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QuEChERS sample preparation for the determination of pesticides and other organic residues in environmental matrices: a critical review

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Abstract
QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) is an extraction and clean-up technique originally developed for recovering pesticide residues from fruit and vegetables.
Since its introduction, and until December 2013, about 700 papers have been published using the QuEChERS technique, according to a literature overview carried out using SciFinder®, Elsevier SciVerse, and Google search engines. Most of these papers were dedicated to pesticide multiresidue analysis in food matrices and this topic has been thoroughly reviewed over recent years.
The QuEChERS approach is now rapidly developing beyond its original field of application to analytes other than pesticides, and matrices other than food, such as biological fluids and non-edible plants, including Chinese medicinal plants.
Recently, the QuEChERS concept has spread to environmental applications by analysing not only pesticides but also other compounds of environmental concern in soil, sediments and water. To the best of our knowledge, QuEChERS environmental applications have not been reviewed so far; therefore, in this contribution, after a general discussion on the evolution and changes of the original QuEChERS method, a critical survey of the literature regarding environmental applications of conventional and modified QuEChERS methodology is provided.
The overall recoveries obtained with QuEChERS and other extraction approaches (e.g. accelerated solvent extraction, ultrasonic solvent extraction, liquid/solid extraction and soxhlet extraction) were compared, evidencing for QuEChERS higher recoveries for various classes of compounds, such as biopesticides, chloroalkanes, phenols, and perfluoroalkyl substances.
The role of physicochemical properties of soil (i.e. clay and organic carbon content, as well as cation exchange capacity) and target analytes (i.e. log K_{OW}, water solubility and vapour pressure) was also evaluated in order to interpret recovery and matrix effect data.

Key Words: QuEChERS, environmental pollutants, soil, sediment, water

Introduction

QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) is an extraction and clean-up technique originally developed in 2003 by Anastassiades, Lehotay, Stajnbaher, and Schenck [1], and subsequently validated by Lehotay et al. [2] and Anastassiades et al. [3] for the recovery of more than two hundreds pesticide residues from fruit and vegetables.
The QuEChERS method was introduced as a "green", user-friendly and cheap approach to meet the changing needs of multiresidue analysis arising from the introduction of relatively polar pesticides, the recovery of which was poor with previously developed methods, such as the Mills [4] and the Luke [5] ones. Moreover, these last two methods have a limited compatibility with the modern instrumental approach based on liquid chromatography (LC) coupled with tandem mass spectrometry (MS/MS), which is suitable for the analysis of compounds with a very wide polarity range.
According to a literature overview performed using SciFinder®, Elsevier SciVerse, and Google search engines, more than 700 papers have been published so far using the QuEChERS technique. Most of these papers were dedicated to pesticide multiresidue analysis in food matrices [6]; this topic has been thoroughly reviewed over recent years by the "fathers" of QuEChERS technique [3,7] and other researchers [8,9].
As stated elsewhere [7], QuEChERS should not be intended as an analytical method, but, rather, as a sample preparation approach characterized by high flexibility, which can therefore be adapted to a number of applications, including the analysis of biological fluids [10,11] and environmental matrices such as water, sediments and, above all, soil.
To the best of our knowledge, QuEChERS environmental applications have not been critically reviewed so far. A review focusing on the fundamentals, procedure and applications of the most recently developed sample preparation techniques, including QuEChERS, for environmental analysis has been published very recently [12]. However, the section dedicated to the QuEChERS method is mainly descriptive and comprises only a few applications published so far. Therefore, in this contribution, after a general discussion on the evolution of the QuEChERS method, a critical survey of the literature regarding its environmental applications is provided. Particular attention was devoted to the comparison of the overall recoveries obtained with different QuEChERS procedures or other sample treatment approaches. To this aim we included in this overview only the recovery data reported in literature, calculated in agreement with IUPAC recommendations [13,14], by applying a whole analytical procedure to a spiked sample, in absence of a matrix effect or after its correction.

The original approach

According to the original QuEChERS approach, the sample is accurately weighed in a Teflon centrifuge tube and acetonitrile is added at 1/1 v/w ratio for promoting the extraction of pesticide residues; after manual shaking, anhydrous $MgSO_4$ and NaCl are then added and the mixture obtained is shaken again to promote the water partition from the organic phase and its dehydration. Triphenylphosphate is then added as an internal standard and after brief shaking the mixture is centrifuged. An aliquot of acetonitrile supernatant is recovered for the clean-up step which is performed by a dispersive solid-phase extraction (d-SPE) approach. Operatively, the extract is transferred into a micro-centrifuge vial containing the "primary secondary amine" (PSA) sorbent and anhydrous $MgSO_4$. Since PSA sorbent is a weak anion exchanger, it interacts strongly with previously co-extracted acidic compounds (e.g. sugars, fatty acids and organic acids), thus removing them from the acetonitrile phase. The addition of $MgSO_4$ removes the water content in the extract and consequently enhances the partition of the above-mentioned matrix interfering compounds (in particular fatty acids) on PSA sorbent. After brief shaking and centrifugation, the

supernatant is recovered and analysed via gas chromatography (GC) or liquid chromatography (LC) coupled to mass spectrometry (MS).

