

Analytical Methods for Environmental Contaminants of Emerging Concern: Pesticides

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1.1. Overview of pesticides

There are thousands of chemicals that can enter the environment and pesticides are one of the most significant. They are used in the last decades in several areas but agricultural activity is the main source of the impact of pesticides in the environment and therefore they can be present in soil, water, crops as well as in the atmosphere [1].

1.1.1. Properties

Pesticides are a class of chemicals used to limit, inhibit or prevent the growth of harmful animals, insects, weeds or fungi [2]. They can be classified according to different criteria, as target organism, origin or chemical structure, but the most common is considering the target organism, being herbicides, fungicides, insecticides, etc., among others [3]. There are more than 800 active components and they are available in different accessible products [4]. Despite the benefits of the use of these compounds, they can be toxic to humans and many of them have been classified as endocrine disruptors, and carcinogenic effects have also been reported [5].

The widespread use of pesticides in combination with their physicochemical properties, such as water solubility, octanol/water partition coefficient, volatility, and stability against degradation by abiotic and biotic factors, are the reasons for their distribution and occurrence in different environmental matrices as water, soil, air and biota [6] by physical processes as sedimentation leaching, sorption, and volatilization.

Once pesticides are in the environment, they can be transformed by biotic or abiotic process [7], increasing the number of potential transformation products (TPs) that can be detected, and most of them are still unknown [8]. In this sense, TPs could also have environmental concern and so in addition to the parent compounds, they should also be monitored in order to get a comprehensive overview of the environmental fate of pesticides.

1.1.2. Legislation

The presence of these pollutants poses a potential risk for the environment and human health and, therefore, international organizations have set legal limits, regarding the presence of pesticides in water and other environmental matrices, for controlling and preventing contamination of environmental ecosystems.

For instance, in Europe, the Water Framework Directive (WFD) is intended to protect transitional waters, inland surface waters, coastal waters, and groundwater. Strategies against the chemical pollution of surface waters led to the Directive 2008/105/EC [9], establishing concentration limits of 33 priority substances and 8 other pollutants, including some pesticides as simazine and trifluralin among others. Priority substances are considered to pose a significant risk to or via the aquatic environment so environmental quality standards (EQSs) were set for each of them. Then, amending Directive 2013/39/EU [10] introduced 12 new compounds to the list and the need to establish an additional list of potential water pollutants (Watch List) that should be carefully monitored to support future reviews of the priority substances list. Currently, among the priority substances are 24 pesticides with Annual Average EQS (AA-EQS) values ranging from $1 \times 10^{-8} \mu\text{g l}^{-1}$ for heptachlor and heptachlor epoxide to $1 \mu\text{g l}^{-1}$ for simazine. In 2020, the European Union (EU) established a new watch list of substances, includingazole compounds and providing maximum acceptable method detection limits for them from 29 to 199 ng l^{-1} [11]. Additionally, the Drinking Water Directive 98/83/EC, amended by EU 2015/1787 [12], set special quality requirements for water for human consumption. It set concentration limits for a range of hazardous substances, including pesticides, establishing a general maximum individual concentration of $0.1 \mu\text{g l}^{-1}$ for individual pesticides, ($0.030 \mu\text{g l}^{-1}$ in the case of aldrin, dieldrin, heptachlor and heptachlor epoxide), and $0.5 \mu\text{g l}^{-1}$ for the sum of all individual pesticides and relevant metabolites/TPs detected. The same values, 0.1 and $0.5 \mu\text{g l}^{-1}$, for individual and total pesticides respectively, are established as groundwater quality standards in the Directive 2006/118/EC [13] on the protection of groundwater against pollution and deterioration.

In the same way, the Clean Water Act (CWA) in the United States (US) establishes the basic structure for regulating quality standards for surface waters discharges of pollutants into the waters. In addition, the Safe Drinking Water Act (SDWA) was aiming at protecting drinking water and its sources (rivers, lakes, reservoirs, springs, and groundwater wells). SDWA authorizes the US Environmental Protection Agency (US EPA) to set national health-based standards for drinking water to protect against contaminants, such as pesticides, that may be found in drinking water [14-16]. In this case, the proposed substance priority list is based on a combination of their frequency, toxicity, and potential for human exposure at National Priorities List (NPL) sites, setting criterion maximum concentration (CMC) values for each of the pollutants listed. Aldrin, dieldrin, heptachlor and heptachlor epoxide showing the lowest CMC values between 7.7×10^{-7} to $3.2 \times 10^{-5} \mu\text{g l}^{-1}$.

Whereas different countries have set pesticide regulation in water matrices, regulation in soils is scarce. For instance, Spain set a generic reference levels for a limited number of substances (< 60), some of the considered as persistent organic contaminants, as dichloro-diphenyl-trichloroethane (DDT) or dichloro-diphenyl-dichloroethane (DDE), whose reference levels were 0.2 mg kg⁻¹ and 0.6 mg kg⁻¹ respectively [17]. These reference levels, in terms of human protection, are the maximum concentration of a substance in the soil that guarantee that contamination does not pose an unacceptable risk to humans. In addition to comply with generic reference levels, it is necessary to determine through toxicological tests that these substances do not present a serious risk to the ecosystem.

1.1.3. Reported or potential metabolites and/or transformation products

Pesticides in the environment may experience different chemical reactions leading to the appearance of TPs and metabolites. These compounds have potentially harmful impacts on organisms, even more than their precursors [18], making their monitoring essential. However, because the high variety of TPs, it is difficult to carry out a comprehensive analysis of their presence, and in consequence, a risk assessment evaluation.

The metabolic/transformation pathways of pesticides can be affected by biological or/and physico-chemical factors in the environment [19]. Hydrolysis is an important degradation mode of pesticides; however, multiple TPs may be produced from different processes, even after hydrolysis [20, 21].

It was noted that the number of substances that must be considered for environmental risk significantly multiplied by a factor of 7.5, just when the precursor compounds were subjected to a photolysis process [22]. This has been observed for terbutryn, mecoprop, penconazole, boscalid diuron and octhilinone pesticides in Figure 1.1, where the number of compounds that should be monitored in environmental samples considerably increase because the presence of TPs. After evaluating genotoxicity of the proposed TPs, it was suggested that the number of substances that pose a risk onto the aquatic environment increased by a factor of > 4. This fact, together with the high incidence of TPs and metabolites in natural waters constitutes a major concern that needs to be addressed from an analytical and legislative point of view.

Several studies have revealed the presence of TPs and metabolites in waters at higher concentrations than the parent compounds [23,24]. The physico-chemical properties (higher mobility and polarity) of the TPs and metabolites might facilitate the migration between surface water and groundwater. Since groundwater is the greatest source of freshwater in the world, the occurrence of some relevant metabolites and/or TPs led to the restriction in the use of certain pesticides, as was recently the case of chlorothalonil and previously simazine and atrazine among others. Most of the TPs/metabolites

found in natural waters are related to acetanilide and triazine herbicides [25]. Such is the case of ethanesulfonic acid (ESA) and oxanilic acid (OA) degradation products of alachlor, metolachlor, as well as acetochlor and atrazine-desethyl (DEA), atrazine-desisopropyl (DIA), terbutometon-desethyl (TED), terbutylazine-desethyl (TD) and terbutylazine-2-hydroxy (T2H). Different analysis have also revealed the occurrence of 2,6-dichlorobenzamide (BAM) from dichlobenil, aminomethyl phosphonic acid (AMPA) from glyphosate, desphenyl chloridazon and methyl-desphenyl chloridazon of the herbicide chloridazon, and N,N-dimethylsulfamide (DMS) formed from the fungicide tolylfluanid [23, 25-27].

