Chapter 3
Analytical Detection of Pesticides, Pollutants, and Pharmaceutical Waste in the Environment

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Abstract The rapid population growth and industrialization have led to widespread use of pesticides, drugs, personal care products, and dyes, some of which are so-called emerging contaminants (ECs). These compounds have obviously brought great benefits in controlling diseases and for increasing agricultural and industrial production, but their indiscriminate use has caused problems to human health and the environment. They can be found in surface water and groundwater at concentrations from ng L^{-1} to mg L^{-1}, which may seem negligible. However, some

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contaminants can accumulate or transform in other more toxic products in the human body and induce such problems as antibiotic resistance. Unfortunately, since there is no regulation for some emerging contaminants, they are not monitored in the environment or cannot be detected with conventional analytical techniques.

The purpose of this chapter is to present the state-of-the-art methodology for detecting the emerging contaminants, e.g., pesticides and pharmaceutical products. The chapter will be divided into subtopics – pesticides, pollutants, and pharmaceutical waste – with adverse environment effects also commented upon. The analytical methodologies for detection will be highlighted, with emphasis on recent advances in sensors and biosensors that may offer low-cost, sensitive, selective, and accurate analysis.

Keywords Sensors · Biosensors · Pesticides · Pollutants · Pharmaceutical waste · Emerging contaminants

3.1 Introduction

Contamination in the environment is generally linked with global warming, being mainly caused by extensive industrialization, high population density, and highly urbanized areas (Akpor and Muchie 2011). Negative consequences to human and animals' health arise from improper discarding of pharmaceutical waste, endocrine disrupting compounds, personal care products, and household care products. They may include hormones, glucocorticoids, analgesics – ibuprofen, estriol, additives in drugs, etc. – and cosmetics containing siloxanes and parabens. Figure 3.1 shows a flowchart depicting sources and fate of the so-called emerging contaminants (ECs) (Gogoi et al. 2018). Unfortunately, since there is no regulation for emerging contaminants, they are not monitored in the environment (Noguera-oviedo and Aga 2016). Hence, pesticides are detected in groundwater and drinking water, even though there is a growing effort of environmental protection companies to replace these products with environmentally friendly substitutes (Aamand et al. 2015). Furthermore, existing treatments of wastewater or drinking water are not efficient to remove estrogens, androgens, or detergent compounds (Adeel et al. 2017; Kot-wasik et al. 2007).

Potential health problems have been usually associated with excessive amounts of emerging contaminants in drinking water, as illustrated in Fig. 3.2, including breast and prostate cancer. The effects of prolonged hormone exposure in aquatic ecosystems, even at low levels (<0.001 mg L^{-1}), can lead to adverse effects on aquatic organisms (Jennifer et al. 2017; Kot-wasik et al. 2007) such as estrogens which may affect fish physiology and reproductive maturity in domestic and wild animals. Estrogens and steroid precursors affect roots, flowering, and germination of plants (Adeel et al. 2017). The awareness about environmental issues is crucial to forge environmentally friendly technologies according to the rules of sustainable

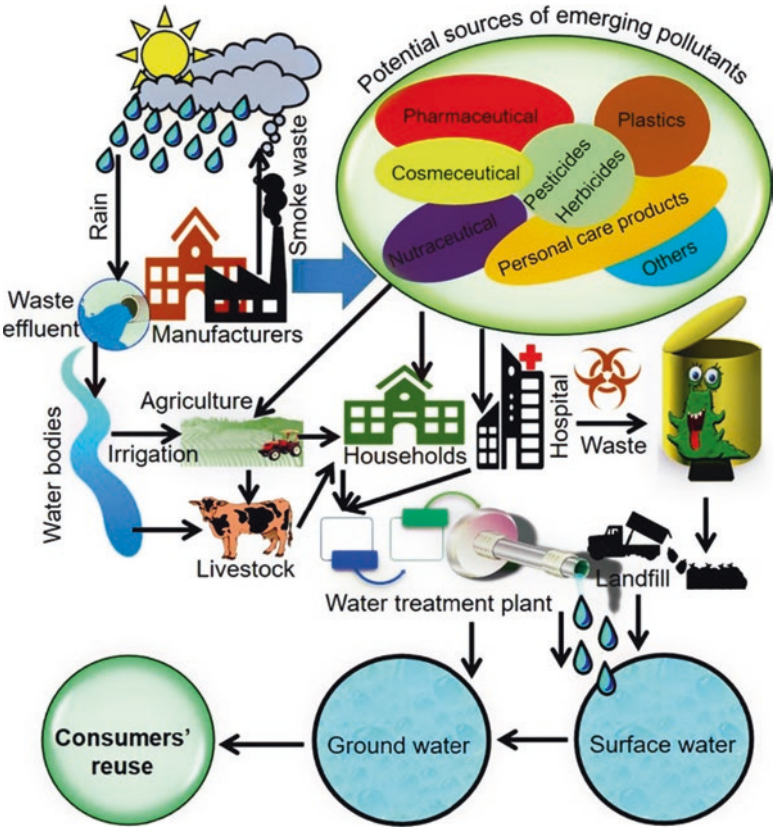


Fig. 3.1 Schematic design with the potential sources of emerging pollutants in the environment. (Reproduced from Ref. (Rasheed et al. 2019) with permission from Elsevier, 2018)

growth (in other words, green chemistry plus green technology). In this context, also relevant are the analytical methodologies to detect trace concentrations of a broad spectrum of pollutants (Kot-wasik et al. 2007).

This chapter reviews the state of the art of groups of emerging contaminants (pesticides, polluters, and pharmaceutical chemicals) and their negative impacts on the environment. In addition, a brief description of standard analytical methodologies is provided, with emphasis on biosensors and sensors to detect emerging contaminants.

3.2 Side Effects of Pesticides

Pesticides are used in agriculture to prevent and control the spread of weeds, bacteria, insects, and rodents. Their use has increased agricultural productivity, helping to secure nearly one-third of the global crop production (Samsidar et al. 2018). In

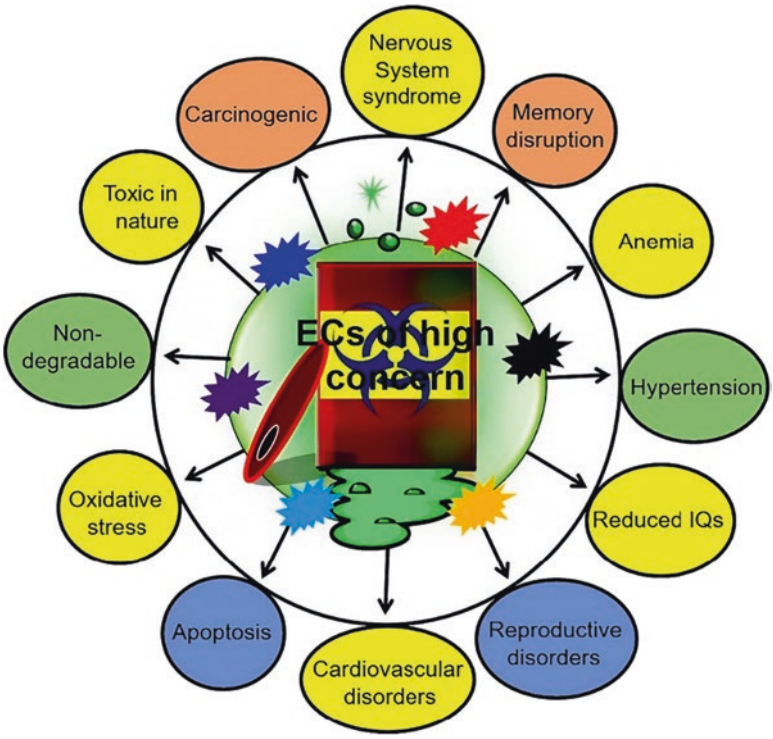


Fig. 3.2 Schematic design on side effects of emerging contaminants. (Reproduced from Ref. (Rasheed et al. 2019) with permission from Elsevier, 2018)

addition, pesticides are useful for controlling vegetation growth, in pet care products, and preventing disease vectors from spreading. More than 1000 pesticides are commercialized, and this number keeps increasing owing to the emergence of resistant pests (Rejczak and Tuzimski 2015). Unfortunately, most of these compounds are toxic, and their indiscriminate use yields major risks to human health, especially for agricultural workers and people living close to farms. Also, exposure to pesticides can cause long-term health effects such as cancer, Parkinson's, Alzheimer's, multiple sclerosis, and cardiovascular diseases (Mostafalou and Abdollahi 2013).

Pesticides are classified based on the target pests and their origin – chemical or biological (Rawtani et al. 2018) – as shown in Fig. 3.3. Biopesticides are derived from natural sources, including animals, plants, bacteria, and minerals. Chemical pesticides have been synthesized to kill different types of pests and are classified as insecticides, herbicides, fungicides, rodenticides, and nematicides (Samsidar et al. 2018). Organophosphates, carbonates, and organochlorines are among the most known chemical pesticides. Compounds such as dichlorodiphenyltrichloroethane (DDT), atrazine, malathion, and parathion have been related to adverse effects on the environment, which include destruction of the habitat of different species (Rawtani et al. 2018).

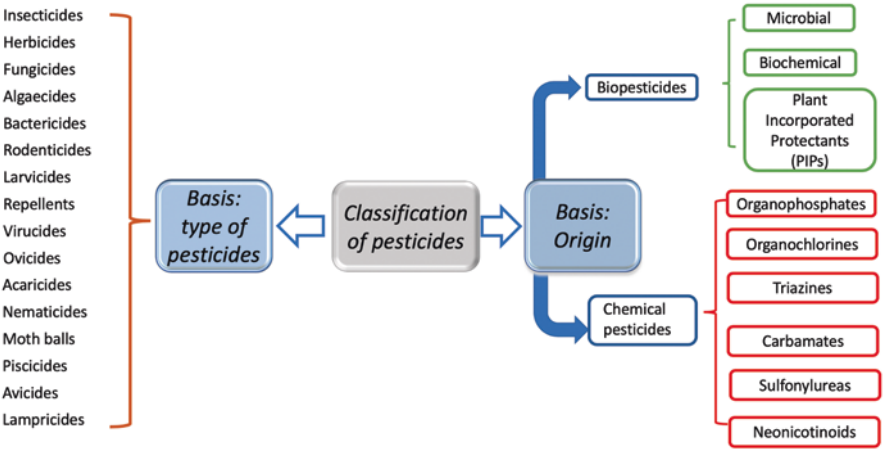


Fig. 3.3 Classification of pesticides. (Figure based on Rawtani et al. (2018))

3.2.1 Analysis of Pesticides

Many countries have established regulations to control the level of pesticides in the environment, especially in water, raw vegetables, and fruits (Samsidar et al. 2018; Yan et al. 2018). In order to enforce these regulations, there is an increasing demand for sensitive and accurate analytical tools to detect low concentrations of pesticides. Analytical methods have been based on conventional techniques – high-performance liquid chromatography (LC) (Picó et al. 2004; Thurman et al. 2001), capillary electrophorese (CE) (Hsu and Whang 2009), and gas chromatography (GC) (Guan et al. 2010). These techniques can be used in combination with several detectors depending on the pesticide and sample analyzed (Rejczak and Tuzimski 2015). For instance, nonvolatile pesticides have been detected using LC coupled to UV detectors, fluorescence detectors, diode-array detectors (DAD), and mass spectrometry (MS). Polar and easily vaporizable compounds are normally detected using GC coupled to detectors such as flame photometric detector (FPD), flame ionization detector (FID), and nitrogen phosphorus detectors (NPD) (Rejczak and Tuzimski 2015).

A crucial step toward the efficient detection of pesticides in complex matrices, e.g., soil, natural waters, and food, is a sample pretreatment to remove potential interferents that may impair an accurate analysis. Efforts have been made to develop procedures for sample extraction and purification, including liquid-liquid extraction (LLE), solid-phase extraction (SPE), matrix solid-phase dispersion (MSPD), solid-phase microextraction (SPME), stir bar sorptive extraction (SBSE), and quick, easy, cheap, effective, rugged, and safe (QuEChERS) extraction (Rejczak and Tuzimski 2015). In addition to removing impurities, many of these methodologies allow one to concentrate the analytes, which is more suitable to detect trace concentrations. An alternative to pretreatment methods is to employ molecularly imprinted polymers (MIPS), which are 3-D polymeric matrices with complementary cavities

designed for a template molecule (Sarafraz-yazdi and Razavi 2015). They are suitable for this protocol owing to their high selectivity, relatively low cost, stability, and easy preparation. MIPs have been used as sorbents for SPE, MSPD, and SPME methods for selective extraction of pesticides from food (Djozan et al. 2009) and human serum (Zhang et al. 2019a). Magnetic MIPs have also been used (Karimian et al. 2017), and these hybrid materials show high selectivity, with their magnetism effect allowing an effect of sample separation without requiring additional filtration or centrifugation steps.

Combining sample pretreatment approaches and analytical characteristics from more conventional techniques has made it possible to detect single molecules and mixtures of pesticides, as illustrated in Table 3.1. It should be mentioned, however, that many experimental methods require sophisticated equipment and trained operators and usually are time-consuming, limiting their application for real-time and on-site detection.

Table 3.1 Analytical methods for detecting pesticides residues

Analyte	Detection technique	Extraction method	Sample	LODs	References
Organophosphates	LC-MS/MS	Liquid-liquid extraction	Fruits and berry juice	3×10^{-4} mg L^{-1} – 3×10^{-2} mg L^{-1}	Timofeeva et al. (2017)
Organochlorine	GC-EDC	Solid-phase extraction	Water	1.7 ng L^{-1}	Moawed and Radwan (2017)
Pyrethroids	GC-ECD	Solid-phase microextraction	Fruits and vegetables	0.1–0.5 ng L^{-1}	Zhang et al. (2017)
Organophosphates	LC-DAD	–	Water	32.8 ng L^{-1} – 104.5 ng L^{-1}	Mahajan and Chatterjee (2018)
Carbamates	LC- MS/MS	Solid-phase extraction	Water	0.5–6.9 ng L^{-1}	Shi et al. (2014)
Multiclass pesticides	GC-FID	Liquid-liquid extraction	Water	0.34–5 μg L^{-1}	Farajzadeh et al. (2015)
Diazinon	LC-UV	Magnetic molecular imprinted polymers	Water	2.19 mg L^{-1}	Karimian et al. (2017)
Ametryn	LC-UV	Magnetic molecular imprinted polymers	Tomato, capsicum, and strawberry	25 nmol L^{-1}	Khan et al. (2018)

LC-MS/MS high-performance liquid chromatography mass spectroscopy, *GC-ECD* gas chromatography-electron capture detector, *LC-DAD* high-performance liquid chromatography with diode-array detection, *GC-FID* gas chromatography-flame ionization detector, *LC-UV* high-performance liquid chromatography with UV detection, *LOD* limit of detection

3.2.2 *Sensors and Biosensors for Pesticide Detection*

The growing need for analytical methods for a rapid, selective, and accurate detection of pesticides has motivated the development of relatively low-cost sensors and biosensors. These devices normally contain nanomaterials: carbon nanotubes (Kaur et al. 2019), graphene derivatives (Hashemi et al. 2019), quantum dots (Wang et al. 2019b), and metal nanoparticles (Jiang et al. 2018). Transduction methods for these sensors include electrochemistry (Velusamy et al. 2019), fluorescence (Wu et al. 2019), surface-enhanced Raman scattering (SERS) (Jiang et al. 2018), and surface plasmon resonance (SPR) (Cakir et al. 2019). A large enhancement in SERS signal may arise from plasmonic nanostructures, then permitting detection of analytes at very low concentrations. For example, a SERS sensor containing Ag-coated Au nanoparticles (Au@Ag NPs) detected insecticide residues in peach simultaneously (Yaseen et al. 2019). Figure 3.4 shows the results for Au@Ag NPs with 26 nm Au core size and 6 nm Ag shell yielded to enhance Raman signals for pesticides, in which the limits of detection were 0.1 mg kg^{-1} for thiacloprid and 0.01 mg kg^{-1} for profenofos and oxamyl.

