev Sci Eau* 22(4):461–471
- Côté P, Buisson H, Praderie M (1998) Immersed membranes activated sludge process applies to the treatment of municipal wastewater. *Water Sci Technol* 38(4–5):437–442
- EC (1986) Directive 86/278/EEC of 12 June 1986 of the European Parliament and of the Council on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. *Official Journal L* 181 of 04.07.1986
- EC (1991) Directive 91/271/EEC of 21 May 1991 of the European Parliament and of the Council concerning urban wastewater treatment. *Official Journal L* 135 of 30.05.1991
- EC (2000a) Working Document on Sludge, 3rd Draft. ENV.E.3/LM. Council of the European Community, Brussels, 27 April, 2000

- EC (2000b) Directive 2000/60/EC of 23 October 2000 of the European Parliament and of the Council establishing a framework for Community action in the field of water policy. Official Journal L 327 of 22.12.2000
- EC (2001a) Pollutants in urban waste water and sewage sludge. Final Report. February, 2001. Office for Official Publications of the European Communities, 2001
- EC (2001b) Disposal and recycling routes for sewage sludge. Part 3-Scientific and technical report. European Commission. DG Environment. Office for Official Publications of the European Communities, 23 October 2001
- EC (2001c) Disposal and recycling routes for sewage sludge. Part 2-Regulatory report. European Commission. DG Environment. Office for Official Publications of the European Communities, October 2001
- EC (2002) Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment. Official Journal L 37 of 13.02.2003
- EC (2007) REACH in brief. Environment Directorate General, European Commission, Brussels
- EC (2011) Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment. Official Journal L 174 of 01.07.2011
- EC (2013) Directive 2013/39/EU of 12 August 2013 of the European Parliament and of the Council amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Official Journal L 226 of 24.08.2013
- Emmanuel E, Perrodin Y, Keck G, Blanchard J-M, Vermande P (2005) Ecotoxicological risk assessment of hospital wastewater: a proposed framework for raw effluents discharging into urban sewer network. *J Hazard Mater* A117:1–11
- Engelhardt N, Firk W, Warnken W (1998) Integration of membrane filtration into the activated sludge process in municipal wastewater treatment. *Water Sci Technol* 38(4–5):429–436
- Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: a review. *J Environ Manage* 92:407–418
- Fuentes A, Loréns M, Sáez J, Soler A, Aguilar MI, Ortuno JF, Meseguer VF (2004) Simple and sequential extractions of heavy metals from different sewage sludges. *Chemosphere* 54:1039–1047
- Goldstone ME, Lester JN (1991) The balance of heavy metals through sewage treatment works. *Sci Total Environ* 105:259–266
- Goldstone ME, Kirk PWW, Lester JN (1990a) The behaviour of heavy metals during wastewater treatment. I. Cadmium, Chromium and Cooper. *Sci Total Environ* 95:233–252
- Goldstone ME, Kirk PWW, Lester JN (1990b) The behaviour of heavy metals during wastewater treatment. II. Lead, Nickel and Zinc. *Sci Total Environ* 95:253–270
- Goldstone ME, Kirk PWW, Lester JN (1990c) The behaviour of heavy metals during wastewater treatment. III. Mercury and Arsenic. *Sci Total Environ* 95:271–294
- Gray NF (2005) *Water Technology: An Introduction for Environmental Scientists and Engineers*, 2nd edn. Elsevier Butterworth-Heinemann, Oxford
- Henze M, Gujer W, Mino T, van Loosdrecht M (2002) *Activated Sludge Models ASM1, ASM2, ASM2d and ASM3*. IWA Publishing, London
- Højbye L, Clauson-Kaas J, Wenzel H, Larsen HF, Jacobsen BN, Dalgaard O (2008) Sustainability of advanced wastewater treatment technologies. *Water Sci Technol* 58(5):963–968
- Huang CP, Wang JM (2001) Factors affecting the distribution of heavy metals in wastewater treatment processes: role of sludge particulate. *Water Sci Technol* 44(10):47–52
- Judd S (2006) *The MBR book: principles and applications of membrane bioreactors in water and wastewater treatment*. Elsevier, London
- Judd S (2008) The status of membrane bioreactor technology. *Trends Biotechnol* 26(2):109–116
- Karvelas M, Katsoyiannis A, Samara C (2003) Occurrence and fate of heavy metals in the wastewater treatment process. *Chemosphere* 53:1201–1210
- Katsoyiannis A, Samara C (2007) The fate of dissolved organic carbon (DOC) in the wastewater treatment process and its importance in the removal of wastewater contaminants. *Environ Sci Pollut Res* 14(5):284–292
- Khudenko BM (1996) Comprehensive fate model for metals in municipal wastewater treatment—discussion by Boris M. Khudenko. *J Environ Eng* 122:164–165
- Lasheen MR, Ammar NS (2009) Assessment of metals speciation in sewage sludge and stabilized sludge from different wastewater treatment plans, Greater Cairo, Egypt. *J Hazard Mater* 164(1–2):740–749