Metabolites were also detected in soils, especially when dissipation studies have been carried out. For instance, nine metabolites of famoxadone were detected in soil samples [28], being IN-JS940 the metabolites detected at the highest percentage relation to the parent compound as it can be observed in Figure 1.2. Therefore, risk assessment is needed to evaluate potential hazards to the fauna and flora. Tiwari et al. [29] evaluated the presence of endosulfan and chlorpyrifos metabolites in soils because the higher toxicity of some of these compounds as chlorpyrifos oxon. They determined that metabolite concentrations increased throughout the study when the concentration of the parent molecule decreased. Moreover, it was observed that concentration of metabolites was higher in soil matrices than in water. In the same way, when 2,4-dichlorophenoxyacetic acid (2,4-D) is applied on crops or on soil, it will undergo chemical, biological, and physical degradation processes depending on the environmental factors, which will determine the formed metabolites. For example, 2,4-D DMA (2,4-D dimethylamine salts) is dissociated to 2,4-D acid after its application on the soil [30], so in addition to the parent compound, different TPs should be monitored.

1.1.4. Occurrence in the environment

Pesticides and their TPs/metabolites are widely distributed in the environment and they can be detected in water, soil, sediments, aquatic biota and air [31] as it can be observed in Figure 1.3, because surface runoff from arable lands, leaching from drainage systems, volatilization, etc. They can have toxic effects in population living close to these areas [32]. For instance, when pesticides are applied in agricultural areas, approximately 20-30 % of the amount is lost due to the spray drift process, whereas another significant fraction is located into the soil or surface waters [33].

Pesticides have been widely detected in the aquatic media. Several scientific papers and technical reports have revealed the presence of pesticides in surface water, groundwater, drinking water as well as treated wastewater which are intended to be discharged in surface waters [34].

In 2018 the European Environment Agency (EEA) indicated that chemical status of surface waters, related to pesticides, has improved between the 1st and 2nd River Basin Management Plants (RBMPs)

assessments [35]. However, pesticides listed as priority substances were still detected. Among them, isoproturon and hexachlorocyclohexane were the most frequently reported, followed by endosulfan and chlorpyrifos. Furthermore, the presence of pesticides in groundwater is a failure to achieve good chemical status. As reported by EAA, several groundwater bodies exceed the permitted concentrations set by EU of total pesticides, as well as the level set for desethylatrazine, atrazine and simazine.

Herbicides as atrazine and fungicides as metalaxyl have been detected in aquifer for drinking water in US [25]. The most found pesticide in Ireland drinking water was 2-methyl-4-chlorophenoxyacetic acid (MCPA), widely used for rush control in grassland [36].

A recent study in The Netherlands, intended to assess the occurrence of pesticides in ground and surface water used as drinking water sources, has revealed the detection of 15 recently even authorized pesticides, such as fluopyram and thiamethoxam, which demonstrates the importance to keep routine monitoring methods [36].

Non-agricultural uses of pesticides are also common in urban environments, such as indoor uses or applications in gardens, roads, sealed areas, among others. As a result, triazine herbicides (atrazine, simazine and prometon) and organophosphate insecticides (chlorpyrifos and diazinon) are frequently detected in U.S. urban surface waters [34].

Pesticide occurrence in soils was inversely related to the occurrence in surface water, and one of the main factors is the hydrophobicity of the compounds, expressed by the n-octanol/water partition coefficient (K_{ow}). Thus, pesticides with $\log K_{ow} > 3$ were more detectable in soils than in water. In a study performed in Argentine ecosystem, it was observed that the most detected herbicide residues (>30% of detection frequency) were acetochlor, atrazine and its metabolite (hydroxyatrazine), flurochloridone, glyphosate and its metabolite (aminomethylphosphonic acid, AMPA) and metolachlor, whereas the most frequently detected insecticides were chlorpyrifos and imidacloprid [37]. In this study, glyphosate and its metabolite AMPA, were also found in all the environmental samples (soil, sediments and surface water), detecting AMPA up to 713 mg kg^{-1} , glyphosate at 32 mg kg^{-1} and 5 mg l^{-1} in sediments and water respectively.

Another group of pesticides really known for their persistence were 2,4-D-based herbicides. The two chlorine that are present in their molecules confers persistence with an estimate half-life between 7 and 312 days, which depends on the environmental conditions [38]. Several studies have reported the presence of 2,4-D and derivates in the environment because different activities, such as agricultural ones and rain and irrigation water. Discharges from manufacturing plants, leaching and accidental spills [39] represent an important source of the aforementioned herbicide.

The key properties that determine the presence of pesticides and their accumulation in biota are hydrophobicity and persistence. Thus, if water solubility is $< 1 \text{ mg l}^{-1}$ or $\log K_{ow}$ is > 3 , they have the potential to accumulate in biota and it may be an indicator of contamination [40]. For instance, earthworms are used as indicators to the response of pesticides [41], but fish are considered as major reservoirs of pesticides and their concentration in fish tissues has been used as an indicator of bioaccumulation [42]. High concentrations of organochlorine pesticides (OCPs) have been found in fish tissues from aquatic environments in Africa [43], detecting DDTs, lindane, mirex and endosulfan at concentrations up to $100 \mu\text{g kg}^{-1}$. Other studies, developed in South-America (southeastern Brazil and the coast of the Argentinean Pampas), showed that lindane and endosulfan levels could cause long-term or short-term damage to biota [44]. Additionally, it was observed that OCPs were highly bioaccumulated in soil mesofauna (up to $260 \mu\text{g g}^{-1}$) [45].

In the last years, several river basins were monitored in the Iberian Peninsula, and in addition to water and sediment, biota was also analyzed. Thus, 50 pesticides were monitored in Guadalquivir river basin, but none of them were detected in biota, although there were detected in water and sediments, specially organophosphorus and triazines at concentrations up to 13 ng l^{-1} in water and 13.2 ng g^{-1} dry weight (dw) in sediment [46]. However, azinphos-ethyl, chlorpyrifos, diazinon, dimethoate and ethion were detected in different species of fish from Júcar river basin, observing that the maximum average concentration was found in European eel (up to 0.024 ng kg^{-1}), whereas in water, dichlofenthion, imazalil pyriproxyfen and prochloraz, commonly used in farming activities, were mainly detected [47]. In biota from Llobregat river basin, chlorpyrifos and azinphos-ethyl were detected at 44.75 ng g^{-1} dw and 105.81 ng g^{-1} dw, indicating possible bioaccumulation. Nevertheless, authors concluded that these values do not represent a high risk to biota. On the other hand, triazines, organophosphorus, and neonicotinoids were mainly detected in water, at concentrations $> 600 \text{ ng l}^{-1}$ as it can be observed in Figure 1.4, being chlorpyrifos the compound most widely detected in soils at concentrations up to 130 ng g^{-1} dw [48]. Additionally, Ebro river basin was also monitored, detecting imazalil and diuron at the highest concentrations in water (410 and 150 ng l^{-1} respectively), chlorpyrifos, diazinon and diclofenthion in sediments, whereas the only compound detected in biota was chlorpyrifos, which was detected at concentrations up to 840.2 ng g^{-1} [49].