Biosensors have been preferred for detecting pesticides due to their selectivity provided by biological components acting as recognition units, viz., enzymes, antibodies, nucleic acids, microorganisms, biological tissues, and organelles. They can be used in combination with a physical transducer to generate intense signals due to changes in concentration of a specific analyte (Madrid et al. 2017). The selectivity of biosensors may allow for analyte detection even in complex matrices (Saini et al. 2017). Enzymes are utilized in electrochemical biosensors to detect pesticides since many products of enzymatic reactions show electroactive responses. Enzymes are

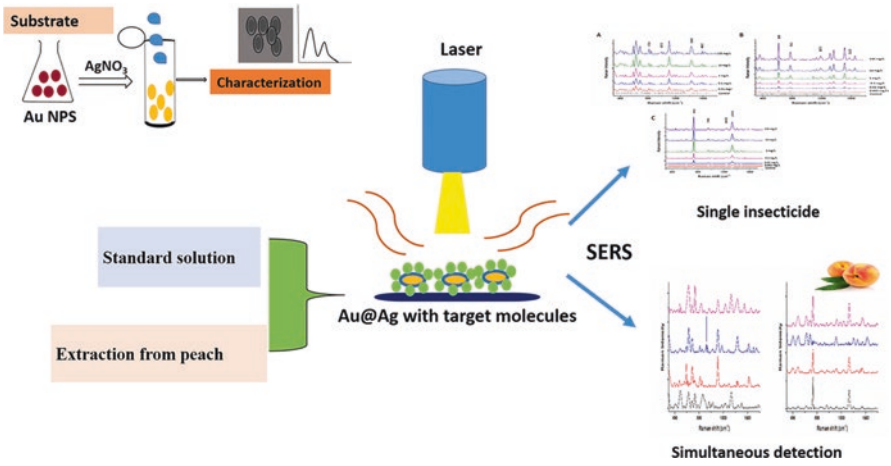


Fig. 3.4 Schematic design for a surface-enhanced Raman scattering (SERS) sensor for detecting thiacloprid, profenofos, and oxamyl in peach. (Reproduced with permission from Yaseen et al. 2019)

usually more stable and less expensive than other common biomolecules such as antibodies (Fabiana Arduini et al. 2016). The detection protocols using enzymatic biosensors involve monitoring changes in pesticide concentration by means of either enzymatic reactions or enzyme-inhibition mechanisms.

Many catalytic biosensors contain organophosphorus hydrolase (OPH), which catalyzes the hydrolysis of organophosphorus compounds, including parathion and methyl parathion, by breaking P-O, P-S, and P-CN bonds (Sassolas et al. 2012). The hydrogen ions and alcohols generated as enzymatic products can be monitored by electrochemical and optical techniques (Sassolas et al. 2012). Wearable potentiometric tattoo biosensors have been built with OPH immobilized onto screen-printed transducers to detect diisopropyl fluorophosphate (DFP) (Mishra et al. 2018). Figure 3.5 shows the principle of detection for these biosensors made with electrodes printed onto a temporary tattoo paper after being modified with a pH-sensitive polyaniline (PANI) film. This PANI film helps to monitor hydrogen ion released from the enzymatic hydrolysis of DFP. This biosensor was also efficient to detect other organophosphates. Catalytic biosensors, nonetheless, have drawbacks that restrict their widespread use, including a limited number of enzymes available for catalyzing the hydrolysis of pesticides. For example, OPH-based biosensors detect only some organophosphorus compounds, since large molecules with more complex structures do not interact effectively with active enzymatic sites (Mulyasuryani and Prasetyawan 2015).

Biosensors based on enzymatic inhibition mechanisms, where the analyte is quantified through its ability to inhibit enzyme function, are more sensitive for detecting pesticides than catalytic biosensors. Figure 3.6 shows the operation principle in which the enzymatic activity can be monitored. After addition of the inhibitor, the catalytic activity decreases and so does the analytical signal (Amine et al. 2015). The properties and operation parameters for these biosensors depend on the enzyme-inhibitor interaction, which is classified as reversible or irreversible. When the interaction is irreversible, covalent bonds are formed between the inhibitor and the active site of the enzyme leading to permanent loss of enzymatic activity (Aziz Amine et al. 2006). For biosensors based on reversible inhibition, on the other hand,

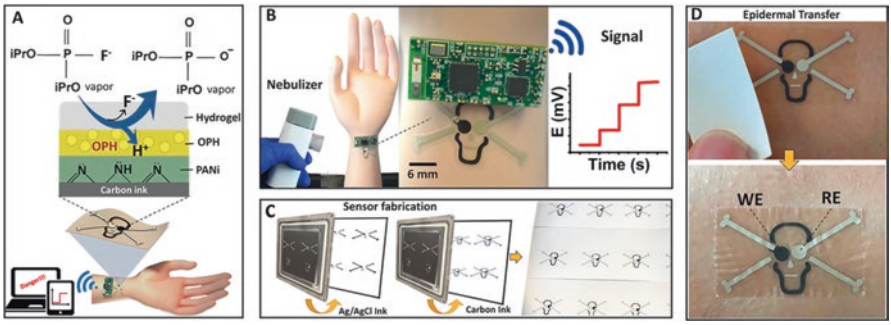


Fig. 3.5 Illustration of tattoo biosensors for detecting nerve agents. (Reproduced with permission from Mishra et al. 2018)

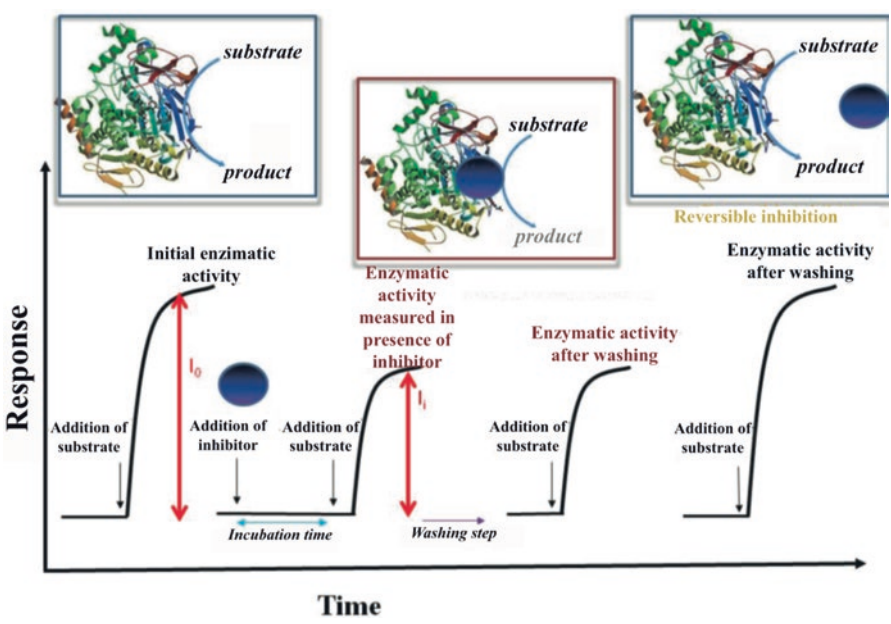


Fig. 3.6 Reversible and irreversible inhibition detection using biosensors based on enzyme inhibition mechanism. (Reproduced with permission from Amine et al. 2015)

the enzymatic activity can be restored by washing them with water or buffer solutions, which allows one to perform multiple measurements with a single device (Amine et al. 2015).

The activity of cholinesterase is inhibited irreversibly by organophosphorus and carbamate pesticides (Fabiana Arduini et al. 2010; Pundir and Chauhan 2012). These enzymes are found in insects and vertebrates, being responsible for catalyzing the hydrolysis of the acetylcholine neurotransmitter, a crucial step in the transmission of nerve impulses. Two types of cholinesterase are known, which are mainly distinguished by their substrate specificity: acetylcholinesterase (AChE), which has a higher catalytic activity toward acetyl esters, e.g., acetylcholine, and butyrylcholinesterase (BChE), which preferentially hydrolyzes butyrylcholine (Saini et al. 2017). The reaction products can be monitored using potentiometry or optical methods with pH-sensitive indicators (Sassolas et al. 2012). A simpler methodology involves artificial substrates such as acetylthiocholine and butyrylthiocholine, whose hydrolysis product – thiocholine – can be detected electrochemically at relatively low potentials. Bi-enzymatic and tri-enzymatic biosensors have also been developed, in which enzymes such as choline oxidase and peroxidase can be used to produce electrochemically detectable species (Andreescu and Marty 2006).

Paper-based biosensors relying on enzymatic inhibition have been reported for low-cost, user-friendly determination of pesticides. Arduini et al. (2019) developed paper-based biosensors using butyrylcholinesterase, alkaline phosphatase, and tyrosinase on screen-printed electrodes modified with carbon black and Prussian

blue nanoparticles to improve sensitivity. Paraoxon, 2,4-dichlorophenoxyacetic acid, and atrazine were detected in standard solutions and river water samples using amperometry. A relevant limitation of biosensors based on enzymatic inhibition is the low selectivity for several enzymes, and this may impair pesticide detection in complex matrices of environmental interest owing to the presence of other, competitive inhibitors. Therefore, most of these sensors are used for screening purposes and not for detecting specific molecules (Jiang et al. 2008).

Immunosensors and aptasensors are useful to detect pesticides, since antibodies and aptamers are able to recognize analytes. For immunosensors, the interaction between antibodies (Ab) and antigens (Ag) is affected by the concentration of a specific analyte (Jiang et al. 2008). In addition to their use for detecting biomarkers of various diseases, immunosensors serve to detect pesticides and other compounds through advances in biotechnology where antibodies are generated which are specific for several molecules (Fernández-Benavides et al. 2019; Jiao et al. 2018). Aptasensors are promising for performing selective, fast, and sensitive detection of pesticides at low concentrations. They can be used in sensors as recognition elements as short oligonucleotides of RNA or DNA synthetized using the selection evolution of ligands by exponential enrichment (SELEX) technique (Liu et al. 2019). With SELEX, molecules can be obtained which possess high binding affinity and selectivity against a target analyte without using animals or cell cultures. In addition to the advantages in the production process, aptamers are more stable than antibodies and enzymes, allowing the use of aptasensors under harsh conditions. Aptasensors exploiting electrochemical techniques (Fu et al. 2019; Xu et al. 2019) and fluorescence (Cheng et al. 2018) have been used to detect pesticides.

3.3 Pollutants and Side Effects

The rapid population growth and industrialization have led to discarding a huge number of contaminants into the environment, which is why the twenty-first century was coined the Century of the Environment (Azam et al. 2016). Most pollutants are hazardous and poisonous, as the case of volatile organic compounds (VOCs) (Liu et al. 2018; Malik et al. 2018), heavy metals (Kamilari et al. 2018), toxic inorganic gases (Joshi et al. 2018), dyes (Nguyen and Saleh 2016), food preservatives, and personal care products. They pose severe threats for human beings and the environment. VOCs, for instance, can easily evaporate from household products such as paints, cleansers, and furnishings, causing short- and long-term adverse effects (Spinelle et al. 2017). Real-time monitoring of VOCs is now required for several types of industries, including cosmetics, medical diagnosis, food, and beverages, and long-term exposure can cause damage to the liver, kidney, and central nervous system (Jung et al. 2012).

The International Agency for Research on Cancer (IARC) has stated that online monitoring of formaldehyde should be performed in indoor environments because formaldehyde has been linked to cancers in the nasal cavity, mouth, throat, skin, and

digestive tract (Mandayo and Castaño 2013). A major concern is water contamination in community services, particularly with heavy metals (Tchounwou et al. 2012). Metals such as Hg, Pb, As, and Cd are known as bioaccumulative compounds in the human body, resulting in multi-organ disruption (Jaishankar et al. 2014; Karri et al. 2016). Another class of pollutants includes additives and dyes in foods and textile industries (Sorouraddin et al. 2015). A synthetic diazo colorant, allura red, used in beverages, ice cream, and bakery products, is known for its carcinogenic effect, also being the main cause of hyperactivity in children. In addition to those linked to air and water quality systems (Scotter 2015), there are pollutants such as brominated flame retardants (Darnerud 2003) and textile dyes used for dyeing and finishing operations. Table 3.2 shows a list of air and water pollutants and adverse effects on mankind and animals.

3.3.1 Analytical Techniques for Pollutant Detection

Quantitative and qualitative measurements of pollutants are necessary to control air and water pollution. However, these measurements are not straightforward, especially owing to the presence of interferents (Qin et al. 2013). Moreover, managing pollution requires detection of pollutants at low concentrations (Gauquie et al. 2015), which depend on mainly on:

- Pollutant state (liquid, gaseous, aerosols, or particulate matter)
- Sample preparation and concentration level
- Measurement period (short or long term)
- Measurement site (in lab or on-site)
- Temperature and humidity effect and control
- Cross-sensitivity with other analytes
- Reliability and stability check with commercial sensor

For monitoring air quality, there are methods to detect hazardous analytes in the environment, as illustrated in Table 3.3. However, stability and selectivity are still a challenge for current sensor technologies. Optical and electrochemical sensors can offer high sensitivity, but bulky dimensions and high-power consumption do not allow them to be widely applied for health-care or mobile applications.

There are also analytical techniques to detect pollutants such as heavy metals, VOCs, food dyes, and brominated flame retardants, as depicted in Table 3.4.

3.3.2 Sensors and Biosensors to Detect Pollutants

The need to detect pollutants in air, soil, and water has sparked research into analytical techniques (Goradel et al. 2017) to replace conventional chromatography that requires expensive, time-consuming sample preparation. Cost-effective, robust, and

Table 3.2 Examples of air and water pollutants – sources and effects (Kaur and Nagpal 2017; Muralikrishna 2017)

No	Pollutants	Sources	Effects
1	Carbon monoxide (CO)	Incomplete combustion of fuels in road transport. Wood stoves, cigarette smoke, and forest fire	Interfering with the blood's ability to carry oxygen, slowing reflexes, and causing drowsiness, headaches, and stress on heart in high concentrations – CO can cause death
2	Sulfur dioxide (SO_2)	Burning fossil fuels (gasoline, oil, natural gas) Released from petroleum refineries, paper mills, chemical, and coal-burning power plants	It is easily dissolved in water and forms acids, contributing to acid rain in lakes and forests. Metals and stones can be also damaged by acid rain
3	Nitrogen oxides (NOx)	Burning fuels in motor vehicles, power plants, industries, and residences that burn fuels	Make the body vulnerable to respiratory infections, lung disease, and possibly cancer
4	Volatile organic compounds	Emitted as gases (fumes) by burning fuels, cleaning supplies, paints, and solvents	Smog formation and can cause serious health problems. They may also harm plants
5	Heavy metals (lead, mercury, cadmium, etc.)	Waste incineration Production of nonferrous metals, iron, steel, and cement	Cause organ and neurological damage in humans and animals. It can also slow down growth rate in plants
6	Organic pollutants Oil and grease pesticides/ weedicides Plastics Detergents	Automobile and machine waste, tanker spills, and offshore oil leakage Chemicals used for better yield from agricultural, industrial, and household waste	Disruption of marine life, aesthetic damage Toxic effects (harmful for aquatic life) Possible genetic defects and cancer Kill fish, eutrophication aesthetics
7	Textile dyes	Natural or synthetic coloring substance which is used in textile industries	They are dangerous and have toxic and carcinogenic effects
8	Brominated flame retardants (BFRs)	Flame retardants containing brominated organic compounds that are applied to combustible materials, such as plastics, wood, paper, electronics, and textiles to meet fire safety regulations	Severe pneumonia by respiratory syncytial virus (RSV) infection to birds and animals. Toxic (acute and chronic) and ecotoxic effects of some BFRs have been observed

portable biosensing and gas sensing devices have been proposed (Materón et al. 2019) with the majority of biosensors incorporating nanomaterials to enhance sensitivity and selectivity (Hernandez-Vargas et al 2018). Electrochemical biosensors, in particular, can detect biological analytes at low concentrations with various techniques, including potentiometric, amperometric, voltammetric, and conductometric measurements (Hernandez-Vargas et al. 2018; Justino et al. 2017). Air pollution caused by hazardous gases from textile and automobile industries has become a serious issue. The major gases that cause air pollution are carbon monoxide and nitrogen oxides, and their main source is fossil fuel combustion (Joshi et al. 2018).