Evolutions in the QuEChERS method

Although the original method proved to be efficient for the recovery of a wide variety of pesticides from a large group of food matrices, during the application of this analytical protocol to real samples several changes were introduced in the procedure in order to make the method perform even better with certain analytes and matrices. According to recent interviews with Lehotay and Anastassiades [15], improvements are related to both the extraction and clean-up steps, as described hereunder.

Extraction pH

In the first approach, no pH control was carried out, thus limiting the performance and also the applicability of the method to certain pesticides, owing to ionization and/or degradation phenomena. In fact, the pesticide class comprises compounds with very different acid-base properties, which strongly influence their water-acetonitrile partition. In this regard, it should be noted that pesticide molecules often contain more than one acid-base moiety, such as protonable nitrogens and carboxylic groups that give rise to charged molecules in a wide range of pH values, thus making it critical to assess an optimal pH for their water-solvent partition. Moreover, some pesticides may undergo degradation processes at both high and low pH-values. For example, pesticides containing the N-trihalomethylthio functional group, such as folpet, captan, dichlofluanid and tolylfluanid are base-sensitive and should be extracted at pH < 4, whereas other pesticides like carbosulphan and pymetrozine are acid-sensitive [16] and their optimal recovery pH should therefore be basic.
It must be underlined how, as with foods, environmental matrices such as soil, may also exhibit different intrinsic acidities. Hence the use of buffers can be useful in making the QuEChERS method suitable for a wider group of matrices and analytes. Two buffered procedures able to keep pH constant around 5 were independently proposed by the two “fathers” of this sample preparation technique, based on acetate [17] or citrate [3] buffers. In fact, this pH value allows for achieving satisfactory recoveries (usually higher than 70%) for acid-sensitive pesticides without any degradation of base-sensitive compounds [15].
The two buffered versions of QuEChERS have been extensively evaluated in inter-laboratory trials, thus giving rise to the two official methods AOAC 2007.01 [18] and EN 15662 [19].

Clean-up

As mentioned above, in the QuEChERS method the clean-up step is based on the simultaneous action of anhydrous $MgSO_4$ and PSA sorbent, the latter added as a dispersive-phase agent, instead of being packed in SPE cartridges. The d-SPE approach is without doubt cheaper and faster than the column SPE and it is usually presented in QuEChERS literature as an almost defect-free technique [7]. However, it should be noted that the d-SPE approach requires the discarding of the dispersive phase, in which some target analytes may be eventually retained. For instance, acidic pesticides such as 2,4-dichlorophenoxyacetic acid (pKa=2.9 [20]) are strongly retained by PSA and must be analysed separately in an aliquot of the extract before adding the PSA itself [21]. In this regard, it is interesting to note the possible advantage of the SPE cartridge approach in allowing the recovery of target analytes retained in the cartridge through a proper fractionated elution.
Graphitized carbon black (GCB) or octadecyl-silanized silica gel (C_{18}) coupled with PSA were proposed by Lehotay et al. for a more efficient clean-up in fatty food matrices [17,22].
However, owing to its specific structure, GCB sorbent is characterized by high retention of planar pesticides such as thiabendazole, terbuphos and hexachlorobenzene. To minimize pesticide losses, GCB-PSA double-layer SPE cartridges were proposed for the clean-up step of the acetonitrile extract using toluene for recovering target analytes [17].
LC-MS/MS and GC-MS (or GC-MS/MS) have been used for pesticide detection. LC-MS/MS covers a broader group of pesticides (including the thermolabile and polar ones) and simplifies the

sample preparation (no need for derivatization, compatibility to aqueous matrix and polar solvents, online clean-up or enrichment procedures); furthermore, LC-MS/MS in most cases allows for obtaining better sensitivities than GC-MS and GC-MS/MS [23]. However, some pesticides such as brompropylate and chlorfenapyr are not amenable to LC and well-analysed by GC, whereas other active molecules, like captan, dicofol and chlorothalonil are problematic analytes with both LC and GC [15]. Irrespective of the detection technique, the clean-up step is of paramount importance for conferring ruggedness and reliability to the chromatographic analysis, which is usually sensitive to matrix-effects.