The presence of pesticides in air depends on the specific agricultural areas, as well as those pesticides that can be transported from nearby places, observing a relationship between the concentration of some of the compounds detected in air and diseases and mortality [50].

Several studies were performed to monitor the presence of pesticides in outdoor and indoor air [51], bearing in mind that volatile pesticides, such as OCPs, can largely remain in the atmosphere after volatilizing from contaminated soils and water. For instance, p,p'-DDT and p,p'-DDD were detected in

Africa air at concentrations of 47 pg m^{-3} and 12 pg m^{-3} respectively, whereas other compounds as dieldrin, hexachlorobenzene (HCB), aldrin, lindane and chlordane were also detected but at lower concentrations [52].

In a study developed in Vietnam, 452 pesticides were included in a database, detecting 18 (12 insecticides, 4 herbicides, and 2 fungicides) in the collected air samples, and the total concentration ranged from 3.35 to 89.0 ng m^{-3} , being the most detected pesticides permethrin-2, carbofuran, fenobucarb and chlorpyrifos as well as metolachlor [53]. Some prohibited pesticides in the EU such as chlorpyrifos, permethrin, deltamethrin, cypermethrin and carbofuran, were also detected [53]. In the same country, 26 pesticides (13 pesticides, 7 fungicides and 6 herbicides) were detected in the air samples, at higher concentrations, ranging from 43 to 370 ng m^{-3} . Permethrins, chlorpyrifos and propiconazole were detected and this may result from their widespread use for both agricultural and domestic purposes in rural areas [54].

Due to their high persistence, OCPs were monitored in addition to current use pesticides (CUPs) in two National Parks in the Rio de Janeiro State. The highest concentrations of endosulfan (up to 3202 pg m^{-3}), cypermethrin (881 pg m^{-3}) and chlorpyrifos (270 pg m^{-3}) indicated background air levels of OCPs. On the other hand, CUPs seemed to behave like pseudo persistent organic pollutants (POPs) although it was believed that they are not persistent in the environment [55].

In another study, carbendazim, metalaxyl, myclobutanil and terbuthylazine were detected in air from rural areas of Valencia (Spain) at concentrations ranging from 16 to 174 pg m^{-3} [56].

Bearing in mind that pesticides can easily adhere to the particulate matter, they have also been analyzed in this matter. Thus, 40 CUPs were determined in PM₁₀ of Valencia Region (Spain) observing that omethoate was detected at the highest average level (141 pg m^{-3}) [57]. A similar study was performed in "Todos los Santos Bay" region (Brazil), were 13 pesticides were analyzed in PM_{2.5} samples, and concentrations ranged from 20 to 315 pg m^{-3} , being carbofuran, malathion and permethrin the compound most widely detected [58].

1.2. Sample preparation and collection

In order to ensure accurate pesticide determination in environmental samples, sample collection and preparation should be carefully designed to minimize potential errors during these steps and therefore error propagation will be limited.

1.2.1. Protocols for collecting and preparing samples

Sample collection is critical to get representative samples as well as to avoid any modification of the initial chemical composition of the sample.

For instance, a guidance on sampling water techniques can be found in the ISO Standard on Water Quality – Sampling 5667. The selection of sampling point, which should cover the area of surveillance, must be subject to local conditions, such as water homogeneity and vertical and lateral mixing.

The sample containers as well as transport and storage arrangements should not lead to changes in the relevant chemical status. Therefore, according to sampling for synthetic organic compounds, water samples must be stored in glass, polytetrafluoroethylene (PTFE) or stainless-steel containers, and they should be analysed within 24 h and stored in the dark at 1-5 °C.

On the other hand, the development and application of passive sampling techniques are highly recommended [59]. Those techniques allow for the accumulation of pesticides by passive diffusion onto a liquid or solid absorbent showing affinity for a certain type of substances. The semipermeable membrane device (SPMD) and the polar organic chemical integrative sampler (POCIS) are the most common passive samplers for organic pollutants. SPMD based on triolein sorbent can be applied for neutral organic chemicals with a log Kow > 3 (lipophilic pesticides) while POCIS, that uses Oasis HLB phase, is intended to the sorption of more water-soluble organic chemicals with Kow < 3 (polar pesticides). To insurance the monitoring of a high number of pollutants different types of passive samplers could be used together [6]. In this sense, an interlaboratory study on passive sampling of emerging water pollutants showed low within laboratory variability in the analysis of replicate samplers when POCIS was used for the monitoring of 7 polar pesticides. The same study established a series of recommendations to take into consideration, especially when passive samplers are combined with liquid chromatographic-mass spectrometric (LC-MS) methods [60].

In the same way, soil samples should be collected from growing fields using a grid pattern uniformly distributed. For instance, a 3 x 3 grid is commonly used for smaller fields, whereas 5 x 5 or even larger grids are used for very large fields and a “W” or “Z” pattern is commonly used. Each sample site represents one portion of the total sample, and then, a composite sample can be formed, ensuring homogeneity. Normally, samples are collected at a 15 cm depth. Additionally, additional steps as removing litter, plant roots, and big stones from the soil samples could be needed [61] and sometimes, soils should be dried with [62] or without temperature [63], homogenized and finally stored at – 18 °C until analysis [64]. Finally, an exhaustive characterization of the soils according to several parameters, as pH, percentage of organic matter, carbon monoxide, sand, silt, clay and grit [28, 65], is advisable to provide useful information and set a relationship between pesticide presence and physico-chemical characteristics of the soil.

In relation to air sampling, other important criteria should be considered as material do not react with target compounds; it must be located in a place where free air masses can be arrived; the sampler should be protected from rainfall, dust or other sources of contamination as well as low maintenance

is required [33]. Furthermore, it should be planned bearing in mind if only gas phase, particulate matter or both of them are going to be collected among other factors.

Finally, for biota sampling, special care should be taken with small biota samples, which are more sensitive to contamination, and degradation or loss of analytes. Long term storage should be performed in darkness and low temperature, and before sample treatment, dry or wet homogenization is needed [66].

1.2.2. Sample extraction and clean-up

For the monitoring of ultra-trace levels of pesticides in water, extraction and concentration steps are required prior to the analytical determination. Liquid-liquid extraction (LLE) allows for the detection of a large range of non-polar pesticides while requires minimal instrumentation being, at the same time, a simple and precise technique. Although fewer and fewer, this technique is still used for the extraction of pesticides from water samples prior to gas chromatography (GC) analysis [67, 68]. However, one major drawback is the large solvent volumes, usually dichloromethane, required in LLE. Therefore, solid phase extraction (SPE) has become the most common extraction technique [69]. Indeed, it is the most powerful sampling and enrichment approach for complex mixtures of known and unknown contaminants, and different sorbent phases can be used, allowing for the extraction of a wide range of pesticides with different physico-chemical properties.

As shown in Table 1.1, the polymeric reversed phase sorbent, Oasis HLB, is commonly used for the extraction of pesticides in water samples providing quantitative recoveries in most cases [18, 23, 70-72]. Furthermore, other sorbents have been successfully applied for the analysis of pesticides and their TPs in natural waters, such as a mixture of hydrophilic–lipophilic balance, weak anion, and cation exchange sorbents (2:1:1, w/w/w) [73] and Strata-X reversed in combination with the mixture of Strata X-mixed mode (AW and CW) and Isolute+ [74].