Table 3.3 Air quality sensors and detection principle (Aswal and Gupta 2006)

Type of sensors	Sensor	Detection principle
Solid-state sensors	Chemiresistive	A change in conductivity of semiconductor is measured when it interacts with the analyte gas
	Chemical field-effect transistors (ChemFET)	Current-voltage (I-V) curves of a field-effect transistor (FET) are sensitive to a gas when it interacts with gate
	Calorimetric	The concentration of a combustible gas is measured by detecting the temperature rise resulting from the oxidation process on a catalytic element
	Potentiometric	The signal is measured as the potential difference between the working electrode and the reference electrode. The working electrode's potential must depend on the concentration of the analyte in the gas phase
	Amperometric	Diffusion limited current of an ionic conductor is proportional to the gas concentration
Mass-sensitive sensors	Acoustic	Change in frequency of surface acoustic waves (SAW) excited on a quartz or piezoelectric substrate upon absorption of gas in a suitable sorption layer (e.g., metals, polymers)
	Microelectromechanical systems (MEMs) based	Change in mechanical bending of micro- or nanocantilevers upon adsorption of gas
Optical sensors	Surface plasmon resonance (SPR)	Change in SPR signals is proportional to the refractive index close to the sensor surface and is therefore related to the amount of bound gas molecules
	Optodes	The change of optical properties measured can base on absorbance, reflectance, luminescence, light polarization, Raman, and others

Volatile organic compounds (VOCs) are produced by construction materials and paint industries, which may even cause headache and skin trouble for people moving into a new apartment (Campos and Sarkis 2018). For example, formaldehyde is produced in industries in the manufacture of resins, as a disinfectant, or as a preservative in consumer products; it is a dangerous indoor pollutant as it can harm all kinds of organisms (Chung et al. 2013; Lawal et al. 2017). The allowed concentration of formaldehyde is only 0.1 ppm in Netherlands and Germany (Chmielewski 2011). Also, the US Environmental Protection Agency (US EPA) has imposed strict regulations on the concentrations of environmental contaminants in air and water. In this section we will discuss the sensors and biosensors for detecting heavy metals, hazardous gases and VOCs, food dyes, and brominated flame retardants.

- *Heavy Metal Detection*

Due to increasing industrial activity, heavy metals such as Hg, AS, Pb, and Cd have been entering into the environment which are highly toxic and carcinogenic

Table 3.4 Detection techniques and detection principles for heavy metals, food dyes, VOCs, and brominated flame retardants (Holbrook et al. 2012; Hori et al. 2013; Zhu et al. 2017).

Type of analytes	Detection method	Detection principle
Heavy metal ions	Inductively coupled plasma (ICP) by mass spectrometry (MS)	The ICP is used to ionize the sample, while the mass spectrometer is used to separate and quantify those ions. Calibrating the instrument with known standards allows for an unknown sample to be quantified
	Cold vapor atomic absorption (CV-AA)	This analysis detects mercury by measuring the absorption of light by mercury in an elemental gaseous state
	Optical	Optical sensors can be described as small devices that respond to the presence of heavy metals by generating an optical signal proportional to the type and concentration of the heavy metal
	Electrochemical	The working principle of such sensors is based on having a transducing element covered with recognition element, which can be either a biological or a chemical element
	Microelectromechanical systems (MEMs) based microspectrometers	Microspectrometer is a tool designed to measure the spectrum of microscopic areas or microscopic samples to measure the transmittance, absorbance, reflectance, polarization, and fluorescence of sample areas smaller than a micron
Volatile organic compounds	Electrochemical (amperometric) sensors	In these sensors, analyte particles diffuse through a membrane and the internal electrolyte toward the surface of working electrode suitably polarized with respect to a reference electrode
	Chemiresistive	Change in conductivity on exposure to analyte gas
	Nondispersive infrared sensors (NDIR)	Sensor consists in arranging a source of infrared radiation along an optical line with a detector. When an analyzed gas appears in a measurement chamber, it absorbs radiation of a particular wavelength and decreases in radiation which is converted into electrical signal.
Food dyes	Paper chromatography (extraction techniques)	The principle involved is partition chromatography, wherein the substances are distributed or partitioned between liquid phases
	Ultraviolet-visible (UV- VIS) spectrophotometer	Principle of UV-visible spectrophotometer is mainly based on Beer's law and Lambert's law

(continued)

Table 3.4 (continued)

Type of analytes	Detection method	Detection principle
Brominated flame retardants	Gas chromatography/mass spectrometry (GC/MS)	The GC works on the principle that a mixture will separate into individual substances when heated. The heated gases are carried through a column with an inert gas (such as helium). As the separated substances emerge from the column opening, they flow into the MS

even at a trace level. They are not biodegradable and will therefore remain for decades once released in the environment and appear at detectable levels in food resources (Tangahu et al. 2011). The sensitive conventional methods to detect heavy metals include atomic absorption spectroscopy and atomic emission spectroscopy. These methods require laborious preparation and pretreatment procedures and professional personnel (Chinna et al. 2018).

Electrochemical, optical, and field-effect transistor (FET)-based sensors have been developed using nanostructures and nanomaterials (Fig. 3.7). Luo et al. (Luo et al. 2009) used silicon nanowires (SiNWs) in FET sensors for detecting toxic heavy metal cations with a LOD of 10^{-7} mol L^{-1} for Hg^{2+} and 10^{-4} mol L^{-1} for Cd^{2+}. The chemical gating effect and strong chelation between thiol groups with positively charged cations is the main reason for the high sensing behavior, and sensors could also be recycled with nearly the same sensitivity as before. Figure 3.7a shows the measuring setup, while Fig. 3.7b shows the I-V behavior of the SiNW before and after thiol modification. The ohmic contacts are formed between electrodes and SiNW, and the modification induces slight decreases in the conductance of SiNW. Figure 3.7c indicates the current change by varying Cd^{2+} concentration in solution. Compared to distilled water (pH = 4), the change in current was increased by 10%. When Cd^{2+} ion of 10^{-4} mol L^{-1} was introduced and as Cd^{2+} concentration further increased to 1×10^{-3}, 3×10^{-3}, 1×10^{-2}, 2×10^{-2}, and 4×10^{-2} mol L^{-1}, the current increased by 28.1%, 40.2%, 56.6%, 66.7%, and 67.4%, respectively. Similarly, the current changed with the Hg^{2+} concentration, as illustrated in Fig. 3.7d.

Optical sensors to detect heavy metals can exploit various principles, including colorimetry, surface plasmon resonance (SPR), and surface-enhanced Raman scattering (SERS) (Meyer et al. 2011; Prabowo et al. 2018; Jiangcai Wang et al. 2017). SERS sensors have been used for chemical and biological sensing and medical diagnostics, but few reports exist of detection of heavy metals. SERS is the molecular spectroscopy which provides spectral fingerprints of target analytes. It is unable to detect heavy metals directly, so the plasmonic nanostructures are functionalized with organic ligands that bind specifically to heavy metal ions. Jinglian Li et al. (2011) developed SERS sensors for As^{3+} detection in aqueous media with glutathione (GSH)/4-mercaptopyridine (4-MPY)-modified silver nanoparticles (AgNPs). Figure 3.8a shows increased SERS signal with addition of As^{3+} ions owing to the As-O linkage established when the distance among AgNPs was shortened with a moderate amount of GSH and 4-MPY. The sensor achieved a limit of detection

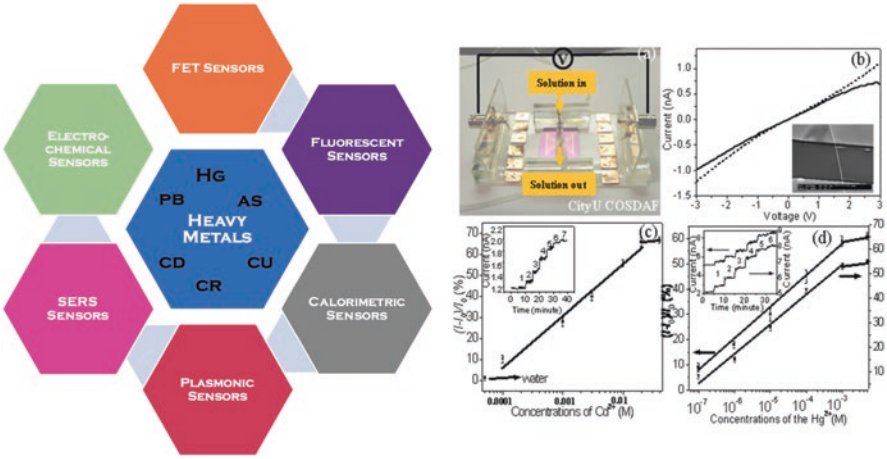


Fig. 3.7 Sensors for detecting heavy metals (**a**) Sensing setup system; (**b**) I-V characteristics of a SiNW before (dotted line) and after thiol modification; (**c**) current changing with increasing Cd^{2+} concentration; (**d**) current variation with increasing Hg^{2+} concentrations. (Reproduced with permission from (Luo et al. 2009), Copyright 2009, American Institute of Physics)

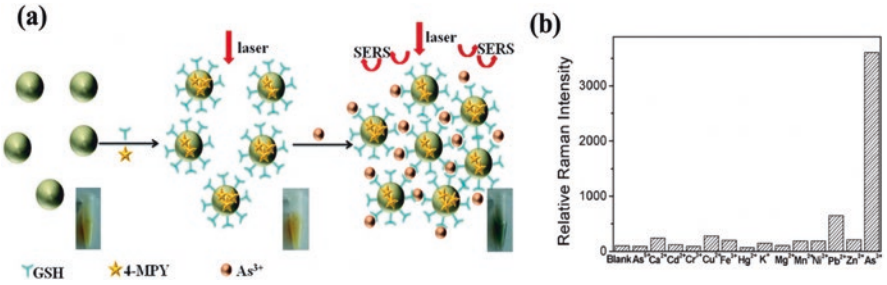


Fig. 3.8 (**a**) Representation of glutathione (GSH) and 4-MPY-modified AgNPs; (**b**) SERS sensor for selective As^{3+} detection using silver nanoparticles. (Reproduced with permission from Jinglian Li et al. (2011). Copyright 2011, American Chemical Society)

(LOD) of 0.76 ppb with selectivity over various metal ions (Fig. 3.8b). However, long-term stability and repeatability of the SERS-based sensors are still a major concern.

- *Chemical Sensors for Detection of Toxic Pollutants*

Chemical sensors are a crucial part of modern life with applications in environmental monitoring, domestic safety, public security, and food quality assessment among others (Swager and Mirica 2019). They are increasingly being integrated into mass-market applications, for instance, in air quality control in buildings and motor vehicles and in traditional areas of toxic and explosive gas detection. The market for gas sensors is growing with new applications driving innovation, for

instance, the analysis of gases from the gut and breath for noninvasive diagnosis of diseases (Bogue 2017). Chemiresistive sensors comprise an important part of the gas sensor market, against a host of competing technologies, due to their low cost, high sensitivity, fast response, and relative simplicity (Liu et al. 2012). The materials used in these sensors are typically wide-bandgap semiconducting metal oxides, such as tin oxide, tungsten oxide, indium oxide, or zinc oxide (Domènech-gil et al. 2017; Joshi et al. 2016; Jinwei Li et al. 2015b; Sayago et al. 2019). They function as gas sensors because adsorbed gaseous species form surface states in the metal oxide by exchange of electrons with the bulk material. The concentration of the surface states is proportional to the partial pressure of the gas impinging on the metal oxide, and hence the conductivity of the material changes in response to changes in gas concentration. These chemically induced changes can then be transduced into electrical signals by means of simple conductivity measurements.

Metal oxides are the most common and even commercially available sensors; however, they rely on high temperature modulation to achieve high sensitivity and selectivity which decreases the sensor lifetime and makes the system more complex (Zhou et al. 2014b). In order to obtain room temperature sensing, 2D materials have been investigated owing to their high surface to volume ratio, but the speed of recovery is still a limitation. Liu et al. (2018) demonstrated new AC phase sensing of graphene FETs for chemical vapors with fast recovery, with a new concept illustrated in Fig. 3.9. To get rid of the effects of trap states and defects, those authors used the reversible and stable phase change as the sensing parameter instead of the vulnerable DC resistance (see Fig. 3.9a). The phase lag between channel resistance and the gate voltage was detected with the AC voltage applied on the gate electrode, as shown in Fig. 3.9b. The recovery speed is ten times faster than with DC resistance signals. Figure 3.9c illustrates the key difference between AC and DC measurements where AC measurements are more sensitive to weak adsorption of vapor molecules, while DC measurement results are sensitive to a strong adsorption-desorption process. Malik et al. (2018) employed Au-TiO_2@g-CN nanohybrids to detect volatile organic amines (VOAs), such as triethylamine (TEA), using a two-step method (hydrothermal and nanocasting). The average times for response and recovery of the Au-TiO2@m-CN sensor toward TEA gas are 9–16 and 6–12 s for 1–50 ppm range.

- *Detection of Food Dyes*

Manufacturing industries use large amounts of cost-effective artificial ingredients for improving their consumer characteristics and appearance (Leo et al. 2017; Lipskikh et al. 2018; Nambiar et al. 2018; Zhu et al. 2017). Monitoring the quality of food dyes in drinks has therefore become of paramount importance. Brilliant Blue (E133), Tartrazine (E102), Sunset Yellow (E110), and Amaranth (E123) (molecular structure and commercial name and details in Table 3.5) are synthetic dyes added to nonalcoholic beverages. The Brazilian Agency for Public Surveillance (ANVISA) has issued legal provision in 2002 to regulate the use of food dyes, since their high consumption could induce skin allergies and bronchial asthma. The maximum level allowed is 0.01 g/100 mL for Sunset Yellow, Tartrazine, and

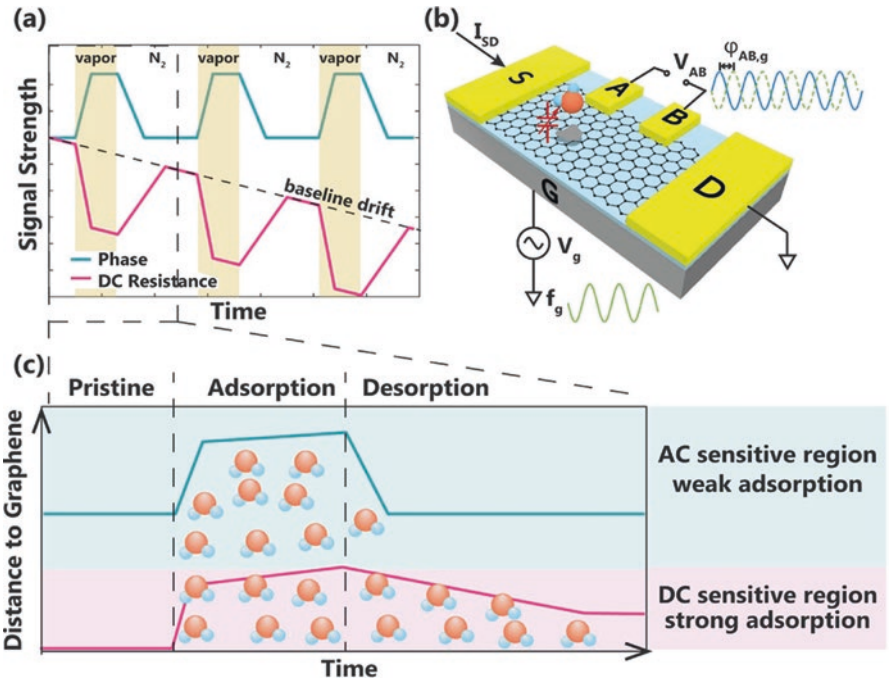
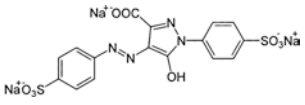
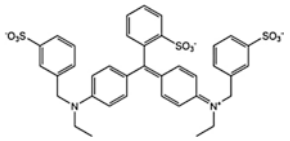
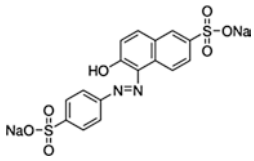
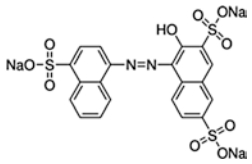


Fig. 3.9 (**a**) Schematic of gas sensing performance using the phase lag detection method with fast recovery compared to the DC resistance method. (**b**) Schematic of phase lag $\varphi_{AB,g}$ between V_{AB} and V_g on a CVD graphene FET sensor under the exposure to chemical vapor. (**c**) Vapor adsorption process and desorption on the graphene surface illustrating that the AC sensing scheme is more effective to detect weakly adsorbed gases away from the graphene surface, while the DC sensing scheme is more effective to detect molecules close to the surface. (Reproduced with permission from (Liu et al. 2018) Copyright 2018, Elsevier)

Brilliant Blue in nonalcoholic beverages, while the value for Amaranth is 0.005 g/100 mL.