LC-MS/MS response is generally improved by the purification of the extracts. In GC, the non-volatile matrix components can be trapped in the injection system and/or in the column, altering the chromatographic response and increasing the need for maintenance [24,25]. However, this phenomenon does not necessarily produce a suppression of the chromatographic response; conversely, in the case of polar pesticides, the presence of matrix components in the injected extract gives rise to a signal increase compared to the injection of standard solutions in solvent; this phenomenon is known as "matrix induced chromatographic response enhancement" (MICRE). In fact, polar pesticides, such as organophosphates, but also polar matrix components, have both a strong affinity for hydrogen-bonding adsorption sites in the injector (e.g. liner and glass wool) and the column. In the absence of matrix components, the target analytes are retained, thus giving rise to peak broadening and loss of sensitivity [26]. It should also be noted that degradation phenomena may occur in the injector due to the high temperature.

The most widely used approach to account for suppression or enhancement phenomena related to the presence of matrix components in the extract entails the use of the "matrix-matched calibration" (MMC) method [15], even though it is expensive and laborious.

To minimize the GC MICRE, the use of so-called "analyte protectants", originally proposed by Erney et al. [27], was successively investigated [26,28,29]. These compounds should have strong hydrogen bonding capabilities to de-activate the adsorption sites of the GC system and are added to the final extract before injection. Analyte protectants should provide antioxidant activity as well, in order to minimize oxidative degradation of the target analytes [30].

QuEChERS applications to soil analysis

Since its first application to soil analysis in 2008 [31], the QuEChERS procedure has been increasingly used for the extraction of organic compounds of environmental concern, even though this application was not encouraged by the QuEChERS fathers owing to the possible negative influence on the recovery arising from the retention properties of the soil matrix [6,15]. Target analytes, overall extraction procedures and instrumental techniques adopted for soil analysis, together with recoveries and relative standard deviation percentages (RSD%) are illustrated in detail in Table 1. As shown in this table, in a few cases the QuEChERS method has been applied in its original form, while most studies have adopted more or less modified procedures. As usually performed for dry food samples, water has often been added to the soil before the analysis, in the aim of reconstituting a matrix with a high water percentage, for which the QuEChERS method was originally designed; in these cases, mixing times from one minute [32] up to 30 minutes [33] between water and soil have been adopted.

More drastic changes to the original procedure, such as the use of the ultrasonic-assisted extraction [34-36] and/or the modification and/or the elimination of the clean-up step [33,37-43], have been introduced for improving the recovery.

Many organic compound classes, both pesticide and non-pesticides molecules, have been determined in soil using the QuEChERS approach.

In order to facilitate the reading comprehension, the studies reported in literature have been reviewed by splitting the investigated molecules into "pesticide" and "non-pesticide" categories and discussing them separately.

Pesticides

The QuEChERS method has been applied to the extraction from soil of more than 150 pesticide molecules belonging to the most important chemical and functional classes. Below, the literature data are reviewed and discussed according to the chemical characteristics of the investigated molecules which are organized in structurally homogeneous groups.

Organochlorine

Organochlorine pesticides (OCPs) are chemicals generally characterized by high toxicity, high persistence in the environment and high lipophilicity, thus they potentially accumulate in fatty tissue and are magnified to higher trophic levels. Consequently, OCPs have been banned in Europe, the United States and other countries as plant protection products. However, some OCPs are still produced for other scopes (e.g. DDT for malaria control programs in Africa) and due to their persistent nature are subject to long-range transport. Hence OCPs analysis in soil is still of current interest and over recent years some authors have used the QuEChERS method for OCPs determination.

The citrate buffered QuEChERS approach was applied to a re-hydrated agricultural soil by Yang et al. [44], for the multiresidual determination of 38 pesticides, including the OCPs dicofol, α-endosulfan and β-endosulfan, using 2/1 CH_3CN/soil v/w ratio and GC-MS as an instrumental detection technique. The method proposed was not affected by the matrix effect and provided quantitative recoveries for α- and β-endosulfan, irrespective of the spiked concentration in soil; conversely, for dicofol the recovery was spike-level dependent and ranged from 53% (50 ng/g spiked) to 94% (10 ng/g spiked).