On-site integrate large-volume SPE has also been proven to be a promising tool for the monitoring of pollutants, including pesticides, in water sources [75]. On the other hand, the possibility of using on-line SPE systems allows for minimizing sample manipulation and cross-contaminations as well as improving sample throughput [76]. Hence the development of fully automated methods, based on the combination of on-line SPE and LC-MS has given much attention in the last few years, being applied for the monitoring of ca. 100 pesticides in natural and drinking waters [24, 77], as well as 51 pesticides, covering highly polar compounds, in surface and groundwaters [78].

Simple and miniaturized sample preparation techniques have been considered in recent years as optimal alternatives [79]. Among them, solid-phase microextraction (SPME) is the most used technique, although the application of QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe)

based protocols [21, 80], stir bar sorptive extraction (SBSE) [77] as well as liquid-phase microextraction (LPME) [81, 82] have also been suitable for the extraction of pesticides from water matrices.

SPME is a simple, sensitive, rapid, and solvent free technique in which the organic compounds are adsorbed/absorbed (depending on fiber coating) directly from the aqueous sample into the fiber and then thermally desorbed at the injection port of the GC, considerably simplifying the analysis procedure. In this sense, the availability of SPME devices in latest GC equipment leads to the complete automatization of the analytical process, allowing for improving data quality, the productivity of staff and instruments, and increasing the sample throughput [83]. This has been demonstrated in recent methodologies involving the on-line combination of SPME and GC coupled to high resolution mass spectrometry (HRMS) allowing for the determination of priority substances, including pesticides, in surface and wastewaters [84, 85] providing limits of quantification (LOQs) at ng l^{-1} levels. Novel SPME sorbents, as magnetic deep eutectic solvent (DES)-based polymeric hydrogel [86] and carbon nanomaterials [87, 88], have been successfully applied for the monitoring of pesticides in different water resources as can be seen in Table 1.1.

On the other hand, vacuum-assisted evaporative concentration has been effective for the monitoring of organic micropollutants [89], including pesticides as chlorothalonil and TPs (sulphonic acids and phenols) by LC-Orbitrap-MS [90]. However, sometimes these extraction procedures are avoided, and direct injection of water samples, after filtration, can be considered when using LC. In fact, its combination with tandem MS (MS/MS) has allowed for the determination of pesticides at ultra-trace levels in surface and groundwaters [25, 27, 91].

In relation to solid samples, as soils, the most common methods were based on solid-liquid extraction (SLE), pressurized liquid extraction (PLE), and QuEChERS (see Table 1.2). In SLE methods, solvent mixtures as acetonitrile and water have been widely used. For example, a mixture of water/acetonitrile (10:90, v/v) was utilized to monitor pesticide residues in soils from Argentina [62], or a mixture of water/acetonitrile (40:60, v/v) was used for the extraction of oxanilic and sulfonic acids metabolites [92]. Hu et al. employed methanol:water (50:50, v/v) instead of acetonitrile for the extraction of acetochlor and propisochlor in soils from Beijing (China) [63]. Colazzo et al. tested different solvents and mixtures, as acetonitrile, methanol, water and methanol/water, choosing methanol as the best option (recoveries ranged from 45 to 90%) to determine pesticide residues in paddy fields and sugar cane from Uruguay [93].

PLE method is based on the use of a solvent that is applied at high pressure and temperature through a solid or semisolid sample (e.g. soils) to effectively extract the analytes, being faster than conventional SLE. The selection of optimum experimental parameters, such as extraction temperature, flush volume, and preheat time, can allow the extraction of a large number of pesticides

within a wide polarity range in only one step [94]. Two different extraction solvents, as dichloromethane:acetone (1:1, v/v) and acetonitrile:water (2:1, v/v), were used for the determination of triazines, phenylureas, and phenoxy acid pesticides [95]. Fungicides and insecticides were also extracted using PLE, applying two extraction solvents as methanol:acetonitrile (70:30, v/v) and methanol:acetonitrile:formic acid (65:30:5, v/v), obtaining recoveries from 57 to 136 % [96].

QuEChERS approach has been widely used to extract pesticides from soils [3] and several modifications were carried out to improve sample extraction. One of them was matrix hydration, which consisted of the addition of water before solvent addition [97]. This approach was used for the extraction of pydiflumetofen enantiomers, obtaining recoveries between 84-103% or for the determination of afidopyropen and its metabolite residues in cotton field with acceptable recoveries (85-100%) [98]. Other modification was the acidification of the solvent to improve the extraction of target analytes. For instance, acetonitrile, acidified with 2.5% formic acid, provided acceptable recoveries (70-120%) for the simultaneous monitoring of 218 pesticide residues in clay loam soil [99]. Clean-up step was not commonly used in soil samples and only a few studies employed dispersive solid phase extraction (d-SPE). The sorbents and salts commonly used were primary secondary amine (PSA) and anhydrous magnesium sulphate ($MgSO_4$) [98, 100]. Other sorbents, as C18, were also used in combination with PSA [61] or with $MgSO_4$ [97].

Finally SPE, using OASIS HLB cartridges, was also applied to concentrate the extract before chromatographic analysis [93].

Tissue analysis is more challenging than water or soil analysis due to the complexity of those matrices. Thus, for the extraction of pesticides from biota, different extraction techniques can be applied such as SPME [40], PLE, SPE, ultrasonic-assisted extraction, dispersive liquid-liquid extraction, and SBSE [101], adding a freezing-lipid filtration in fatty materials. Other procedures such as QuEChERS have been widely used in the last few years, using in the clean-up step based on d-SPE a mixture of sorbents that includes $MgSO_4$, PSA, C18 and graphitized carbon black (GCB) [46, 47, 49], as it can be indicated in Table 1.3.

Finally, pesticides are usually extracted from air using active or passive samplers (see Table 1.4). The active ones are mainly based on SPE by pumping high volumes of air through different sorbents as Tenax TA, Carbotrap or polyurethane foam filter (PUF) [54, 102]. Passive samplers are based on diffusion through a well-defined barrier or membrane (e. g. Radiello) PUF disks or semipermeable membrane devices [33]. Then, compounds are desorbed from the passive sampler using Soxhlet extraction [55, 103], microwave-assisted extraction [104], PLE [105] or ultrasound-assisted extraction [33]. In this sense, different solvents can be used for the extraction of pesticides from filters or membranes, such as ethyl acetate [57], acetone or petroleum ether [55]. Additionally, miniaturized

methods can also be applied, and for instance, pesticides were extracted from PM_{2.5} using a miniaturized device with 500 µL of 18 % acetonitrile in dichloromethane followed by sonication and injection into GC-MS [58].

3. Determination of pesticides

Current analytical methods for pesticide residue analysis are mainly based on the use of chromatographic techniques (GC or LC), depending on their polarity and volatility among other factors, coupled to MS analyzers. As example, Figure 1.5 shows the chromatograms of blank soil sample spiked with 218 pesticides by LC-MS/MS and GC-MS/MS, observing the potentiality of these techniques to analyse a wide range of compounds.