The analytical techniques to determine concentrations of food colorants include thin-layer chromatography (TLC), spectrophotometry in the visible region, high-performance liquid chromatography, and capillary electrophoresis. Reverse phase LC and ion-pair high-performance liquid chromatography (LC IP) are the most used in drinks. For instance, sulfonated azo dyes used in 330 commercial samples of orange and grape carbonated soft drinks were determined using ion-pair LC combined with photodiode array and thin-layer chromatography (TLC) (Andrade et al. 2014). A liquid chromatography diode-array detector (LC-DAD) was utilized to distinguish natural and synthetic colorants in dairy samples such as milk shakes, yogurts, and ice creams (Gallego and Valca 2003). Second-order derivative linear sweep voltammetry was used to detect tartrazine where glassy carbon electrodes were coated with a TiO_2-reduced graphene oxide composite (He et al. 2018).

Table 3.5 Food colorants and their structures and commercial names. European Community (EC) number, and food (F) and drug (D) number (Oplatowska-stachowiak and Elliott 2015)

Molecular structure	Commercial name	EC number	FD&C number
	Tartrazine	E102	Yellow #5
	Brilliant Blue FCF	E133	Blue #1
	Sunset Yellow FCF	E110	Yellow #6
	Amaranth	E123	Red #2

- *Detection of Brominated Flame Retardants*

Brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) are mainly used in plastics and electronic equipment to prevent combustion. Exposure to PBDEs may lead to endocrine disruption and neurodevelopmental toxicity in humans and hepatotoxicity, endocrine disruption, gene expression, and impaired reproductive physiology in animals. They have been banned in Europe, North America, and Australia (Mcgrath et al. 2017). Most BFRs are detected with gas chromatography/mass spectrometry (Geng et al. 2017).

3.4 Pharmaceutical and Personal Care Products (PPCPs)

Pharmaceutical (human and veterinary therapeutic drugs) and personal care products (PPCPs) comprise a well-known group of emerging contaminants (Boxall 2004; Boxall et al. 2012; Jennifer et al. 2017). Some of this pollution comes from human excretion of contraceptives and other medicines (e.g., acetaminophen, acetylsalicylic acid, ibuprofen, naproxen, and carbamazepine), which are eventually found in water (Boxall 2004). These drugs are absorbed, metabolized, and excreted

to the sewage system, with some metabolized products being even more toxic than the non-metabolized drugs. Furthermore, many of the water treatment systems are not capable of removing the drugs and may transform the products into more toxic ones (Boxall 2004; Boxall et al. 2012; Jennifer et al. 2017; Kümmerer 2009; Vieno and Sillanpää 2014). The main sources of environmental pollution from pharmaceutical products are:

- Effluents from manufacturing and hospital waste
- Excretion by animals treated with antibiotics or other drugs
- Human excretion of pharmaceutical and personal care products (Richardson and Bowron 1985; Rzymski et al. 2017)

The traditional methods to treat water include adsorption, solvent extraction, reduction, flocculation, coagulation, chemical or biological oxidation, ultrasound, and membrane filtration (Fan et al. 2018; Jing Wang et al. 2019a). The reported concentrations of pharmaceutical products are low, between ng L^{-1} (groundwater) and μg L^{-1} (wastewater), but many drugs can have cumulative effects and bring health problems, such as cancer (Boxall 2004; Christou et al. 2018).

3.4.1 Current Analysis of Pharmaceutical Products

The large number of recent reports of emerging pollutants in the environment may give the impression that this is a new problem. However, this is not new, and such pollution was simply ignored in the past owing to the lack of analytical methods with sufficient sensitivity to detect trace amounts (Buchberger 2011). Indeed, already in 1977 Hignite and Azarnoff found clofibric acid (used to lower plasma triglycerides and cholesterol concentrations in humans) and salicylic acid at low ppb levels in sewage treatment plant effluents (Hignite and Azarnoff 1977). Kolpin et al. (2002) detected 95 pharmaceutical contaminants such as hormones and other organic wastewater contaminants (OWCs) in water resources in the USA in 1999 and 2000 (Kolpin et al. 2002). Ternes reported the discovered drugs in the aquatic environment at concentrations up to approximately 1 μg l^{-1} in the UK (Ternes 1998). Pharmaceutical and chemotherapeutic drugs were found in the sewage, sewage effluents, river, and potable water (Richardson and Bowron 1985). Unfortunately, some drug residues could survive the various water treatment processes and remain at low concentrations <μg L^{-1} (Richardson and Bowron 1985; Ternes 1998).

In a review about ecotoxicity of hospital waste effluents, Orias and Perrodin (2013) listed a variety of toxic substances (Jean et al. 2012; Orias and Perrodin 2013), and human and veterinary pharmaceutical substances were found in surface water, groundwater, tap/drinking water, and soil (Beek et al. 2016). The anti-inflammatory drug diclofenac was found in higher-than-expected concentrations in 50 countries (aus der Beek et al. 2016). Also relevant are the effects of cocktails of drugs released in the environment after human consumption or/and incomplete removal at the waste treatment plant, which increase ecotoxicity (Vasquez et al.

2014) that is increasing over the years owing to their availability in town pharmacies (Parrella et al. 2014), (Besse et al. 2012). Ferrando-Climent and co-workers found tamoxifen and ciprofloxacin in the river upstream the sewage discharge (Ferrando-Climent et al. 2014), and Miller et al. (2018) discussed bioaccumulation of pharmaceuticals and its metabolite products in aquatic fauna, including anticancer drugs (Miller et al. 2018).

The increasing environmental contamination with pharmaceutical products requires alternative analytical techniques (Webb et al. 2003) to liquid (LC) and gas chromatography (GC) coupled to mass spectrometry (MS) (Fatta et al. 2007; Miller et al. 2018). Other methodologies to detect emerging pollutants are given in Table 3.6, including titrimetric measurements, UV-vis spectroscopy, near-infrared spectroscopy (NIRS), fluorometry, phosphorimetry, and nuclear and magnetic resonance spectroscopy (NMR) (Turci et al. 2003).

3.4.2 Sensors and Biosensors to Detect Pharmaceutical and Personal Care Products (PPCPs)

Pharmaceutical products and derivatives are among the most demanding contaminants to detect in the environment. Highly frequent are the antibiotics introduced into the ecosystem via excretion from humans and animals (Khor et al. 2011). Antibiotics have been found in water resources, effluent from industries, sludge, manure, soil, plants, and organisms, the most common being b-lactams, sulfonamides, monobactams, carbapenems, aminoglycosides, glycopeptides, lincomycin, macrolides, polypeptides, polyenes, rifamycin, tetracyclines, chloramphenicol, quinolones, and fluoroquinolones (Gothwal and Shashidhar 2014). Negative effects from antibiotics include reduction of the growth, photosynthesis, content of photosynthetic pigments, chlorophylls, and carotenoids in plants. Moreover, fluoroquinolones inhibit DNA synthesis in eukaryotic cells, and b-lactams affect the plastid division in lower plants (Gothwal and Shashidhar 2014). In humans, fluoroquinolones may cause side effects such as nausea, dyspepsia, vomiting, dizziness, insomnia, and headache (Norrby 1991). The most serious problem, though, is the potential resistance development in human and animal pathogens (Norrby 1991; Larsson 2014).

Detection of pharmaceutical products has also been performed with electrochemical techniques that may offer low cost, robustness, easy miniaturization, low detection limits, small analyte volume, and real-time monitoring (Wang et al. 2008). Electroanalytical methods may also be combined with standard techniques to improve sensitivity (Brett 2001). They employ enzymes, antibodies, nucleic acids, or whole cells immobilized onto amperometric or potentiometric electrode transducers, without requiring sample pretreatment (Joseph Wang 2002). Biosensors with a chemically selective layer (Stradiotto et al. 2003) may encompass immunosensors, such as the one to detect the fluoroquinolone antibiotic enrofloxacin in milk

Table 3.6 Methods to detect pharmaceutical products in the environment

Drug determined	Technique	LOD	Real sample	References
Acetaminophen	UPLC-MS/MS	3.5 ng L^{-1}	Wastewater	Hong et al. (2015)
Amoxicillin	LC-ESI-MS/MS	9.49 ng L^{-1}	Hospital Wastewater	Gros et al. (2013)
Amoxicillin	LC-ESI-MS/MS	2.65 ng L^{-1}	Urban Wastewater Effluent	Gros et al. (2013)
Amoxicillin	LC-ESI-MS/MS	3.32 ng L^{-1}	Urban Wastewater Influent	Gros et al. (2013)
Amoxicillin	LC-ESI-MS/MS	1.32 ng L^{-1}	River Water	Gros et al. (2013)
Caffeine	UPLC-MS/MS	3.4 ng L^{-1}	Wastewater	Hong et al. (2015)
Cefalexin	LC-ESI-MS/MS	4.32 ng L^{-1}	Hospital Wastewater	Gros et al. (2013)
Cefalexin	LC-ESI-MS/MS	1.43 ng L^{-1}	Urban Wastewater Effluent	Gros et al. (2013)
Cefalexin	LC-ESI-MS/MS	3.40 ng L^{-1}	Urban Wastewater Influent	Gros et al. (2013)
Cefalexin	LC-ESI-MS/MS	0.77 ng L^{-1}	River Water	Gros et al. (2013)
Clindamycin	LC-ESI-MS/MS	4.89 ng L^{-1}	Hospital Wastewater	Gros et al. (2013)
Clindamycin	LC-ESI-MS/MS	1.48 ng L^{-1}	Urban Wastewater Effluent	Gros et al. (2013)
Clindamycin	LC-ESI-MS/MS	3.13 ng L^{-1}	Urban Wastewater Influent	Gros et al. (2013)
Clindamycin	LC-ESI-MS/MS	0.48 ng L^{-1}	River Water	Gros et al. (2013)
Chloramphenicol	LC-MS	0.03–0.83 ng g^{-1}	Mussels	Fedeniuk et al. (2015)
Ciprofloxacin	U-LC-Q-Extractive Orbitrap	12.6 ng L^{-1}	River water	Lidia et al. (2015)
Diclofenac	UPLC-MS/MS	8.6 ng L^{-1}	Wastewater	Hong et al. (2015)
Doxycycline	LC-ESI-MS/MS	33.65 ng L^{-1}	Hospital Wastewater	Gros et al. (2013)
Doxycycline	LC-ESI-MS/MS	77.49 ng L^{-1}	Urban Wastewater Effluent	Gros et al. (2013)
Doxycycline	LC-ESI-MS/MS	59.79 ng L^{-1}	Urban Wastewater Influent	Gros et al. (2013)
Doxycycline	LC-ESI-MS/MS	11.23 ng L^{-1}	River Water	Gros et al. (2013)
Diclofenac	U-LC-Q-Extractive Orbitrap	5.0 ng L^{-1}	River water	Lidia et al. (2015)
Erythromycin	UPLC-MS/MS	0.22–0.26 ng g^{-1}	Fish	Liu et al. (2014a)

(continued)

Table 3.6 (continued)

Drug determined	Technique	LOD	Real sample	References
FQs	LC-FLD	0.3 ng g^{-1}	Fish liver and muscle, sediment	He et al. (2012)
FQs	LC-MS	0.5–3.9 ng g^{-1}	Frog legs, fishes	Turnipseed et al. (2012)
FQs	LC-MS/MS	0.06–0.9 ug kg^{-1}	Mollusks	Li et al. (2012a)
FQs	LC-MS/MS	0.31–38.4 ng g^{-1}	Plants	Sabourin et al. (2012)
FQs	LC-MS/MS	0.08–0.25 ng g^{-1}	Fish	Liu et al. (2015)
FQs	UPLC-MS/MS	Nd	Fish	Zhao et al. (2015a)
Ketoprofen	UPLC-MS/MS	5.0 ng L^{-1}	Wastewater	Hong et al. (2015)
Metronidazole	LC-ESI-MS/MS	6.49 ng L^{-1}	Ho spital Wastewater	Gros et al. (2013)
Metronidazole	LC-ESI-MS/MS	1.80 ng L^{-1}	Urban Wastewater Effluent	Gros et al. (2013)
Metronidazole	LC-ESI-MS/MS	4.45 ng L^{-1}	Urban Wastewater Influent	Gros et al. (2013)
Metronidazole	LC-ESI-MS/MS	0.43 ng L^{-1}	River Water	Gros et al. (2013)
Naproxen	U-LC-Q-Extractive Orbitrap	3.7 ng l^{-1}	River water	Lidia et al. (2015)
Oxacillin	UPLC-MS/MS	5.5 ng L^{-1}	Wastewater	Hong et al. (2015)
Oxytetracycline	LC-MS	2.6–4.4 µg kg^{-1}	Plants	Lidia et al. (2015)
Penicillin G	LC-ESI-MS/MS	2.55 ng L^{-1}	Hospital Wastewater	Gros et al. (2013)
Penicillin G	LC-ESI-MS/MS	3.48 ng L^{-1}	Urban Wastewater Effluent	Gros et al. (2013)
Penicillin G	LC-ESI-MS/MS	8.62 ng L^{-1}	Urban Wastewater Influent	Gros et al. (2013)
Penicillin G	LC-ESI-MS/MS	4.00 ng L^{-1}	River Water	Gros et al. (2013)
Penicillin V	LC-ESI-MS/MS	11.31 ng L^{-1}	Hospital Wastewater	Gros et al. (2013)
Penicillin V	LC-ESI-MS/MS	7.04 ng L^{-1}	Urban Wastewater Effluent	Gros et al. (2013)
Penicillin V	LC-ESI-MS/MS	22.82 ng L^{-1}	Urban Wastewater Influent	Gros et al. (2013)
Penicillin V	LC-ESI-MS/MS	5.37 ng L^{-1}	River Water	Gros et al. (2013)

(continued)

Table 3.6 (continued)

Drug determined	Technique	LOD	Real sample	References
PCs	LC-UV/VIS	11.0–20.4 ug kg^{-1}	Fish	Evaggelopoulou and Samanidou (2013)
Piroxicam	U-LC-Q-Extractive Orbitrap	3.9 ng L^{-1}	River Water	Lidia et al. (2015)
QLs	LC-MS/MS	Nd	Fish, crustacean	Na et al. (2013)
QLS	LC-MS/MS	0.81–4.60 ug kg^{-1}	Crustacean	Na et al. (2013)
Roxithromycin	UPLC-MS/MS	0.25–0.35 ng g^{-1}	Fish	Liu et al. (2014b)
SAs	LC-MS/MS	0.01–0.1 ng L^{-1}	Aquatic plants	Li et al. (2012b)
SAs	LC-MS/MS	0.01–1 μg kg^{-1}	Fish, sediment	Gao et al. (2012)
SAs	LC-MS/MS	Nd	Plants	Tanoue et al. (2012)
Sulfadiazine	U-LC-Q-Extractive Orbitrap	2.3 ng L^{-1}	River Water	Lidia et al. (2015)
Sulfadiazine	LC-MS/MS	5 ng L^{-1}	Plants	Michelini et al. (2012)
Sulfadiazine	LC-FLD	Nd	Plants	Li et al. (2013)
Sufamethoxazole	LC-MS	9.28–16.07 g g^{-1}	Plants	Holling et al. (2012)
Tetracycline	LC-ESI-MS/MS	24.30 ng L^{-1}	Hospital Wastewater	Gros et al. (2013)
Tetracycline	LC-ESI-MS/MS	13.42 ng L^{-1}	Urban Wastewater Effluent	Gros et al. (2013)
Tetracycline	LC-ESI-MS/MS	16.25 ng L^{-1}	Urban Wastewater Influent	Gros et al. (2013)
Tetracycline	LC-ESI-MS/MS	4.72 ng L^{-1}	River Water	Gros et al. (2013)
Triclosan	UPLC-MS/MS	16 ng L^{-1}	Wastewater	Hong et al. (2015)
Tylosin	LC-ESI-MS/MS	11.97 ng L^{-1}	Hospital Wastewater	Gros et al. (2013)
Tylosin	LC-ESI-MS/MS	28.11 ng L^{-1}	Urban Wastewater Effluent	Gros et al. (2013)
Tylosin	LC-ESI-MS/MS	34.00 ng L^{-1}	Urban Wastewater Influent	Gros et al. (2013)
Tylosin	LC-ESI-MS/MS	2.37 ng L^{-1}	River Water	Gros et al. (2013)
Vancomycin	LC-MS/MS	8.8 ng L^{-1}	Wastewater	Hong et al. (2015)
Warfarin	UPLC-MS/MS	14 ng L^{-1}	Wastewater	Hong et al. (2015)

nd no data, *FLD* fluorescence detection, *LC* high-performance liquid chromatography, *ESI* electrospray ionization, *UPLC* ultra-performance liquid chromatography, *LC-MS/MS* liquid chromatography mass spectroscopy

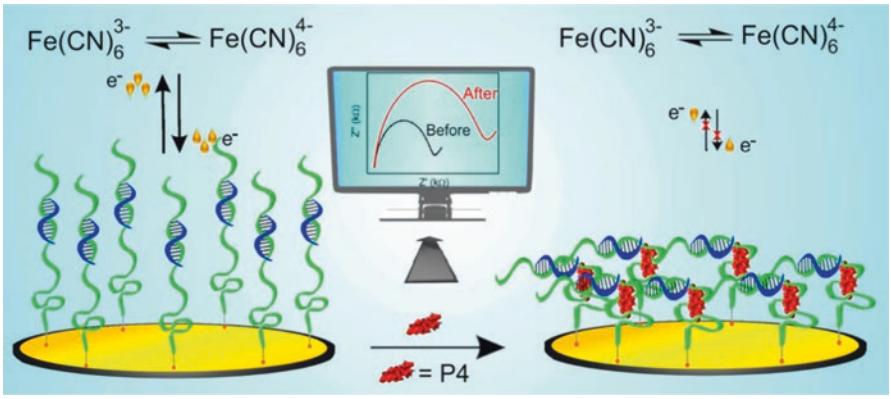


Fig. 3.10 Design of the impedimetric aptasensor to detect progesterone (P4). (Reproduced with permission from (Jiménez et al. 2014). Copyright 2019, American Chemical Society)

and waters (Khor et al. 2011). An immunosensor prepared in a microfluidic device modified with antibodies was used to detect ibuprofen in water from various sources with a limit of detection at 0.25 pg mL^{-1} (Nagaraj et al. 2014), where the principle of detection was impedance spectroscopy. Aptasensors have been used to detect the hormone progesterone (P4) in a concentration range from 10 ng mL^{-1} to 60 ng mL^{-1} with a detection limit of 0.90 ng mL^{-1} (Jiménez et al. 2014). This impedimetric aptasensor was fabricated by immobilizing an aptamer on gold electrodes, as depicted in Fig. 3.10.