- Mantis I, Voutsas D, Samara S (2005) Assessment of the environmental hazard from municipal and industrial wastewater treatment sludge by employing chemical and biological methods. *Ecotoxicol Environ Saf* 62:397–407
- Mattsson A, Mattsson J, Davidsson F (2012) A strategy for reducing pollutants at source in order to obtain sustainable agricultural recycling of wastewater sludge. *Water Sci Technol* 66(9):1879–1884
- Meng F, Chae S-R, Drews A, Kraume M, Shin H, Yang F (2009) Recent advances in membrane bioreactors (MBRs): membrane fouling and membrane material. *Water Res* 43:1489–1512
- Merrington G, Oliver I, Smernik RJ, McLaughlin MJ (2003) The influence of sewage sludge properties on sludge-borne metal availability. *Adv Environ Res* 8:21–36
- Metcalf & Eddy Inc (2003) *Wastewater engineering. Treatment and reuse*, 4th edn. McGraw Hill International Editions, New York
- Mudho A, Kumar S (2013) Effects of heavy metals as stress factors on anaerobic digestion processes and biogas production from biomass. *Int J Environ Sci Technol* 10:1383–1398
- Murillo J, Busquets D, Dalmau J, López B, Muñoz V, Rodríguez-Roda I (2011) Improving urban wastewater management through an auction-based management of discharges. *Environ Model Softw* 26:689–696
- Nabizadeh R, Mahvi A, Mardani G, Yunesian M (2005) Study of heavy metals in urban runoff. *Int J Environ Sci Technol* 1(4):325–333
- NRC (2002) *Biosolids applied to land: advancing standards and practices*. National Research Council, National Academy Press, Washington, DC
- Olofsson U, Lundstedt S, Haglund P (2010) Behaviour and fate of anthropogenic substances at a Swedish sewage treatment plant. *Water Sci Technol* 62(12):2880–2888
- Olofsson U, Bignert A, Haglund P (2012) Time-trends of metals and organic contaminants in sewage sludge. *Water Res* 46:4841–4851
- Olofsson U, Brorström-Lundén E, Kylin H, Haglund P (2013) Comprehensive mass flow analysis of Swedish sludge contaminants. *Chemosphere* 90:28–35
- Parker WJ, Monteith HD, Bell JP, Melcer H, Berthouex PM (1994) Comprehensive fate model for metals in municipal wastewater treatment. *J Environ Eng* 120(5):1266–1283
- Plósz BG, Benedetti L, Daigger GT, Langford KH, Larsen HF, Monteith H, Ort C, Seth R, Steyer JP, Vanrolleghem PA (2013) Modelling micro-pollutant fate in wastewater collection and treatment systems: status and challenges. *Water Sci Technol* 67(1):1–15
- Pomiès M, Choubert J-M, Wisniewski C, Coquery M (2013) Modelling of micropollutant removal in biological wastewater treatments: a review. *Sci Total Environ* 443:733–748



- Rossin AC, Sterrit RM, Lester JN (1982) The influence of process parameters on the removal of heavy metals in activated sludge. *Water Air Soil Pollut* 17:185–198
- Ruel SM, Choubert J-M, Ginestet P, Coquery M (2008) Semi-quantitative analysis of a specific database on priority and emerging substances in wastewater and sludge. *Water Sci Technol* 57(12):1935–1942
- Ruel SM, Choubert J-M, Budzinski H, Miège C, Esperanza M (2012) Occurrence and fate of relevant substances in wastewater treatment plants regarding Water Framework Directive and future legislations. *Water Sci Technol* 65(7):1179–1189
- Rule KL, Comber SDW, Ross D, Thornton A, Makropoulos CK, Rautiu R (2006) Diffuse sources of heavy metals entering an urban wastewater catchment. *Chemosphere* 63:64–72
- Salado R, Daly E, Vencovsky D, Zamparutti T, Palfrey R (2008) Environmental, economic and social impacts of the use of sewage sludge on land. Consultation report on options and impacts prepared by RPA, Milieu Ltd and WRc for the European Commission, DG Environment under Study Contract DG ENV.G.4/ETU/2008/0076r
- Scancar J, Milacic R, Strazar M, Burica O (2000) Total metal concentrations and partitioning of Cd, Cr, Cu, Fe, Ni and Zn in sewage sludge. *Sci Total Environ* 250:9–19
- Sörme L, Lagerkvist R (2002) Sources of heavy metals in urban wastewater in Stockholm. *Sci Total Environ* 298:13–145
- Sörme L, Lindqvist A, Söderberg H (2003) Capacity to influence sources of heavy metals to wastewater treatment sludge. *Environ Manage* 31(3):421–428
- Stephenson T, Lawson PS, Rudd T, Sterrit RM, Lester JN (1987) Mechanism of metal removal in activated sludge. *J Environ Eng* 113:1074–1088
- Stylianou MA, Kollia D, Haralambous K, Inglezakis VJ, Moustakas G, Loizidou MD (2007) Effect of acid treatment on the removal of heavy metals from sewage sludge. *Desalination* 215:73–81
- US EPA (1995) Process Design Manual for land application of sewage sludge and domestic septage. EPA/625/R-95/001, Office of Research and Development, Washington, DC
- Vanhooen H, Meirlaen J, Amerlinck Y, Claeys F, Vangheluwe H, Vanrolleghem A (2003) WEST: modelling biological wastewater treatment. *J Hydroinform* 5(1):27–50
- Wang J, Huang CP, Allen HE (2006) Predicting metals partitioning in wastewater treatment plant influents. *Water Res* 40:1333–1340
- Youshizaki S, Tomida T (2000) Principle and process of heavy metal removal from sewage sludge. *Environ Sci Technol* 34:1572–1575