1.3.1. Development of the instrumental method

1.3.1.1. Chromatography

GC enables the detection of a high number of volatile or semivolatile and thermally stable pesticides, allowing the determination of persistent pesticides in environmental matrices as water, soil, biota and air (Tables 1.1-1.4). Several multiresidue methods have been developed, and for instance, eleven OCPs were determined in soils using GC with a DB-5-MS capillary column with 5% phenyl stationary phase and 95% of methylpolysiloxane [106]. Although this is the stationary phase most commonly used, other stationary phases, as DB-XLB and DB-35-MS, were also tested for the determination of endosulfan, chlorpyrifos, and their metabolites [29], obtaining the best results with DB-XLB (larger differences in the retention time of the compounds). ZB-5MSi was also tested to determine pyrethroid pesticide metabolites in soil samples [64] and a HP-5-MS UI column to analyze 58 pesticides in soils samples [61]. Additionally, pesticides can simultaneously be analysed with other pollutants as polycyclic aromatic hydrocarbons (PAHs), brominated diphenyl ethers (BDEs) and polychlorinated biphenyls (PCBs) in environmental matrices, such as surface waters [84] accomplishing with the Environmental Quality Standards (EQS) fixed by Directive 2013/39/EC [10].

For non-GC amenable compounds, although chemical derivatization can be carried out, LC is recommended and high performance liquid chromatography (HPLC) and, increasingly, ultra-high performance liquid chromatography (UHPLC), are commonly used for the analysis of pesticides, using different particle sizes as 5 µm [107], 3 µm [62] or even lower (1.8 µm) [28]. For LC-amenable pesticides, conventional C18 columns are commonly used [57], with generic mobile phases as methanol and water 0.1% formic acid 4 mM ammonium formate, allowing for instance the determination of parent pesticides (famoxadone) and metabolites [28]. Moreover, hydrophilic interaction liquid chromatography (HILIC) has been proposed as a promising tool for highly polar

pesticides in fresh water [72] whereas a mixed-mode stationary phase is an interesting alternative [108], allowing the separation of a wide range of compounds such as polar, medium and non-polar ones. Thus, mixed column as XDB-C18 was used to determine thirty pesticides (herbicides, fungicides and insecticides), using as mobile phase acetonitrile and water 0.1% formic acid [93], or an EC-C18 column, using mobile phases consisted of methanol 0.1% formic acid and 2 mM ammonium acetate, and water 0.1% formic acid and 2mM ammonium acetate, allowing the determination of 218 pesticides [99].

As it can be observed in Tables 1.1-1.4, different multiresidue and multiclass methods based on LC-MS have been reported in recent years. Robust and reliable analytical methods have been developed, allowing for the monitoring of ca. 500 pesticides in surface and groundwaters [23], 215 pesticides and TPs in groundwater [25], as well as 251 emerging contaminants in surface water [75].

In the last years, chiral columns were also employed to determine enantiomers of pesticides [65], using different specific stationary phases, as Chiralcel OD-RH column and a mobile phase consisting of acetonitrile and water 0.1% formic acid, or a Chiralcel OD-3 [97], that allows the determination of pydiflumetofen enantiomers in soil samples.

On the other hand, despite the proved potential of supercritical fluid chromatography (SFC) [108-110], its application in the analysis of environmental samples is still scarce. For instance, SPE was combined with SFC for the analysis of 8 emerging contaminants, including the diuron herbicide, in river water [111]. Ionic chromatography (IC) coupled with MS has tested for the analysis of polar pesticides, as glyphosate, AMPA, glufosinate and MPPA in surface water [112], being an interesting alternative to HILIC or approaches.

1.3.1.2. Detection

Different classical detectors have been applied for the determination of target pesticides in environmental samples, such as flame ionization detector (FID) [68] and electron capture detector (ECD) [45, 63, 86] in combination with GC. Likewise, LC coupled to UV-vis detector was used for the analysis of organophosphorus pesticides in soils samples [113], or fluorescence detector, which was utilized to monitor pesticides and metabolites in soils [114]. However, in the last two decades, MS has become the main detection system in environmental monitoring as it can be observed in Tables 1.1-1.4. Most of the methodologies involving GC make use of electron ionization (EI) [99], while electrospray (ESI), or heated ESI (HESI) in positive and/or negative ionization modes is mainly used in the case of LC. As can be seen from Tables 1.1-1.4, triple quadrupole (QqQ) analyzer is the most widely used in combination with both GC and LC.

QqQ, operating in selected reaction monitoring (SRM) or multiple reaction monitoring modes (MRM), provides high selectivity and sensitivity for target analytes. Thus, QqQ and ESI+/- was used to determine 218 pesticides in soils, or to analyze propamocarb and fenamidone in soils [100]. Zhao et al. [65] determined LOQ lower than the previous works (0.22 to 1.54 $\mu\text{g kg}^{-1}$) for the analysis of eight chiral pesticides (diniconazole, metalaxyl, paclobutrazol, epoxiconazole, myclobutanil, hexaconazole, napropamide and isocarbophos) in soils and river sediments, employing QqQ and ESI source.

Other types of MS analyzers coupled to LC have also been used. The single quadrupole MS was employed by Belmonte Vega et al. [107] to determine pesticides in environmental matrices, or the triple quadrupole-linear ion trap-mass spectrometer (QTRAP), which was used to detect herbicides, insecticides and fungicides [93], achieving LOQ of 1-10 $\mu\text{g kg}^{-1}$

However, other types of analyzers coupled to LC was employed as. In GC, ion trap mass spectrometer detector was employed to detect endosulfan, chlorpyrifos, and their metabolites in soil matrices [29] and isotope ratio mass spectrometer (IRMS) was used to determine OCPs and metabolites [115]. Additionally, the double-focusing magnetic sector high resolution mass spectrometer is extremely sensitive when multiple ion detection (MID) is used as acquisition mode. It has been utilized in combination with SPME and GC for the fully automated determination of priority substances at ultra-trace levels, including pesticides, in surface water [84], as well as more complex matrixes such as treated and non-treated wastewaters [85].

Although QqQ was still used to monitor the presence of pesticides in environmental samples, when a large number of compounds should be monitored, the sensitivity of these analyzers decreased by the simultaneous monitoring of a huge number of transitions. Therefore, HRMS analyzers are also used in this field, because the number of compounds to be simultaneously analyzed is theoretically unlimited and other strategies can be applied [56]. Additionally, good chromatographic peaks and resolution are still important. The use of HRMS allows that customized database can be built, including CUPs, TPs, banished pesticides, and other pollutants, increasing the scope of the analysis.

HRMS enables the analysis of target, post-target (or suspected) and non-target analytes. The high sensitivity of certain HRMS analyzers, when operating in full scan mode, combined with high resolving power (>30 000 full width at half maximum, FWHM) and accurate mass measurement (1–5 ppm) allows for retrospective analysis.

While most of the HRMS applications have been aimed to targeted pesticide analysis, there are already some studies aimed at the identification of non-target analytes including new contaminants such as metabolites or TPS for a more exhaustive monitoring of water quality.

Some examples of the successful application of HRMS analyzers, concretely Q-Time of Flight (TOF) systems, in combination with LC, in target screenings allowed for the monitoring of 474 emerging

contaminants, including 296 pesticides, in coastal waters [70] and ca. 500 pesticides and TPs in surface and groundwater [23]. Likewise, and as shown in Table 1.1, the potential of Orbitrap analyzers has also been employed in methods involving emerging contaminants belonging different families and classes.