Illicit drugs have also been found in sewage and wastewater (Mccall et al. 2015). Huerta-fontela et al. determined cocaine and metabolites in wastewater at concentrations from 4 ng L^{-1} to 4.7 μg L^{-1} and from 9 ng L^{-1} to 7.5 μg L^{-1}, respectively, while concentrations of amphetamine type stimulatory drugs ranged from 2 to 688 ng L^{-1} (Huerta-fontela et al. 2008). Drugs found in tap water included ecstasy, caffeine, paraxanthine, fentanyl, and methadone (Boleda et al. 2011). Fentanyl exemplifies the risk because it causes death owing to overdoses (Ciccarone 2017). Goodchild and co-workers (2019) developed a sensor to detect fentanyl made with screen-printed carbon electrodes (SPCE) modified with the ionic liquid (RTIL) 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[C_4C_1PYrr][NTF_2]$ using cycling square voltammetry (Goodchild et al. 2019). Data for this sensor, whose limit of detection was 5 μmol L^{-1}, are illustrated in Fig. 3.11:

Table 3.7 shows other examples of sensors and biosensors used for pharmaceutical detection in the environment. The presence of emerging pollutants in the environment, mainly in potable water, is already a worrying reality in many countries. Novel sensors and biosensors need to be developed to detect pollutants, pesticides, and pharmaceutical products in the environment.

As mentioned above, there is no doubt that electroanalytical techniques are an outstanding alternative to monitor contaminants due to low-cost and excellent detection limits.

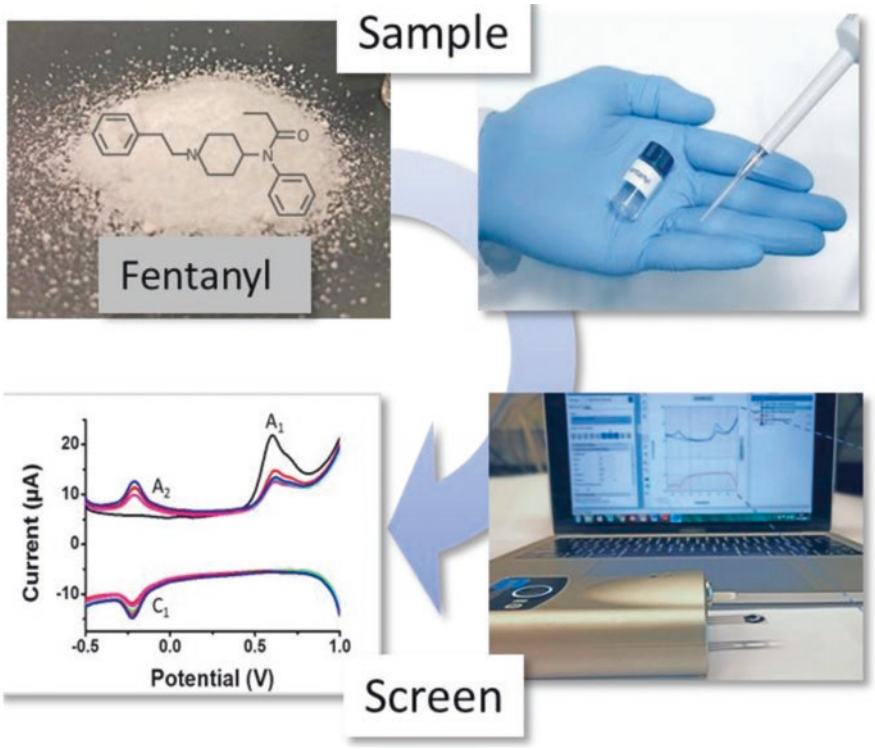


Fig. 3.11 Fentanyl sensor based in screen-printed modified with the room temperature ionic liquid (RTIL). (Reproduced with permission from (Goodchild et al. 2019). Copyright 2019, American Chemical Society)

3.5 Final Remarks

The problem of emergent contaminants has been ignored for an extended time because many environmental entities consider lower concentrations to be harmless. Consequently, these low concentrations lead to serious health problems in humans and animals, due to many products that are accumulated or can cause compounds to be more toxic when metabolized by the body.

Undoubtedly, the emergent contaminants are a significant problem that should be resolved by new regulations about the environmental quality that support green chemistry and the development of devices to monitor these product toxics in the environment – followed by more toxicity studies and rigorous control of products that will be brought to market.

As mentioned in this chapter, the electrochemical techniques have been postulated as a tool for detection of pollutants, pharmaceutical products, and pesticides with a low price, simplicity, and selectivity, rather low detection limits and multiple

Table 3.7 Electrochemical methods to detect pharmaceutical products in the environment

Drug determined	Technique	LOD	Real sample	References
17b-Estradiol	Electrochemical impedance	5.0×10^{-9} µmolL^{-1}	Water sample	Ke et al. (2014)
Acetaminophen	Differential pulse voltammetry	4.4 µg L^{-1}	River water	Berto et al. (2018)
Amiloride hydrochloride	Square wave voltammetry	0.09 µmolL^{-1}	Tap water	Moraes and Salamanca-neto (2017)
Amlodipine besylate	Square wave voltammetry	0.30 µmolL^{-1}	Tap water	Moraes and Salamanca-neto (2017)
Ampicillin	Differential pulse voltammetry	1.09×10^{-9} molL^{-1}	Milk	Wang (2015)
Ampicillin	Differential pulse voltammetry	4.0×10^{-9} molL^{-1}	Milk	Wang et al. (2016)
Ampicillin	Square wave voltammetry	2.8×10^{-10} molL^{-1}	Lake water	Yang et al. (2017)
Ascorbic acid	Cyclic voltammetry	1 µmolL^{-1}	Lemon juice	Emran et al. (2018)
Atenolol	Square wave voltammetry	0.06 µmolL^{-1}	Tap water	Moraes and Salamanca-neto (2017)
Bisphenol-A	Square wave voltammetry	0.6×10^{-9} mol L^{-1}	Tap water	Liu et al. (n.d.)
Bisphenol-A	Square wave voltammetry	0.19×10^{-9} molL^{-1}	Tap water	Yu et al. (2016)
Bisphenol-A	Differential pulse voltammetry	2.1×10^{-11} molL^{-1}	Environmental water	Derikvand et al. (2016)
Bisphenol-A	Differential pulse voltammetry	5.0×10^{-6} molL^{-1}	milk	Zhou et al. (2014a)
Cefalexin	Differential pulse voltammetry	0.01 µmolL^{-1}	River water	Feier et al. (2017)
Cefalexin	Cyclic voltammetry, electrochemical impedance spectroscopy	3.2 nmolL^{-1}	River water	Feier et al. (2019)
Cefalexin	Differential pulse voltammetry, amperometry	1.0×10^{-7} molL^{-1}	Spike river water	Feier et al. (2017)

(continued)

Table 3.7 (continued)

Drug determined	Technique	LOD	Real sample	References
Chloramphenicol	Electrochemical impedance spectroscopy	1.8×10^{-6} molL^{-1}	Buffer solution	Pilehvar et al. (2014)
Chloramphenicol	Square wave voltammetry	1.0×10^{-12} mol L^{-1}	Fish	Chen et al. (2015)
Chloramphenicol	Square wave voltammetry	4.6×10^{-10} mol L^{-1}	Milk	Yan et al. (2016)
Chloramphenicol	Cyclic voltammetry	1.0×10^{-5} mol L^{-1}	Milk	Munawar et al. (2017)
Chloramphenicol	Differential pulse voltammetry	1.0×10^{-10} mol L^{-1}	Milk and honey spiked samples	Yang and Zhao (2015)
Chloramphenicol (CAP)	Square wave voltammetry and cyclic voltammetry	2.0×10^{-7} mol L^{-1}	Milk powder, bee pollen samples spiked with CAP	Sun et al. (2017)
Ciprofloxacin	Differential pulse voltammetry	0.005 µmolL^{-1}	Wastewater effluent	Gayen and Chaplin (2015)
Ciprofloxacin	Electrochemical impedance spectroscopy, cyclic voltammetry	0.5 ng L^{-1}	Milk	Li et al. (2018)
Clenbuterol	Electrochemical impedance spectroscopy	1.3×10^{-12} molL^{-1}	Pork	Chen et al. (2016)
Clonazepam	Differential pulse adsorptive cathodic stripping voltammetry	0.65 µgL^{-1}	Natural rivers	Nunes et al. (2017)
Dexamethasone	Square wave voltammetry	2.8 10^{-8} molL^{-1}	Wastewater	Oliveira et al. (2015)
Diazepam	Differential pulse adsorptive cathodic stripping voltammetry	0.27 µgL^{-1}	Natural rivers	Nunes et al. (2017)
Diclofenac	Square wave voltammetry	1.8×10^{-7} mol L^{-1}	Wastewater	Oliveira et al. (2015)
Dopamine	Flow injection analysis system coupled to multiple pulse	0.011 µmolL^{-1}	Waste river samples	Wong et al. (2018)
Flutamide	Square wave voltammetry	0.21 µmolL^{-1}	Water	Švorc et al. (2017)

(continued)

Table 3.7 (continued)

Drug determined	Technique	LOD	Real sample	References
Flutamide	Cyclic voltammetry	0.016 μmolL^{-1}	Tap water	Kubendhiran et al. (2018)
Hydrazine	Amperometry	0.23 μmol L^{-1}	Natural lake and tap water	Deroco et al. (2018)
Hydrochlorothiazide	Square wave voltammetry	0.08 μmolL^{-1}	Tap water	Moraes and Salamanca-neto (2017)
Hydroquinone	Square wave voltammetry	0.05 μmolL^{-1}	Water samples	Soltani et al. (2016)
Hydroquinone	Flow injection amperometry	0.1 μmolL^{-1}	Water samples	Upan et al. (2015)
Ibuprofen	Differential pulse voltammetry	2.0×10^{-10} molL^{-1}	Wastewater	Roushani and Shahdost-fard (2016)
Kanamycin	Differential pulse voltammetry	8.7×10^{-13} molL^{-1}	Food	Xiong et al. (2012)
	Square wave voltammetry	1.4×10^{-10} molL^{-1}	Milk	Zhou et al. (2015)
	Differential pulse voltammetry	7.6×10^{-12} molL^{-1}	Milk	Sheng et al. (2017)
	Differential pulse voltammetry	0.87×10^{-6} molL^{-1}	Milk	Qin et al. (2015)
Kanamycin	Differential pulse voltammetry	5.8×10^{-9} molL^{-1}	Milk	Sun et al. (2013)
	Square wave voltammetry	1.0×10^{-9} molL^{-1}	Milk	Xu et al. (2015)
	Differential wave voltammetry	9.5×10^{-12} molL^{-1}	Milk	Xu et al. (2014)
Kanamycin	Cyclic voltammetry, electrochemical impedance spectroscopy	0.11 ng mL^{-1}	Spiked milk samples	Sharma et al. (2017)
Levofloxacin	Differential pulse voltammetry	3.61 ng mL^{-1}	Milk	Huang et al. (2016)
Metronidazole	Cyclic voltammetry	1.8×10^{-11} molL^{-1}	Tablets, fish samples	Li et al. (2015a)

(continued)

Table 3.7 (continued)

Drug determined	Technique	LOD	Real sample	References
Metronidazole	Differential pulse adsorption square voltammetry	1.6×10^{-8} molL^{-1}	Milk, honey spiked samples	Chen et al. (2013)
Metronidazole	Linear sweep voltammetry	2.8×10^{-8} molL^{-1}	Lake water	Emran et al. (2018)
Ofloxacin	Differential pulse voltammetry	0.4 ng mL^{-1}	Water, plant sewage	Pilehvar et al. (2016)
Oxacillin	Differential pulse voltammetry, amperometry	1.0×10^{-5} molL^{-1}	Spike river water	Feiera et al. (2017)
Oxytetracycline	Square wave voltammetry	2.2×10^{-10} molL^{-1}	Milk	Rapini and Marrazza (2017)
Paracetamol	Square wave voltammetry	0.01 μmolL^{-1}	Water samples	Kumar et al. (2019)
Paracetamol	Differential pulse voltammetry	1.3×10^{-8} molL^{-1} 8.0×10^{-9} molL^{-1}	Natural water from creek	Raymundo-Pereira et al. (2017)
Penicillin G (beta-lactams)	Amperometry	1.0×10^{-10} molL^{-1}	River wastewater	Merola et al. (2014)
Piroxicam	Square wave voltammetry	0.16 μmolL^{-1}	Tap water	Augusto et al. (2018)
Ractopamine	Electrochemical impedance spectroscopy	1.0×10^{-10} molL^{-1}	Pork	Chen et al. (2016)
Streptomycin	Differential pulse voltammetry	14.1×10^{-6} molL^{-1}	Rat serum, milk	Danesh et al. (2015)
Streptomycin	Differential pulse voltammetry	5×10^{-10} molL^{-1}	Porcine, kidney, honey (spiked samples)	Wen et al. (2017)
Sulfadimethoxine	Square wave voltammetry	7.0×10^{-9} molL^{-1}	Lake water	Yang et al. (2017)
Sulfaguanidine	Impedance spectroscopy, differential pulse voltammetry	0.20 pg mL^{-1}	Honey samples	El et al. (2018)
Sulfamethoxazole	Square wave voltammetry	0.024 μmolL^{-1}	Surface water samples	Zhao et al. (2015b)
Sulfamethoxazole	Electrochemical impedance	1.0×10^{-12} molL^{-1}	Seawater	Ait-lahcen et al. (2016)

(continued)

Table 3.7 (continued)

Drug determined	Technique	LOD	Real sample	References
Sulfamethoxazole	Square wave voltammetry	0.024 μmolL^{-1}	Lake water	Zhao et al. (2015b)
Sulfamethoxazole	Electrochemical impedance spectroscopy	1.0×10^{-12} molL^{-1}	Spiked seawater	Ait-lahcen et al. (2016)
Sulfanilamide	Amperometry	0.016 μ molL^{-1}	Pork	He and Chen (2016)
Sulfathiazole	Amperometry	0.001 μg mL^{-1}	Milk	Bueno et al. (2014)
Sulfonamides	Cyclic voltammetry	0.12 ng mL^{-1}	Water samples	Zhang et al. (2019b)
Tetracycline	Cyclic voltammetry	0.035 μgL^{-1}	Water samples	Alawad et al. (2019)
Tetracycline	Voltammetry	0.22 fM	Honey	Bougrini et al. (2016)
Tetracycline	Differential pulse voltammetry	5.6×10^{-12} molL^{-1}	Milk	Guo et al. (2015)
Tetracycline	Differential pulse voltammetry	4.5×10^{-11} molL^{-1}	Milk	Mohammad, et al. (2016)
Tetracycline	Linear sweep voltammetry	2.2×10^{-16} molL^{-1}	Honey	Bougrini et al. (2016)
Tetracycline	Adsorptive stripping differential pulse voltammetry	3.6×10^{-7} mol L^{-1}	River water	Wong et al. (2015)
Theophylline	Differential pulse voltammetry	1.2×10^{-9} molL^{-1}	Tea	Gan et al. (2017)
Timolol maleate	Pulse adsorptive anodic stripping voltammetry	7.1×10^{-10} mol L^{-1}	Tap water	Mohammed et al. (2018)
Triclosan	Cyclic voltammetry	0.23 pg mL^{-1}	Water samples	Motia et al. (2019)

designs that allow miniaturization. These techniques also have the possibility of being coupled with conventional measurement methods improving their sensitivity.

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References

Aamand J, Gavrilescu M, Agathos S, Fava F (2015) Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation. New Biotechnol 32(1):147–156

Adeel M et al (2017) Environmental impact of estrogens on human, animal and plant life: a critical review. Environ Int 99:107–119. https://doi.org/10.1016/j.envint.2016.12.010

Ait-lahcen A, Mercante LA, Amine A (2016) Molecularly imprinted polymer-decorated magnetite nanoparticles for selective sulfonamide detection. Anal Chem 88:3578–3584

Akpor OB, Muchie M (2011) Environmental and public health implications of wastewater quality. Afr J Biotechnol 10(13):2379–2387

Alawad A, Istamboulié G, Calas-blanchard C, Noguer T (2019) A reagentless aptasensor based on intrinsic aptamer redox activity for the detection of tetracycline in water. Sensors Actuators B Chem 288(February):141–146. https://doi.org/10.1016/j.snb.2019.02.103

Amine A, Mohammadi H, Bourais I, Palleschi G (2006) Enzyme inhibition-based biosensors for food safety and environmental monitoring. Biosens Bioelectron 21(8):1405–1423

Amine A, Arduini F, Moscone D, Palleschi G (2015) Recent advances in biosensors based on enzyme inhibition. Biosens Bioelectron 76:180–194. https://doi.org/10.1016/j.bios.2015.07.010

Andrade FID et al (2014) TLC and ion-pair HPLC 1 MSc in Public Health from State University of Ceará. Food Chem:1–25. https://doi.org/10.1016/j.foodchem.2014.01.100

Andreescu S, Marty J-L (2006) Twenty years research in cholinesterase biosensors: from basic research to practical applications. Biomol Eng 23(1):1–15

Arduini F, Amine A, Moscone D, Palleschi G (2010) Biosensors based on cholinesterase inhibition for insecticides, nerve agents and aflatoxin B1 detection (review). Microchim Acta 170(3–4):193–214

Arduini F, Cinti S, Scognamiglio V, Moscone D (2016) Nanomaterials in electrochemical biosensors for pesticide detection: advances and challenges in food analysis. Microchim Acta:2063–2083. https://doi.org/10.1007/s00604-016-1858-8

Arduini F et al (2019) Origami multiple paper-based electrochemical biosensors for pesticide detection. Biosens Bioelectron 126(October 2018):346–354

Aswal DK, Gupta SK (2006) Science and technology of chemiresistor gas sensors. Nova Science Publishers. https://books.google.com.br/books?id=fmw6nQAACAAJ

Augusto H et al (2018) Sensitive voltammetric method for piroxicam determination in pharmaceutical, urine and tap water samples using an anodically pretreated boron-doped diamond electrode. Braz J Anal Chem 5(18):40–50

aus der Beek T, Weber FA, Bergmann A, Hickmann S, Ebert I, Hein A, Küster A (2016) Pharmaceuticals in the environment -global occurrence and perspectives. Environ Toxicol Chem 35(4):823–835

Azam AG, Zanjani BR, Mood MB (2016) Effects of air pollution on human health and practical measures for prevention in Iran. J Res Med Sci\:1–12

Berto S et al (2018) Application of an electro-activated glassy-carbon electrode to the determination of acetaminophen (paracetamol) in surface waters. Electrochim Acta. https://doi.org/10.1016/j.electacta.2018.07.145

Besse JP, Latour JF, Garric J (2012) Anticancer drugs in surface waters. what can we say about the occurrence and environmental significance of cytotoxic, cytostatic and endocrine therapy drugs? Environ Int 39(1):73–86

Bogue R (2017) Emerging applications driving innovations in gas sensing. Sens Rev 37(2):1–15

Boleda MR, Huerta-fontela M, Ventura F, Teresa Galceran M (2011) Chemosphere evaluation of the presence of drugs of abuse in tap waters. Chemosphere 84(11):1601–1607. https://doi.org/10.1016/j.chemosphere.2011.05.033

Bougrini M et al (2016) Development of a novel sensitive molecularly imprinted polymer sensor based on electropolymerization of a microporous-metal- organic framework for tetracycline detection in honey. Food Control 59:424–429. https://doi.org/10.1016/j.foodcont.2015.06.002
Boxall ABA (2004) The environmental side effects of medication. EMBO Rep 5(12):1110–1116
Boxall ABA et al (2012) Review pharmaceuticals and personal care products in the environment: what are the big questions? Environ Health Perspect 120(9):1221–1229
Brett CMA (2001) Electrochemical sensors for environmental monitoring. Strategy and examples. Pure Appl Chem 73(12):1969–1977
Buchberger WW (2011) Current approaches to trace analysis of pharmaceuticals and personal care products in the environment. J Chromatogr A 1218(4):603–618. https://doi.org/10.1016/j.chroma.2010.10.040
Bueno AM, Contento AM, Rios A (2014) Determination of sulfonamides in milk samples by HPLC with amperometric detection using a glassy carbon electrode modified with multiwalled carbon nanotubes. J Sep Sci 37:382–389
Cakir O, Bakhshpour M, Yilmaz F, Baysal Z (2019) Novel QCM and SPR sensors based on molecular imprinting for highly sensitive and selective detection of 2, 4-dichlorophenoxyacetic acid in apple samples. Mater Sci Eng C 102(April):483–491. https://doi.org/10.1016/j.msec.2019.04.056
Campos MSG, Sarkis JES (2018) New methodology for the analysis of volatile organic compounds (VOCs) in bioethanol by gas chromatography coupled to mass spectrometry. J Phys Conf Ser 975:012015
Chen D et al (2013) A core – shell molecularly imprinted polymer grafted onto a magnetic glassy carbon electrode as a selective sensor for the determination of metronidazole. Sensors Actuators B Chem 183:594–600. https://doi.org/10.1016/j.snb.2013.04.050
Chen M et al (2015) Electrochemical simultaneous assay of chloramphenicol and PCB72 using magnetic and aptamer-modified quantum dot-encoded dendritic nanotracers for signal amplification. Microchim Acta:1–8
Chen D et al (2016) A novel aptasensor for electrochemical detection of ractopamine, clenbuterol, salbutamol, phenylethanolamine and procaterol. Biosens Bioelectron:1–18. https://doi.org/10.1016/j.bios.2016.01.025
Cheng N et al (2018) Aptasensor based on fluorophore-quencher nano-pair and smartphone spectrum reader for on-site quantification of multi-pesticides. Biosens Bioelectron 117(May):75–83
Chinna P et al (2018) Anthracene-based highly selective and sensitive fluorescent 'turn-on' chemodosimeter for Hg2+. ACS Omega 3:12341–12348
Chmielewski A (2011) Monitoring, control and effects of air pollution. ed. IntechOpen
Christou A, Michael C, Fatta-kassinos D, Fotopoulos V (2018) Can the pharmaceutically active compounds released in agroecosystems be considered as emerging plant stressors? Environ Int 114:360–364. https://doi.org/10.1016/j.envint.2018.03.003
Chung P-r et al (2013) Formaldehyde gas sensors: a review. Sensors 13:4468–4484
Ciccarone D (2017) International Journal of Drug Policy fentanyl in the US heroin supply: a rapidly changing risk environment. Int J Drug Policy 46:107–111. https://doi.org/10.1016/j.drugpo.2017.06.010
Danesh NM et al (2015) A novel electrochemical aptasensor based on arch- shape structure of aptamer-complimentary strand conjugate and exonuclease I for sensitive detection of streptomycin. Biosens Bioelectron. https://doi.org/10.1016/j.bios.2015.08.017
Darnerud PO (2003) toxic effects of brominated flame retardants in man and in wildlife. Environ Int 29:841–853
Derikvand Z et al (2016) Design of ultrasensitive bisphenol A-aptamer based on Pt nanoparticles loading to polyethyleneimine functionalized carbon nanotubes. Anal Biochem. https://doi.org/10.1016/j.ab.2016.06.007
Deroco PB et al (2018) Carbon black supported Au – Pd core-shell nanoparticles within a dihexadecylphosphate film for the development of hydrazine electrochemical sensor. Sensors Actuators B Chem 256:535–542. https://doi.org/10.1016/j.snb.2017.10.107

Djozan D, Mahkam M, Ebrahimi B (2009) Preparation and binding study of solid-phase microextraction fiber on the basis of ametryn-imprinted polymer application to the selective extraction of persistent triazine herbicides in tap water, rice, maize and onion. J Chromatogr A 1216:2211–2219

Domènech-gil G et al (2017) Chemical gas sensors based on individual indium oxide nanowire. Sensors Actuators B Chem 238:447–454. https://doi.org/10.1016/j.snb.2016.07.084

El N et al (2018) Development of a highly sensitive and selective molecularly imprinted electrochemical sensor for sulfaguanidine detection in honey samples. J Electroanal Chem 823:647–655. https://doi.org/10.1016/j.jelechem.2018.07.011

Emran MY, Mohamed AS, Abdelwahab AA, Abdelmottaleb SA E-s (2018) Facile synthesis of microporous sulfur-doped carbon spheres as electrodes for ultrasensitive detection of ascorbic acid in food and pharmaceutical products. New J Chem 42:5037–5044

Evaggelopoulou EN, Samanidou VF (2013) Development and validation of an HPLC method for the determination of six penicillin and three amphenicol antibiotics in gilthead seabream (Sparus Aurata) tissue according to the European Union Decision 2002/657/EC Cloxacillin Dicloxacillin. Food Chem 136(3–4):1322–1329. https://doi.org/10.1016/j.foodchem.2012.09.044

Fan M et al (2018) A review on experimental design for pollutants removal in water treatment with the aid of artificial intelligence. Chemosphere 18:1–52. https://doi.org/10.1016/j.chemosphere.2018.02.111.

Farajzadeh MA, Feriduni B, Afshar Mogaddam MR (2015) Development of counter current salting-out homogenous liquid-liquid extraction for isolation and preconcentration of some pesticides from aqueous samples. Anal Chim Acta 885:122–131

Fatta D, Nikolaou A, Achilleos A, Meric S (2007) Analytical methods for tracing pharmaceutical residues in water and wastewater. Trends Anal Chem 26(6):515–533

Fedeniuk RW, Mizuno M, Neiser C, Byrne CO (2015) Development of LC – MS/MS methodology for the detection/determination and confirmation of chloramphenicol, chloramphenicol 3-O-ᴺʟ – d -glucuronide, florfenicol, florfenicol amine and thiamphenicol residues in bovine, equine and porcine liver. J Chromatogr B 991:68–78. https://doi.org/10.1016/j.jchromb.2015.04.009

Feier B, Gui A, Cristea C, Săndulescu R (2017) Electrochemical determination of cephalosporins using a bare boron-doped diamond electrode. Anal Chim Acta. https://doi.org/10.1016/j.aca.2017.04.050

Feier B et al (2019) Electrochemical sensor based on molecularly imprinted polymer for the detection of cefalexin. Biosensors 9

Feiera B, Ionela I, Cristeaa C, Săndulescua R (2017) Electrochemical behaviour of several penicillins at high potential. N J Chem 41:12947–12955

Fernández-Benavides DA et al (2019) A novel bismuth-based lead-free piezoelectric transducer immunosensor for carbaryl quantification. Sensors Actuators B Chem 285(August 2018):423–430

Ferrando-Climent L, Rodriguez-Mozaz S, Barceló D (2014) Incidence of anticancer drugs in an aquatic urban system: from hospital effluents through urban wastewater to natural environment. Environ Pollut 193:216–223

Fu J et al (2019) Electrochemical aptasensor based on one step Co-electrodeposition of aptamer and GO-CuNPs nanocomposite for organophosphorus pesticide detection. Sensors Actuators B Chem 287:503–509. https://doi.org/10.1016/j.snb.2019.02.057

Gallego M, Valca M (2003) Determination of natural and synthetic colorants in prescreened dairy samples using liquid chromatography-diode array detection. Anal Chem 75(3):685–693

Gan T et al (2017) An electrochemical sensor based on SiO_2 @ TiO_2 -embedded molecularly imprinted polymers for selective and sensitive determination of theophylline. J Solid State Electrochem 21(12):3683–3691

Gao L, Shi Y, Li W, Cai Y (2012) Occurrence, distribution and bioaccumulation of antibiotics in the Haihe. J Environ Monit 14:1248–1255

Gauquie J, Devriese L, Robbens J, De Witte B (2015) A qualitative screening and quantitative measurement of organic contaminants on different types of marine plastic debris. Chemosphere 138:348–356. https://doi.org/10.1016/j.chemosphere.2015.06.029

Gayen P, Chaplin BP (2015) Selective electrochemical detection of ciprofloxacin with a porous nafion/multi-walled carbon nanotube composite film electrode. Appl Mater Interfaces 8(3):1615–1626

Geng D, Kukucka P, Jogsten IE (2017) Analysis of brominated flame retardants and their derivatives by atmospheric pressure chemical ionization using gas chromatography coupled to tandem quadrupole mass spectrometry. Talanta 162(June 2016):618–624. https://doi.org/10.1016/j.talanta.2016.10.060

Gogoi A et al (2018) Groundwater for sustainable development occurrence and fate of emerging contaminants in water environment: a review. Groundw Sustain Dev 6(January):169–180. https://doi.org/10.1016/j.gsd.2017.12.009

Goodchild SA et al (2019) Ionic liquid-modified disposable electrochemical sensor strip for analysis of fentanyl. Anal Chem 91(5):3747–3753

Goradel NH et al (2017) Biosensors for the detection of environmental and urban. J Cell Biochem 119(1):207–212

Gothwal R, Shashidhar T (2014) Review antibiotic pollution in the environment: a review. CLEAN Soil Air Water 42(9999):1–11

Gros M, Rodríguez-mozaz S, Barceló D (2013) Rapid analysis of multiclass antibiotic residues and some of their metabolites in hospital, urban wastewater and river water by ultra-high-performance liquid chromatography coupled to quadrupole-linear ion trap tandem mass spectrometry. J Chromatogr A 1292:173–188. https://doi.org/10.1016/j.chroma.2012.12.072

Guan H, Brewer WE, Garris ST, Morgan SL (2010) Disposable pipette extraction for the analysis of pesticides in fruit and vegetables using gas chromatography/mass spectrometry. J Chromatogr A 1217:1867–1874

Guo Y, Shen G, Sun X, Wang X (2015) Electrochemical aptasensor based on multiwalled carbon nanotubes and graphene for tetracycline detection. IEEE Sensors J 15(3):1951–1958

Hashemi P et al (2019) Reduced graphene oxide decorated on Cu / CuO-Ag nanocomposite as a high- performance material for the construction of a non-enzymatic sensor: application to the determination of carbaryl and fenamiphos pesticides. Mater Sci Eng C 102(May):764–772. https://doi.org/10.1016/j.msec.2019.05.010

He B-s, Chen W-b (2016) Voltammetric determination of sulfonamides with a modified glassy carbon electrode using carboxyl multiwalled carbon nanotubes. J Braz Chem Soc 27(12):2216–2225

He X et al (2012) Residues of fluoroquinolones in marine aquaculture environment of the Pearl River Delta, South China. Environ Geochem Health 34:323–335

He Q et al (2018) Sensitive and selective detection of tartrazine based on TiO 2 -electrochemically reduced graphene oxide composite-modified electrodes. Sensors 18(1911):1–12

Hernandez-Vargas G et al (2018) Electrochemical biosensors: a solution to pollution detection with reference to environmental contaminants. Biosensors 8(29):1–21

Hignite C, Azarnoff DL (1977) Drugs and drug metabolites as environmental contaminants: chlorophenoxyisobutyrate and salicylic acid in sewage water effluent. Life Sci 20(2):337–341

Holbrook RD, Davis JM, Scott KCK, Szakal C (2012) Detection and speciation of brominated flame retardants in high-impact polystyrene (HIPS) polymers. J Microsc 246(2):143–152