Most of the non-target screenings have been applied to wastewater samples [116], which are considered an important source of contamination of natural waters when discharged into rivers and coastal compartments. This approach was also applied in soils, detecting suspected metabolites of famoxadone in samples [28].

Nevertheless, a recent study, making use of UHPLC-Q-Orbitrap MS and software Compound Discoverer 3.0 to perform non-target analysis of pollutants in surface water, has revealed that pesticides and plastic additives were the two main types of pollutants found in Dianshan Lake in China. Once the pollutants were identified, a target screening allowed for their confirmation and quantification [117].

Moreover, HRMS is a powerful tool for the identification of unknown TPs and metabolites. In fact, novel TPs resulting from the chlorination of clothianidin, imidacloprid, desnitro-imidacloprid, imidacloprid-urea, and hydrolysis products of thiamethoxam were identified in drinking water by using HPLC-TOF MS system [18].

1.3.2. Figures of merit

The use of the analytical methods described in previous sections provides sensitive and reliable methods that allows for low LOQs and suitable recoveries, as it can be observed in Tables 1.1-1.4. Thus, despite the lower EQS set by EU legislation for some pesticides, lower LOQs can be achieved and for instance, concentrations down to $0.0001 \mu\text{g l}^{-1}$ can be quantified (see Table 1.1), combining preconcentration techniques, as SPE or SPME and sensitive analyzers. For instance, 51 pesticides, covering highly polar compounds, were determined in surface and groundwaters by using on-line SPE in combination with (U)HPLC and tandem mass spectrometry, providing LOQ values in the range of $0.005\text{-}0.025 \mu\text{g l}^{-1}$ [78]. Higher limits were obtained in soils, allowing the quantification at $\mu\text{g kg}^{-1}$ or even lower (see Table 1.2), as well as in biota, where concentrations below $\mu\text{g kg}^{-1}$ (ng g^{-1}) can be detected (Table 1.3). Additionally, the use of passive sampling, such as in air, allows for achieving adequate recovery and precision values (Table 1.4) and low LOQs ($< 6.5 \text{ pg m}^{-3}$) for most of the compounds [56].

In terms of recovery, most of the current analytical methods provided recoveries between 70 and 120 %, although when multiresidue methods are developed, recoveries $< 70 \%$ or $> 120 \%$ are sometimes achieved. In the case of lower recoveries, if precision is $< 20 \%$, correction factors can be used for

quantification purposes. In this sense, the use of generic methods, such as QuEChERS, which has been widely used in soils (see Table 1.2), provides acceptable recoveries (70-120%) for the simultaneous environmental monitoring of 218 pesticide residues in clay loam soil [99], or the quantitative extraction of parent pesticides, as afidopyropen, and metabolites (recovery values: 85-100%) [98].

1.3.3. Hints and tips

There are several hints and tips that should be considered in order to fulfill current legislation as well as to ensure reliable results:

- Sample collection: Apply a statistical-based sampling procedure to ensure spatial and/or time variation and collect representative samples. Avoid compound degradation, selecting suitable storage and transport conditions. For air or water sampling, in addition to active sampling procedures, passive sampling is an interesting alternative, which is easy to deploy and minimum maintenance is required.
- Extraction: Use sensitive and/or generic extraction procedures. Thus, for aqueous samples, SPE or SPME, selecting suitable sorbents, are the most widely extraction techniques to ensure lower LOQs as well as suitable recovery. For solid samples, such as biota and soils, although PLE, combining different sorbents depending on the target compounds is a good option, nowadays, QuEChERS approach is the first choice, because its versatility, wide range of application and simplicity. Depending on the complexity of the matrix, an additional clean-up step could be necessary. The final extract can be injected in both GC and LC equipment or it can easily be evaporated and redissolved in a GC solvent as ethyl acetate.
- Analytical determination: Select LC or GC depending on the characteristics of the monitored compounds (GC for non-polar compounds and LC for polar pesticides). Either LC or GC should be coupled to QqQ, providing reliable, sensitive, fast and wide-scope analysis.
- LRMS vs HRMS: Use QqQ (LRMS analyser) for targeted analysis of pesticide residues in environmental samples, whereas HRMS ((Q)-Orbitrap or (Q)-TOF) must be utilized if suspect or unknown analysis is also required.
- Data treatment: Well-set workflows and software are available for targeted analysis whereas when suspect or unknown analysis is performed, large raw data files are obtained, and high expertise and suitable software is needed for data interpretation and pesticide identification.

1.4. Future directions and challenges

Nowadays, in order to increase sample throughput and minimize the number of analyses that should be performed to get a comprehensive view of the presence of pesticides in the environment, current

analytical methods are monitoring a higher number of pesticides. However they have different physico-chemical properties (from non-polar to highly polar pesticides, and from low to high volatility) and this is hampered the development of an all-in-one approach, where a wide-scope analysis can be performed, analyzing pesticides and TPs. Therefore, the combination of different platforms (GC-MS & LC-MS) is a suitable approach to minimize the number of analyses to be carried out, covering a wide-scope of pesticides, although several compounds will still require specific methods to be detected (e. g. highly polar pesticides or metabolites).

Simplification of sample treatment is still necessary in order to minimize sample handling and therefore, error or bias associated to this step. Thus, automated methodologies that allowing for monitoring of many priority substances and specific pollutants at concentrations below EQSs (e. g. water samples) are still demanding, because they are fast and cost-effective

One of the main challenges of environmental analytical chemistry is that there is a huge number of pesticides and/or TPs present in the environment, but many of them are still unknown because for instance, the dissipation of the parent compounds has not been evaluated. Therefore, targeted approach should be combined with suspect and unknown analyses to comprehensively assess chemical pollution related to pesticides. Special interest should be paid to the identification of new metabolites and/or TPs, and other emerging contaminants and therefore, faster acquisition rate in HRMS analyzers and the development of efficient and user-friendly software are still needed to carry out a deconvolution process for the generation of clean mass spectra of coeluting peaks as well as an accurate putative identification. In this sense, the development of databases that include detected transformation products are needed to make this process much easier and this will facilitate the inclusion of TPs in future legislation.

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Figure Captions

Figure 1.1. Forty-five TPs originating from six pesticidal parent compounds. Illustration of the multiplication of known substances that should be further investigated by an environmental risk assessment. Source [22]. Reproduced with permission of Elsevier B.V.

Figure 1.2. Metabolite behaviour according to the concentration of famoxadone during monitoring period (100 days) for soil experiments at: a) normal dose (2.4 mg g^{-1} soil) and b) double dose (4.8 mg g^{-1} soil). Source [28]. Reproduced with permission of Elsevier B.V.

Figure 1.3. Neonicotinoid insecticides in the environment: sources, pathways, receptors and related process. Source [31]. Reproduced with permission of Elsevier B.V.

Figure 1.4. Pesticide families detected in A) water, B) sediment and C) fish samples from Llobregat basin in 2010 and 2011 according to the sampling point. Source [48]. Reproduced with permission of Elsevier B.V.

Figure 1.5. Chromatograms of the targeted pesticides by LC-MS/MS (A) and GC-MS/MS (B) of a blank soil sample spiked at 20 ng g^{-1} . Source [99]. Reproduced with permission of Elsevier B.V.