Holling CS, Bailey JL, Heuvel V, Kinney CA (2012) Uptake of human pharmaceuticals and personal care products by cabbage (Brassica Campestris) from fortified and biosolids-amended soils. J Environ Monit 14:3029–3036

Hong Y, Sharma VK, Hyunook P-c C (2015) Fast-target analysis and hourly variation of 60 pharmaceuticals in wastewater using UPLC-high resolution mass spectrometry. Arch Environ Contam Toxicol 69(4):525–534

Hori H, Ishimatsu S, Fueta Y (2013) Evaluation of a real-time method for monitoring volatile organic compounds in indoor air in a Japanese University. Environ Health Prev Med (2013) 18:285–292

Hsu CC, Whang CW (2009) Microscale solid phase extraction of glyphosate and aminomethylphosphonic acid in water and guava fruit extract using alumina-coated iron oxide nanoparticles followed by capillary electrophoresis and electrochemiluminescence detection. J Chromatogr A 1216(49):8575–8580

Huang J-y et al (2016) Voltammetric determination of levofloxacin using a glassy carbon electrode modified with poly (o-Aminophenol) and graphene quantum dots. Microchim Acta 184(1):127–135. https://doi.org/10.1007/s00604-016-1982-5

Huerta-fontela M, Teresa M, Martin-alonso J, Ventura F (2008) Occurrence of psychoactive stimulatory drugs in wastewaters in North-Eastern Spain. Sci Total Environ 397:31–40

Jaishankar M et al (2014) Toxicity, mechanism and health effects of some heavy metals. Interdiscip Toxicol 7(2):60–72

Jean J et al (2012) Identification and prioritization of bioaccumulable pharmaceutical substances discharged in hospital effluents. J Environ Manag 103:113–121

Jennifer A, Abdallah M A-e, Harrad S (2017) Pharmaceuticals and Personal Care Products (PPCPs) in the freshwater aquatic environment. Emerg Contam 3(1):1–16. https://doi.org/10.1016/j.emcon.2016.12.004

Jiang X et al (2008) Immunosensors for detection of pesticide residues. Biosens Bioelectron 23:1577–1587

Jiang J et al (2018) Surface-enhanced Raman scattering detection of pesticide residues using transparent adhesive tapes and coated silver nanorods. ACS Appl Mater Interfaces:2–8

Jiao S et al (2018) Binding properties of broad-specific monoclonal antibodies against three organophosphorus pesticides by a direct surface plasmon resonance immunosensor. Anal Bioanal Chem 410(28):7263–7273

Jiménez GC et al (2014) Aptamer-based label-free impedimetric biosensor for the detection of progesterone. Anal Chem 87(2):1075–1082

Joshi N et al (2016) Ozone sensing properties of nickel phthalocyanine: ZnO nanorod heterostructures. Proc IEEE Sens:1–3

Joshi N et al (2018) A review on chemiresistive room temperature gas sensors based on metal oxide nanostructures, graphene and 2D transition metal dichalcogenides. Microchim Acta 185:213

Jung J-h et al (2012) The characteristics of the appearance and health risks of volatile organic compounds in industrial (Pohang, Ulsan) and non-industrial (Gyeongju) areas. Environ Health Toxicol 27(0):e2012012

Justino CIL, Duarte AC, Rocha-Santos TAP (2017) Recent progress in biosensors for environmental monitoring: a review. Sensors 17(2918):1–25

Kamilari E et al (2018) Detection and quantitative determination of heavy metals in electronic cigarette refill liquids using total reflection X-ray fluorescence spectrometry. Food Chem Toxicol 116(part B):233–237. https://doi.org/10.1016/j.fct.2018.04.035

Karimian R, Piri F, Hosseini Z (2017) Magnetic molecularly imprinted nanoparticles for the solid-phase extraction of diazinon from aqueous medium, followed its determination by HPLC-UV. J Appl Biotechnol Rep 4(1):533–539

Karri V, Schuhmacher M, Kumar V (2016) Heavy metals (Pb, Cd, MeHg, As) as risk factors for cognitive dysfunction: a general review of metal mixture mechanism in brain. Environ Toxicol Pharmacol. https://doi.org/10.1016/j.etap.2016.09.016

Kaur M, Nagpal AK (2017) Evaluation of air pollution tolerance index and anticipated performance index of plants and their application in development of green space along the urban areas. Environ Sci Pollut Res 24:18881–18895

Kaur N, Thakur H, Prabhakar N (2019) Multi walled carbon nanotubes embedded conducting polymer based electrochemical aptasensor for estimation of malathion. Microchem J 147:393–402. https://doi.org/10.1016/j.microc.2019.03.042

Ke H et al (2014) A fetomolar level 17 -B-stradiol electrochemical aptasensor constructed on hierachical dendritic gold modified boron-doped diamond electrode. Electrochim Acta 137:146–153. https://doi.org/10.1016/j.electacta.2014.06.014

Khan S et al (2018) Synthesis and characterization of magnetic-molecularly imprinted polymers for the HPLC-UV analysis of ametryn. React Funct Polym 122:175–182. https://doi.org/10.1016/j.reactfunctpolym.2017.11.002

Khor SM et al (2011) An electrochemical immunobiosensor for direct detection of veterinary drug residues in undiluted complex matrices. Electroanalysis 23(8):1797–1804

Kolpin D et al (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in U. S. Streams, 1999-2000: a national reconnaissance. Environ Sci Technol 36:1202–1211

Kot-wasik A, De J, Namies J (2007) Analytical techniques in studies of the environmental fate of pharmaceuticals and personal-care products. Trends Anal Chem 26(6):557–568

Kubendhiran S et al (2018) Innovative strategy based on a novel carbon-black−β-cyclodextrin 2 nanocomposite for the simultaneous determination of the 3 anticancer drug flutamide and the environmental pollutant 4-nitrophenol. *Anal Chem* 90(10):6283–6291

Kumar N et al (2019) Electrochemical detection and photocatalytic performance of MoS2/TiO2 nanocomposite against pharmaceutical contaminant: paracetamol. Sens Bio-Sens Res 24:1–8. https://doi.org/10.1016/j.sbsr.2019.100288

Kümmerer K (2009) The presence of pharmaceuticals in the environment due to human use – present knowledge and future challenges. J Environ Manag 90:2354–2366

Larsson DGJ (2014) Antibiotics in the environment. Ups J Med Sci 119:108–112

Lawal O et al (2017) Exhaled breath analysis: a review of 'breath-taking' methods for off-line analysis. Metabolomics 13(10):1–16

Leo L et al (2017) Occurrence of azo food dyes and their effects on cellular inflammatory responses. Nutrition. https://doi.org/10.1016/j.nut.2017.08.010

Li J, Chen L, Lou T, Wang Y (2011) Highly sensitive SERS detection of As^{3+} ions in aqueous media using glutathione functionalized silver nanoparticles. ACS Appl Mater Interfaces 3:3936–3941

Li W et al (2012a) Investigation of antibiotics in mollusks from coastal waters in the Bohai Sea of China. Environ Pollut 162:56–62. https://doi.org/10.1016/j.envpol.2011.10.022

Li W et al (2012b) Chemosphere occurrence of antibiotics in water, sediments, aquatic plants, and animals from Baiyangdian Lake in North China. *Chemosphere* 89(11):1307–1315. https://doi.org/10.1016/j.chemosphere.2012.05.079

Li X, Yu H, Xu S, Hua R (2013) Ecotoxicology and environmental safety uptake of three sulfonamides from contaminated soil by pakchoi cabbage. Ecotoxicol Environ Saf 92:297–302. https://doi.org/10.1016/j.ecoenv.2013.03.010

Li Y et al (2015a) Molecularly imprinted polymer decorated nanoporous gold for highly selective and sensitive electrochemical sensors. Sci Rep 5:33–35

Li J, Liu X, Cui J, Sun J (2015b) Hydrothermal synthesis of self-assembled hierarchically tungsten oxides hollow spheres and their gas sensing properties. Appl Mater Interfaces:1–28

Li Z, Zhu Z, Louis J (2018) Disposable electrochemical aptasensor based on carbon nanotubes-V2O5-chitosan nanocomposite for detection of ciprofloxaci. Sensors Actuators B Chem. https://doi.org/10.1016/j.snb.2018.03.155

Lidia C et al (2015) Science of the total environment high sensitive multiresidue analysis of pharmaceuticals and antifungals in surface water using U-HPLC-Q-exactive orbitrap HRMS. Application to the Danube River Basin on the Romanian Territory. Sci Total Environ 532:501–511. https://doi.org/10.1016/j.scitotenv.2015.06.010

Lipskikh OI et al (2018) Sensors for voltammetric determination of food azo dyes – a critical review. Electrochim Acta 260:974–985. https://doi.org/10.1016/j.electacta.2017.12.027

Liu X et al (2012) A survey on gas sensing technology. Sensors 2:9635–9665

Liu J, Lu G, Ding J et al (2014a) Tissue distribution, bioconcentration, metabolism, and effects of erythromycin in crucian carp (Carassius Auratus). Sci Total Environ 490:914–920. https://doi.org/10.1016/j.scitotenv.2014.05.055

Liu J, Lu G, Wang Y et al (2014b) Chemosphere bioconcentration, metabolism, and biomarker responses in freshwater fish carassius auratus exposed to roxithromycin. Chemosphere 99:102–108. https://doi.org/10.1016/j.chemosphere.2013.10.036

Liu J et al (2015) Science of the total environment occurrence , bioaccumulation and risk assessment of lipophilic pharmaceutically active compounds in the downstream rivers of sewage treatment plants. Sci Total Environ 511:54–62. https://doi.org/10.1016/j.scitotenv.2014.12.033

Liu H et al (2018) Chemical AC phase sensing of graphene FETs for chemical vapors with fast recovery and minimal baseline drift. Sensors Actuators B Chem 263:94–102. https://doi.org/10.1016/j.snb.2018.01.244

Liu M et al (2019) Aptasensors for pesticide detection. Biosens Bioelectron 130:174–184

Liu Y et al (n.d.) Sensitive detection of bisphenol A based on ratiometric electrochemical aptasensor:1–22

Luo L et al (2009) Silicon nanowire sensors for Hg2+ and Cd2+ ions silicon nanowire sensors for Hg2+ and Cd2+ ions. Appl Phys Lett 94(193101):42–45

Madrid RE, Chehín R, Chen T-H, Guiseppi-Elie A (2017) Biosensors and nanobiosensors: the road to bioengineering. In: Further Understanding of the Human Machine, pp 391–462

Mahajan R, Chatterjee S (2018) A simple HPLC – DAD method for simultaneous detection of two organophosphates, profenofos and fenthion, and validation by soil microcosm experiment. Environ Monit Assess:190, 327

Malik R et al (2018) Au–TiO2-loaded cubic g-C3N4 nanohybrids for photocatalytic and volatile organic amine sensing applications. ACS Appl Mater Interfaces 10:34087–34097

Mandayo GG, Castaño E (2013) Conductometric formaldehyde gas sensors. a review: from conventional Fi Lms to nanostructured materials. Thin Solid Films:1–12. https://doi.org/10.1016/j.tsf.2013.04.083

Materón EM et al (2019) Graphene-based electrochemical sensors for biomolecules. In: Graphene-containing microfluidic and chip-based sensor devices for biomolecules. Elsevier Inc. https://doi.org/10.1016/B978-0-12-815394-9.00013-3.

Mccall A-k et al (2015) Critical review on the stability of illicit drugs in sewers and wastewater samples. Water Res:1–38. https://doi.org/10.1016/j.watres.2015.10.040

Mcgrath TJ, Morrison PD, Ball AS, Clarke BO (2017) Detection of Novel Brominated Fl Ame Retardants (NBFRs) in the urban soils of Melbourne , Australia. Emerging Contaminants:1–9. https://doi.org/10.1016/j.emcon.2017.01.002

Merola G, Martini E, Tomassetti M, Campanella L (2014) New immunosensor for B -lactam antibiotics determination in river waste waters. Sensors Actuators B Chem 199:301–313. https://doi.org/10.1016/j.snb.2014.03.083

Meyer SA, Le Ru EC, Etchegoin PG (2011) Combining Surface Plasmon Resonance (SPR) spectroscopy with Surface-Enhanced Raman Scattering (SERS). Anal Chem 83:2337–2344

Michelini L, Reichel R, Werner W, Ghisi R (2012) Sulfadiazine uptake and effects on *Salix Fragilis* L. and *Zea Mays* L. plants. Water Air Soil Pollut 223:5243–5257

Miller TH, Bury NR, Owen SF, MacRae JI, Barron LP (2018) A review of the pharmaceutical exposome in aquatic fauna. Environ Pollut 239:129–146. https://doi.org/10.1016/j.envpol.2018.04.012

Mishra RK et al (2018) Chemical wearable potentiometric tattoo biosensor for on-body detection of G-type nerve agents simulants. Sensors Actuators B 273:966–972

Moawed EA, Radwan AM (2017) Application of acid modified polyurethane foam surface for detection and removing of organochlorine pesticides from wastewater. J Chromatogr B 1044–1045:95–102. https://doi.org/10.1016/j.jchromb.2016.12.041

Mohammad S, Mohammad N, Ramezani M (2016) A novel M-shape electrochemical aptasensor for ultrasensitive detection of tetracyclines. Biosens Bioelectron 85:509–514. https://doi.org/10.1016/j.bios.2016.05.048

Mohammed GI, Khraibah NH, Bashammakh AS, El-shahawi MS (2018) Electrochemical sensor for trace determination of timolol maleate drug in real samples and drug residues using

nafion/carboxylated-MWCNTs nanocomposite modified glassy carbon electrode. Microchem J 143:474–483. https://doi.org/10.1016/j.microc.2018.08.011
Moraes JT, Salamanca-neto CAR (2017) Advanced sensing performance towards simultaneous determination of quaternary mixture of antihypertensives using boron-doped diamond electrode. Microchem J. https://doi.org/10.1016/j.microc.2017.06.001
Mostafalou S, Abdollahi M (2013) Pesticides and human chronic diseases: evidences, mechanisms, and perspectives. Toxicol Appl Pharmacol 268:157–177
Motia S et al (2019) Electrochemical sensor based on molecularly imprinted polymer for sensitive triclosan detection in wastewater and mineral water. Sci Total Environ 664:647–658. https://doi.org/10.1016/j.scitotenv.2019.01.331
Mulyasuryani A, Prasetyawan S (2015) Organophosphate hydrolase in conductometric biosensor for the detection of organophosphate pesticides. Libertas Acad:23–27
Munawar A et al (2017) Investigating nanohybrid material based on 3D CNTs @ Cu nanoparticle composite and imprinted polymer for highly selective detection of chloramphenicol. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2017.08.014
Muralikrishna MV (2017) Environmental management. Chapter One – Introduction
Na G et al (2013) Occurrence, distribution, and bioaccumulation of antibiotics in coastal environment of Dalian, China. Mar Pollut Bull 69(1–2):233–237. https://doi.org/10.1016/j.marpolbul.2012.12.028
Nagaraj VJ, Jacobs M, Vattipalli M (2014) Nanochannel-based electrochemical sensor for the detection of pharmaceutical contaminants in water. Environ Sci Process Impacts 16:135–140
Nambiar AP, Sanyal M, Shrivastav PS (2018) Simultaneous densitometric determination of eight food colors and four sweeteners in candies, jellies, beverages and pharmaceuticals by normal-phase high performance thin-layer chromatography using a single elution protocol. J Chromatogr A 1572:152–161. https://doi.org/10.1016/j.chroma.2018.08.059
Nguyen T, Saleh MA (2016) Detection of azo dyes and aromatic amines in women undergarment. J Environ Sci Health A 51(9):744–753
Noguera-oviedo K, Aga DS (2016) Lessons learned from more than two decades of research on emerging contaminants in the environment. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2016.04.058
Norrby SR (1991) Side-effects of quinolones: comparisons between quinolones and other antibiotics. Eur J Clin Microbiol Infect Dis 10(4):378–383
Nunes CN, dos Anjos VE, Quinaia SP (2017) Determination of diazepam and clonazepam in natural water – a voltammetric study. Electroanalysis 29:1–11
Oliveira TMBF et al (2015) Simultaneous electrochemical sensing of emerging organic contaminants in full-scale sewage treatment plants. Chem Eng J 267:347–354. https://doi.org/10.1016/j.cej.2015.01.003
Oplatowska-stachowiak M, Elliott CT (2015) Critical reviews in food science and nutrition food colours: existing and emerging food safety concerns. Crit Rev Food Sci Nutr Publ (April):37–41
Orias F, Perrodin Y (2013) Characterisation of the ecotoxicity of hospital effluents: a review. Sci Total Environ J 455:250–276
Parrella A et al (2014) Estrogenic activity and cytotoxicity of six anticancer drugs detected in water systems. Sci Total Environ 485–486:216–222. https://doi.org/10.1016/j.scitotenv.2014.03.050
Picó Y, Blasco C, Font G (2004) Environmental and food applications of LC-tandem mass spectrometry in pesticide-residue analysis: an overview. Mass Spectrom Rev 23(1):45–85
Pilehvar S et al (2014) An electrochemical impedimetric aptasensing platform for sensitive and selective detection of small molecules such as chloramphenicol. Sensors 14:12059–12069
Pilehvar S et al (2016) A joint action of aptamers and gold nanoparticles chemically trapped on a glassy carbon support for the electrochemical sensing of ofloxacin. Sensors Actuators B Chem. https://doi.org/10.1016/j.snb.2016.09.075
Prabowo BA, Purwidyantri A, Liu K-C (2018) Surface plasmon resonance optical sensor: a review on light source technology. Biosensors 8(80):26

Pundir CS, Chauhan N (2012) Acetylcholinesterase inhibition-based biosensors for pesticide determination: a review. Anal Biochem 429(1):19–31

Qin Y, Liu J, Wang G, Zhang Y (2013) Evaluation of indoor air quality based on qualitative, quantitative and olfactory analysis. Chin Sci Bull 58(9):986–991

Qin X et al (2015) A novel electrochemical aptasensor based on MWCNTs-BMIMPF6 and amino functionalized graphene nanocomposites film for determination of kanamycin. Anal Methods 7(13):5419–5427

Rapini R, Marrazza G (2017) Bioelectrochemistry electrochemical aptasensors for contaminants detection in food and environment: recent advances. Bioelectrochemistry 118:47–61. https://doi.org/10.1016/j.bioelechem.2017.07.004

Rasheed T et al (2019) Environmentally-related contaminants of high concern: potential sources and analytical modalities for detection, quantification, and treatment. Environ Int 122:52–66

Rawtani D, Khatri N, Tyagi S, Pandey G (2018) Nanotechnology-based recent approaches for sensing and remediation of pesticides. J Environ Manag 206:749–762. https://doi.org/10.1016/j.jenvman.2017.11.037

Raymundo-Pereira PA et al (2017) Printex 6L carbon nanoballs used in electrochemical sensors for simultaneous detection of emerging pollutants hydroquinone. Sensors Actuators B Chem. https://doi.org/10.1016/j.snb.2017.05.121

Rejczak T, Tuzimski T (2015) Recent trends in sample preparation and liquid chromatography/mass spectrometry for pesticide residue analysis in food and related matrixes. J AOAC Int 98:1143–1162

Richardson ML, Bowron JM (1985) The fate of pharmaceutical chemicals in the aquatic environment. J Pharm Pharmacol 37(1):1–12

Roushani M, Shahdost-fard F (2016) Covalent attachment of aptamer onto nanocomposite as a high performance electrochemical sensing platform: fabrication of an ultra-sensitive ibuprofen electrochemical aptasensor. Mater Sci Eng C 68:128–135. https://doi.org/10.1016/j.msec.2016.05.099

Rzymski P, Drewek A, Klimaszyk P (2017) Pharmaceutical pollution of aquatic environment: an emerging and enormous challenge. Limnol Rev 17(2):97–107

Sabourin L et al (2012) Science of the total environment uptake of pharmaceuticals, hormones and parabens into vegetables grown in soil fertilized with municipal biosolids. Sci Total Environ 431:233–236. https://doi.org/10.1016/j.scitotenv.2012.05.017

Saini RK, Bagri LP, Bajpai AK (2017) Smart nanosensors for pesticide detection. In: New pesticides and soil sensors, pp 519–559

Samsidar A, Siddiquee S, Shaarani SM (2018) A review of extraction, analytical and advanced methods for determination of pesticides in environment and foodstuffs. Trends Food Sci Technol 71:188–201

Sarafraz-yazdi A, Razavi N (2015) Application of Molecularly-Imprinted Polymers in Solid-Phase Microextraction Techniques. *Trends Anal Chem* 73:81–90

Sassolas A, Prieto-simón B, Marty J-l (2012) Biosensors for pesticide detection: new trends. Am J Anal Chem 2012:210–232

Sayago I, Aleixandre M, Santos P (2019) Development of tin oxide-based nanosensors for electronic nose environmental applications. Biosensors 9(21):1–12

Scotter MJ (2015) Colour additives for foods and beverages. In: Methods of analysis for food colour additive quality and safety assessment. Elsevier Ltd, York. https://doi.org/10.1016/B978-1-78242-011-8.00006-4.

Sharma A et al (2017) Disposable and portable aptamer functionalized impedimetric sensor for detection of kanamycin residue in milk sample. Sensors Actuators B Chem 245:507–515. https://doi.org/10.1016/j.snb.2017.02.002

Sheng F, Zhang X, Wang G (2017) Novel ultrasensitive homogeneous electrochemical aptasensor based on DsDNA-templated copper nanoparticles for the detection of ractopamine. J Mater Chem B 5(1):53–61. http://xlink.rsc.org/?DOI=C6TB02020H

Shi Z et al (2014) Graphene based solid phase extraction combined with ultra high performance liquid chromatography – tandem mass spectrometry for carbamate pesticides analysis in environmental water samples. J Chromatogr A 1355:219–227

Soltani H, Pardakhty A, Ahmadzadeh S (2016) Determination of hydroquinone in food and pharmaceutical samples using a voltammetric based sensor employing NiO nanoparticle and ionic liquids. J Mol Liq 219:63–67. https://doi.org/10.1016/j.molliq.2016.03.014

Sorouraddin M-h, Saadati M, Mirabi F (2015) Simultaneous determination of some common food dyes in commercial products by digital image analysis. J Food Drug Anal 23(3):447–452. https://doi.org/10.1016/j.jfda.2014.10.007

Spinelle L, Gerboles M, Kok G, Persijn S, Sauerwald T (2017) Review of portable and low-cost sensors for the volatile organic compounds. Sensors 17(1520):1–30

Stradiotto NR, Yamanaka H, Zanoni MVB (2003) Review electrochemical sensors: a powerful tool in analytical chemistry. J Braz Chem Soc 14(2):159–173

Sun X et al (2013) Aptasensor based on the synergistic contributions of chitosan-gold nanoparticles, graphene-gold nanoparticles and multi-walled carbon nanotubes-cobalt phthalocyanine nanocomposites for kanamycin detection. Analyst 139:299–308

Sun Y et al (2017) Voltammetric sensor for chloramphenicol determination based on a dual signal enhancement strategy with ordered mesoporous carbon @ polydopamine and β -cyclodextrin. Sensors Actuators B Chem. https://doi.org/10.1016/j.snb.2017.09.016

Švorc Ľ et al (2017) Advanced electrochemical platform for determination of cytostatic drug flutamide in various matrices using a boron-doped diamond electrode. Electrochim Acta 251:621–630. https://doi.org/10.1016/j.electacta.2017.08.077

Swager TM, Mirica KA (2019) Introduction: chemical sensors. Chem Rev 119:1–2

Tangahu BV et al (2011) A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. Int J Chem Eng 2011:1–31

Tanoue R et al (2012) Plant uptake of pharmaceutical chemicals detected in recycled organic manure and reclaimed wastewater. J Agric Food Chem 60:10203–10211

Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ (2012) Heavy metal toxicity and the environment. ed. Luch A. Springer, Basel

Ternes TA (1998) Occurrence of drug in german sewage treatment plants and rivers. Water Res 32(11):3245–3260. https://doi.org/10.1016/s0043-1354(98)00099-2

Thurman EM, Ferrer I, Barceló D (2001) Choosing between atmospheric pressure chemical ionization and electrospray ionization interfaces for the HPLC/MS analysis of pesticides. Anal Chem 73(22):5441–5449

Timofeeva I et al (2017) On-line in-syringe sugaring-out liquid-liquid extraction coupled with HPLC-MS/MS for the determination of pesticides in fruit and berry juices. Talanta 167:761–767. https://doi.org/10.1016/j.talanta.2017.01.008

Turci R, Sottani C, Spagnoli G, Minoia C (2003) Biological and environmental monitoring of hospital personnel exposed to antineoplastic agents: a review of analytical methods. J Chromatogr B 789:169–209

Turnipseed SB, Clark SB, Storey JM, Carr JR (2012) Analysis of veterinary drug residues in frog legs and other aquacultured species using liquid chromatography quadrupole time-of-flight mass spectrometry. J Agric Food Chem 60(18):4430–4439

Upan J, Reanpang P, Jakmunee J (2015) Flow injection amperometric sensor with a carbon nanotube modified screen printed electrode for determination of hydroquinone. Talanta 146:766–771. https://doi.org/10.1016/j.talanta.2015.06.026

Vasquez MI et al (2014) Environmental side effects of pharmaceutical cocktails: what we know and what we should know. J Hazard Mater 279:169–189. https://doi.org/10.1016/j.jhazmat.2014.06.069

Velusamy V et al (2019) Novel electrochemical synthesis of cellulose microfiber entrapped reduced graphene oxide: a sensitive electrochemical assay for detection of fenitrothion organophosphorus pesticide. Talanta 192:471–477. https://doi.org/10.1016/j.talanta.2018.09.055

Vieno N, Sillanpää M (2014) Fate of diclofenac in municipal wastewater treatment plant – a review. Environ Int 69:28–39. https://doi.org/10.1016/j.envint.2014.03.021

Wang J (2002) Real-time electrochemical monitoring : toward green analytical chemistry. Acc Chem Res 35(9):811–816

Wang H (2015) Target-aptamer binding trigged quadratic recycling amplification for highly specific and ultrasensitive detection of antibiotics at attomole level. Chem Commun 51:8377–8380

Wang Y, Xu H, Zhang J, Li G (2008) Electrochemical sensors for clinic analysis. Sensors 8(4):2043–2081. http://www.mdpi.com/1424-8220/8/4/2043/

Wang X et al (2016) Highly sensitive homogeneous electrochemical dual recycling amplification strategy highly sensitive homogeneous electrochemical aptasensor for antibiotic residues detection based on dual recycling amplification strategy. Biosens Bioelectron. https://doi.org/10.1016/j.bios.2016.03.055

Wang J et al (2017) Fluorescence spectroscopy. Sensors 17(2719):1–19

Wang J, Wang Z, Vieira CLZ, Wolfson JM (2019a) Review on the treatment of organic pollutants in water by ultrasonic technology. Ultrason Sonochem 55:1–27. https://doi.org/10.1016/j.ultsonch.2019.01.017

Wang Q et al (2019b) Double quantum dots-nanoporphyrin fluorescence-visualized paper-based sensors for detecting organophosphorus pesticides. Talanta 199(February):46–53

Webb S, Ternes T, Gibert M, Olejniczak K (2003) Indirect human exposure to pharmaceuticals v Ia drinking water. Toxicol Lett 142:157–167

Wen Y, Liao X, Deng C, Liu G (2017) Imprinted voltammetric streptomycin sensor based on a glassy carbon electrode modified with electropolymerized poly (Pyrrole-3-carboxy acid) and electrochemically reduced graphene oxide. Microchim Acta. https://doi.org/10.1007/s00604-017-2089-3

Wong A et al (2015) Development and application of an electrochemical sensor modified with multi-walled carbon nanotubes and graphene oxide for the sensitive and selective detection of tetracycline. J Electroanal Chem 757:250–257

Wong A, Santos AM, Fatibello-filho O (2018) Simultaneous determination of dopamine and cysteamine by flow injection with multiple pulse amperometric detection using a boron-doped diamond electrode. Diam Relat Mater 85:68–73. https://doi.org/10.1016/j.diamond.2018.03.034

Wu X et al (2019) Fluorescence sensor for facile and visual detection of organophosphorus pesticides using AIE fluorogens-SiO_2 -MnO_2 sandwich nanocomposites. Talanta 198:8–14. https://doi.org/10.1016/j.talanta.2019.01.082

Xiong P et al (2012) an ultrasensitive electrochemical immunosensor for alpha-fetoprotein using an envision complex-antibody copolymer as a sensitive label. Materials 5(12):2757–2772. http://www.mdpi.com/1996-1944/5/12/2757

Xu W et al (2014) A novel sandwich-type electrochemical aptasensor for sensitive detection of kanamycin based on GR–PANI and PAMAM–Au nanocomposites. New J Chem 38:4931–4937. https://doi.org/10.1039/c4nj00858h

Xu Y et al (2015) A label-free and signal-on electrochemical aptasensor for ultrasensitive kanamycin detection based on exonuclease recycling cleavage. Anal Methods 8:726–730

Xu G et al (2019) Chemical dual-signal aptamer sensor based on polydopamine-gold nanoparticles and exonuclease I for ultrasensitive malathion detection. Sensors Actuators B Chem 287:428–436

Yan Z et al (2016) A sensitive electrochemical aptasensor for multiplex antibiotics detection based on high-capacity magnetic hollow porous nanotracers coupling exonuclease-assisted cascade target recycling. Biosens Bioelectron 78:51–57. https://doi.org/10.1016/j.bios.2015.11.019

Yan X, Li H, Su X (2018) Review of Optical Sensors for Pesticides. Trends Anal Chem 103:1–20

Yang G, Zhao F (2015) Electrochemical sensor for chloramphenicol based on novel multiwalled carbon nanotubes @ molecularly imprinted polymer. Biosens Bioelectron 64:416–422. https://doi.org/10.1016/j.bios.2014.09.041

Yang AZ, Ding X, Guo Q, Wang Y (2017) Second generation of signaling-probe displacement electrochemical aptasensor for detection of picomolar ampicillin and sulfadimethoxine. Sensors Actuators B Chem. https://doi.org/10.1016/j.snb.2017.07.119

Yaseen T, Hongbin P, Sun D-w (2019) fabrication of silver-coated gold nanoparticles to simultaneously detect multi-class insecticide residues in peach with SERS technique. Talanta 196:537–545. https://doi.org/10.1016/j.talanta.2018.12.030

Yu P et al (2016) A novel electrochemical aptasensor for bisphenol A assay based on triple-signaling strategy. Biosens Bioelectron 79:22–28. https://doi.org/10.1016/j.bios.2015.12.007

Zhang S et al (2017) A zeolitic imidazolate framework based nanoporous carbon as a novel fiber coating for solid-phase microextraction of pyrethroid pesticides. Talanta 166(January):46–53. https://doi.org/10.1016/j.talanta.2017.01.042

Zhang W-j et al (2019a) Synthesis and application of novel molecularly imprinted solid phase extraction materials based on carbon nanotubes for determination of carbofuran in human serum by high performance liquid chromatography. J Agric Food Chem 67:5105–5112

Zhang Z et al (2019b) A competitive immunosensor for ultrasensitive detection of sulphonamides from environmental waters using silver nanoparticles decorated single-walled carbon nanohorns as labels. Chemosphere 225:282–287. https://doi.org/10.1016/j.chemosphere.2019.03.033

Zhao J-l et al (2015a) Tissue-specific bioaccumulation of human and veterinary antibiotics in bile, plasma, liver and muscle tissues of wild fish from a highly urbanized region. Environ Pollut 198:15–24. https://doi.org/10.1016/j.envpol.2014.12.026

Zhao Y et al (2015b) An electrochemical sensor for selective determination of sulfamethoxazole in surface water using a molecularly imprinted polymer modified BDD electrode. Anal Methods (6):1–6. https://doi.org/10.1039/C4AY03055A

Zhou L, Wang J, Li D, Li Y (2014a) An electrochemical aptasensor based on gold nanoparticles dotted graphene modified glassy carbon electrode for label-free detection of bisphenol A in milk samples. Food Chem 162:34–40. https://doi.org/10.1016/j.foodchem.2014.04.058

Zhou X, Guo J, Zhang W, Zhou P (2014b) Occurrences and inventories of heavy metals and brominated flame retardants in wastes from printed circuit board production. Environ Sci Pollut Res 21(17):10294–10306

Zhou N et al (2015) A label-free electrochemical aptasensor for the detection of kanamycin in milk. Anal Methods 7:1991–1996. https://doi.org/10.1039/C4AY02710H

Zhu S, Zhou J, Jia H, Zhang H (2017) Liquid-liquid microextraction of synthetic pigments in beverages using a hydrophobic deep eutectic solvent. Food Chem 243:351–356. https://doi.org/10.1016/j.foodchem.2017.09.141