Table 1.1 Overview of analytical methods applied to monitor pesticides in environmental waters^a

Pesticides	Matrix	Extraction technique	Determination technique	Recovery (%)	LOQ ($\mu\text{g l}^{-1}$)	Reference
4 OCP and 2 OPPs	Surface water	LLE (dichloromethane)	GC-FID	80-90	0.002	[68]
296 pesticides +156 pharmaceuticals, 18 consumer products, 10 industrial chemicals and 4 others	Coastal waters	SPE (Oasis HLB and SpePak cartridges)	LC-QTOF-MS	70-130	0.00002- 0.300 ^b	[70]
14 pesticides and TPs	Surface water and drinking water	SPE (Oasis HLB cartridge)	UHPLC-QTrap-MS/MS	85-105	0.01-0.1	[71]
19 acidic herbicides + metabolites	River water	SPE (Oasis HLB cartridge)	LC-QqQ-MS/MS	64-111	0.004-0.022	[72]
6 neonicotinoids and metabolites	Drinking water	SPE (Oasis HLB cartridge)	LC-DAD-QqQ-MS/MS & QTOF-MS	57-120	0.000057-0.000488 ^b	[18]
ca. 500 pesticides and TPs	Surface water and groundwater	SPE (Oasis HLB cartridge)	UHPLC-QTOF-MS	---	---	[23]
8 Pesticides + TPs	Surface water	Mix mode SPE: (HLB: WAX: WCX, 2: 1: 1)	HPLC-QqQ-MS/MS	43-141	0.00002-0.0056 ^b	[73]
125 pesticides and metabolites + 130 pharmaceuticals and metabolites + 42 antibiotics and metabolites + 63 others	Surface and marine water	SPE (Strata-X and the mixture Strata-X-AW: Strata-X-CW: Isolute ENV+ (1:1:1.5))	HPLC-LTQ-Orbitrap-MS	83-93	---	[74]
251 contaminants (pesticides, pharmaceuticals or	Surface water	Onsite integrative large-volume SPE (HR-X sorbent)	UHPLC-LTQ-Orbitrap MS	60-123	---	[75]

industrial chemicals and their transformation products)						
96 including pesticides and TPs	Surface water, groundwater and drinking water	On-line SPE	UHPLC-QqQ-MS/MS	---	0.005-0.025	[24]
51 pesticides	Surface water and groundwater	On-line SPE (Prospekt-2-system)	LC-QqQ-MS/MS	80-125	0.010	[78]
8 pesticides	Surface water and groundwater	QuEChERS (Acetonitrile, MgSO ₄ and NaCl)	GC-Q-MS	85-103	0.95-13.69	[80]
Cyflumetofen + 2 metabolites	Surface water	QuEChERS (Acetonitrile, MgSO ₄ and NaCl)	UHPLC-QqQ-MS/MS	79-118	0.7-9.8	[21]
102 pesticides	Surface water and groundwater	SBSE (PDMS) (GC) On-line SPE (LC)	GC-Q-MS (27) UHPLC-QqQ-MS/MS (75)	---	0.015-0.025 (GC) 0.005-0.025 (LC)	[77]
10 pesticides	Surface water	HF-LPME	GC-Q-MS	85-115	0.14-1.69	[82]
14 pesticides + 16 PAHs + 26 PCBs + 6 BDEs	Surface water	On-Line SPME (DI, PA fiber)	GC-DFS-HRMS	87-116	0.0001-0.050	[84]
16 pesticides	Surface water, marine water and groundwater	Magnetic SPME with a magnetic DES-based polymeric hydrogel	GC- μ ECD	61-120	0.006-0.399	[86]
24 pesticides	Surface water	SPME (Novel carbon nanomaterial sorbent)	GC-Q-MS	70-123	0.0007-3.7320	[87]
18 chiral pesticides	Surface water and influent and	Magnetic SPME (Amino modified multiwalled carbon nanotubes)	LC-QqQ-MS/MS	83-105	0.00035-0.00204	[88]

	effluent wastewater					
Chlorothalonil + 6 TPs	Surface water and groundwater	Vacuum-assisted evaporative concentration	LC-Orbitrap-MS	85-110	0.0002-0.010	[90]
215 pesticides and TPs (Method SH2437) 30 pesticides (Method LC9045) 3 herbicides (glyphosate, AMPA and glufosinate) (Method GLYPH)	Groundwater	SH2437 & LC9045: Direct injection GLYPH: derivatization with FMOC prior to on-line SPE	LC-QqQ-MS/MS	78-114	0.001-1.350 ^b 0.001-0.028 ^b 0.020 ^b	[25]
150 pesticide metabolites	Surface water and groundwater	Direct injection	LC-QqQ-MS/MS	-	0.003-2.000	[27]
16 polar pesticides + pharmaceuticals	Groundwater	Extraction from passive sampler (POCIS): acetone:methanol	UHPLC-QqQ-MS/MS	42-116	0.00003-0.00135 ^b	[59]

^a Abbreviations: BDEs: Brominated diphenyl ethers; DAD: Diode array detector; DES: Deep eutectic solvent; DFS-HRMS: Magnetic sector-high resolution mass spectrometry; DI: Direct injection; FID: Flame ionization detection; FMOC: 9-florenylmethyl-chloroformate; GC: Gas chromatography; HF-LPME: Hollow fiber-liquid phase microextraction; HLB: Hydrophilic-lipophilic balanced; LC: Liquid chromatography; LLE: Liquid-liquid extraction; LOQ: Limit of quantification; LTQ: Linear ion trap; MS: Mass spectrometry; MS/MS: Tandem mass spectrometry; μ ECD: Micro electron capture detector; OCPs: Organochlorine pesticides; OPPs: Organophosphorus pesticides; PA: Polyacrilate; PAHs: Polycyclic aromatic hydrocarbons; PCBs: Polychlorinated biphenyls; PDMS: Polydimethylsiloxane; POCIS: Polar organic chemical integrative samples; Q: Single quadrupole; QqQ: Triple quadrupole; QTOF: Quadrupole-time of flight; QTRAP: Hybrid triple quadrupole-linear ion trap; SBSE: Stir bar sorptive extraction; SPE: Solid phase extraction; SPME: Solid phase microextraction; TPs: Transformation products; UHPLC: Ultra high performance liquid chromatography; WAX: Weak anion exchange; WCX: Weak cation exchange.

^b Limit of detection.

Table 1.2 Overview of analytical methods applied to determine pesticides in soil matrices^a

Pesticides	Extraction	Determination technique	Recovery (%)	LOQ ($\mu\text{g kg}^{-1}$)	Reference
Famoxadone and metabolites	SLE: Water/ Acetonitrile 1% acetic acid (50:50, v/v)	LC-Orbitrap-MS	72-113	20	[28]
OCPs, OPPs, pyrethroids (58)	SLE: Water/ Acetonitrile 1% acetic acid. Extraction salts: MgSO_4 and sodium acetate Clean up: MgSO_4 , PSA & C18	GC-QqQ-MS/MS	69-119	100-5000	[61]
30-multiclass	SLE: Methanol Clean-up: SPE (Oasis HLB)	LC-QTRAP-MS/MS	70-120	1-10	[93]
18-multiclass	SLE: Water/Acetonitrile (1:5, v/v)	LC-QqQ-MS/MS	50-120	50	[62]
Fenamidone, propamocarb	SLE: Methanol or Water Clean-up: MgSO_4 & PSA	LC-QqQ-MS/MS	77-108	0.4–2	[100]
Oxanilic and sulfonic acid metabolites of acetochlor	SLE: Acetonitrile /Water (60:40, v/v)	LC-QqQ-MS/MS	91-120	1-2	[92]
Endosulfan, chlorpyrifos, and their metabolites	SLE: Ethyl acetate with a 1:5 (w/v) soil-to-solvent ratio	GC-IT-MS	76-95	10-50 ^b	[29]
Acetochlor and Propisochlor	SLE: Methanol/water (1:1 v/v) Clean-up: PSA	GC-ECD	80-116	10	[63]
10 OCPs	SLE: Water/ Acetonitrile Clean-up: MgSO_4	GC-QqQ-MS/MS	70-115	2-40	[106]
10 OCPs and metabolites	QuEChERS. Clean up: Sulphuric acid and florisil	GC-IRMS	60-100	500	[115]
218	QuEChERS using Acetonitrile 2.5% formic acid. Extraction salts: MgSO_4 & sodium acetate	LC-QqQ-MS/MS GC-QqQ-MS/MS	70-120	0.5-20	[99]
Pydiflumetofen enantiomers	QuEChERS Clean-up: MgSO_4 & C18	UHPLC-QqQ-MS/MS	84–103	5	[97]
Pyrethroid pesticide metabolite	QuEChERS Clean-up: d-SPE	GC-IT-MS	70-94	13	[64]
32-multiclass	UAE: 40mL of methanol–water (4:1 v/v). 20 min	LC-Q-MS	60-110	1.5-5.0	[107]

25-Triazines, phenylureas, phenoxy acid pesticides	PLE: Dichloromethane – acetone (1:1, v/v) and Acetonitrile –water (2:1, v/v)	LC-QqQ-MS/MS	65-120	0.1-3	[95]
51 Fungicides and insecticides	PLE: Methanol:Acetonitrile (70:30, v/v) Methanol: Acetonitrile:formic acid (65:30:5, v/v)	LC-QqQ-MS/MS	57-136	0.3-8.5	[96]
9 OPCs & PAHs	MAE: Hexane/water (3:2 v/v)	GC-QqQ-MS/MS	-	-	[104]
8 Pesticides and metabolites	DLLME	LC-FD	70-120	0.07-80	[114]
8 Chiral Pesticides	MSPD-DLLME	LC-QqQ-MS/MS	87-104	0.2-1.5	[65]
5 OPPs	Deep eutectic solvent embedded sponge	LC-UV-Vis	-	-	[113]

^a Abbreviations: DLLE: Dispersive liquid-liquid microextraction; d-SPE: Dispersive solid phase extraction; ECD: Electron capture detector; FD: Fluorescence detection; GC: Gas chromatography; HLB: Hydrophilic-lipophilic balanced; IRMS: Isotope ratio mass spectrometry; IT: Ion trap; LC: Liquid chromatography; MAE: Microwave assisted extraction; MS: Mass spectrometry; MSPD: Matrix solid-phase dispersion; MS/MS: Tandem mass spectrometry; OPCs: Organochlorine pesticides; OPPs: Organophosphorus pesticides; PAHs: Polycyclic aromatic hydrocarbons; PCBs: Polychlorinated biphenyls; PLE: Pressurized liquid extraction; PSA: Primary secondary amine; Q: Single quadrupole; QqQ: Triple quadrupole; QTRAP: Hybrid triple quadrupole-linear ion trap; SLE: Solid liquid extraction; SPE: solid phase extraction. UAE: Ultrasonic assisted extraction; UHPLC: Ultra high performance liquid chromatography; UV-Vis: Ultraviolet-visible detection.

^b Instrumental method ($\mu\text{g l}^{-1}$)

Table 1.3 Overview of analytical methods applied to determine pesticides in biota^a

Pesticides	Matrix	Extraction technique	Determination technique	Recovery (%)	LOQ (ng g ⁻¹)	Reference
50	Fish	QuEChERS	LC-QqQ	---	---	[49]
50 (TPs)	Fish	QuEChERS Clean-up: d-SPE (MgSO ₄ + C ₁₈ + active coal)	LC-QqQ	58-140	0.90-11.25	[46]
40 (TPs)	Fish	QuEChERS Clean-up: d-SPE (MgSO ₄ + C ₁₈ + PSA + activated charcoal)	LC-QqQ	58-145	0.01-1 ^b	[47]
50	Fish	QuEChERS Clean-up: d-SPE (MgSO ₄ + C ₁₈ + PSA + active coal)	LC-QqQ	58-140	0.90-11.25 ¹	[48]
10 OCPs	Fish	PLE: dichloromethane:hexane 1:1 v/v. Clean-up: silica gel & basic alumina	GC-Q-MS	50-110	0.0055-0.0300 dw ^b	[105]
OCPs	Several species	Soxhlet: Hexane:acetone 3:1 v/v. Clean-up: acid silica	GC-Q-MS	---	1-4	[103]
16 OCPs	Soil & microorganisms	Soxhlet: Hexane:dichloromethane 3:2 v/v. Clean up: GPC Hexane:dichloromethane 1:1 v/v	GC-ECD	---	---	[45]

^a Abbreviations: d-SPE: Dispersive solid phase extraction; dw: dry weight; ECD: Electron capture detector; GPC: Gel permeation chromatography; LC: Liquid chromatography; MS: Mass spectrometry; MS/MS: Tandem mass spectrometry; OCPs: Organochlorine pesticides; PLE: Pressurized liquid extraction; PSA: Primary secondary amine; Q: Single quadrupole; QqQ: Triple quadrupole; TPs: Transformation products;

^b Limit of detection

Table 1.4: Overview of analytical methods applied to determine pesticides in air matrices

Pesticides	Matrix	Extraction technique	Determination technique	Recovery (%)	LOQ (pg m ⁻³)	Reference
20	Indoor air	Passive Sampling (VERAM) MAE: acetone:hexane, 1:1 v/v Clean-up: Alumina-C18 Cartridges	GC-Q-MS	59-174	1-10 ^b	[51]
OCPs	Air samples	PAS: PUF. Soxhlet: acetone	GC-Q-MS	82-126	---	[54]
34 (OCPs & CUPs)	Air samples	PUF. Soxhlet: acetone + petroleum ether. Clean-up: silica column	GC-Q-MS	86-102	0.1-90.7 ^c	[55]
40 & TPs	PM10 (remote, urban and rural areas)	MAE: ethyl acetate	LC-QqQ-MS/MS	---	6.5-32.5	[57]
35	PM10	MAE: Ethyl acetate	UHPLC-Orbitrap	73-116	2.6-75	[56]
13	PM2.5	UAE: 18 % of Acetonitrile in dichloromethane	GC-Q-MS	70.2-124 (ethion 31.2 to 63.0)	7.5-60	[58]
452 (OCPs & CUPs)	Air particles	UAE: dichloromethane	GC-QqQ-MS/MS	---	---	[53]

^a Abbreviations: CUPs: Current use pesticides; GC: Gas chromatography; LC: Liquid chromatography; MAE: Microwave assisted extraction; MS: Mass spectrometry; MS/MS: Tandem mass spectrometry; OCPs: Organochlorine pesticides; QqQ: Triple quadrupole; TPs: Transformation products; UAE: Ultrasound assisted extraction; PAS: Passive air sampler; PUF: Polyurethane foam; UHPLC: Ultra high performance liquid chromatography.

^b Limit of detection provided as ng VERAM⁻¹

^c Limit of detection