The extraction of twenty-two OCPs has been investigated using either the original or modified QuEChERS methods. Fourteen molecules of this group (α-HCH, β-HCH, δ-HCH, HCB, lindane, aldrin, dieldrin, endrin, α-endosulfan, β-endosulfan, p,p'-DDE, p,p'-DDD, o,p'-DDT and methoxychlor), most of which belong to the so-called dirty dozen [45], have been extensively studied by various authors to evaluate recovery under different experimental conditions. Fernandes et al. [46] obtained recoveries lower than 50% for most analytes when the conventional 1/1 CH_3CN/soil v/w ratio was adopted. Interestingly, for the above-mentioned pesticides, we found a significant negative linear correlation (R^2=0.62, P=0.0015) by plotting these recoveries as a function of log K_{OW} values [20]. A noticeable increment of the recovery (increment range: approximately from 10% for HCHs to 50% for dieldrin and p,p'-DDD) was observed with the introduction of a re-hydration step before extraction with CH_3CN and the use of a solvent in excess of the analysed soil amount [46]; the importance of sample re-hydration was also confirmed in another study by the same team [32] (Fig. 1). As a possible explanation of this result, it should be noted that water can successfully compete with pesticides for adsorption sites of soil humic substance, promoting their desorption; moreover, the soil re-hydration step allows acetonitrile to gain better access into the soil pores, thus improving the partitioning process between the aqueous and organic phases.

Conversely, Lesueur et al. [31] achieved good recoveries for γ-HCH (89-116%) and dieldrin (69-101%) applying the original QuEChERS protocol to three non-rehydrated commercially available reference soils, using a 2/1 CH_3CN /soil ratio and GC-MS for quantification. However, since no investigation of the matrix effect was performed and external standard calibration curves in solvent were used for quantification, it is not clear how much the recovery data were affected by the matrix. Accordingly, in agreement with IUPAC recommendations [14], these recovery data should be considered more properly as "apparent recoveries".

According to Fernandes et al. [46], the introduction of an additional ultrasonic-bath treatment before the d-SPE clean-up step, besides the above-mentioned use of a solvent excess (2/1 v/w solvent/soil ratio), represents a modification of the original QuEChERS procedure that allows for achieving a general increase in the recoveries; more in detail, the recovery increase due to the introduction of ultrasounds was particularly significant (> 20%) for δ-HCH, α-endosulfan and β-

endosulfan, whereas the increase in the solvent/soil ratio led in most cases to overall recoveries higher than 80%. Even though a rather low matrix effect was observed, the MMC was chosen for quantification. Time and power of sonication should be optimized according to the soil organic carbon content and its resulting retention properties towards OCPs [32].
The soil re-hydration step before extraction with acidic acetonitrile (see Table 1) was adopted by Rashid et al. [33] for the GC-MS/MS determination of 19 OCPs (including those investigated by Correia-Sá et al. and Fernandes et al. [32,46]), in different soils. A final CH_3CN extract limited the GC injection volume to 1 μL, thus negatively influencing the method sensitivity; in order to overcome this limitation, the authors proposed an unconventional clean-up, consisting of the addition of water to the CH_3CN extract and its liquid-liquid back extraction into n-hexane, for which a higher injection volume is permitted [33]. This approach also allowed for easily reducing the volume of the final extract, thus further increasing sensitivity, even though its application to more polar pesticides seems to be problematic. The recoveries obtained with this method (using MMC) were in most cases higher than or equal to 70% and seemed not to be affected by soil characteristics, which were very similar for all the soils investigated. As noted in other studies [32,40,46,47], the lowest recovery (47-56%) was observed for HCB.
Alpha, beta, gamma and delta HCH isomers, and HCB have been analysed in soaked peat by using QuEChERS and GC-MS [47]. In this study some key-parameters of the extraction and clean-up steps, such as the use of CH_2Cl_2 instead of CH_3CN as the extraction solvent, the elimination of the PSA clean-up step, and the use of different ratios between soil amount and solvent volume, were investigated. With regard to this last parameter, it should be noted that the soil was soaked in order to ensure the same water content for all soil samples investigated; hence, the analysis of different amounts of soil for a certain volume of solvent corresponds to different water contents of the extracted mixtures. Since the salt amount was kept constant, irrespective of the sample amount analysed, for higher sample amounts (3-5 g), the salt was not sufficient for absorbing water, thus resulting in lower recoveries. Moreover peat is rich in organic carbon, mainly of an acidic nature and matrix extracted compounds should therefore exhibit a strong affinity for hydrogen-bonding adsorption sites in the injector and the column. According to this consideration, a significant MICRE was observed and MMC was necessary for HCH isomer quantification. In this regard it should be noted that the analyte protectants tested by Rouvière and co-workers as an alternative solution of the MICRE failed completely, probably due to the different volatility characteristics of the tested protectants and the OCPs analysed. Extraction with CH_3CN provided significantly higher recoveries (range: 82-94%) than CH_2Cl_2, whereas the presence of the d-SPE clean-up did not highlight any great improvement. Interestingly, it should be noted that by using the proposed method, Rouvière and colleagues obtained a very good recovery (94%) even for HCB.

Organophosphorus

Organophosphorus pesticides (OPPs) are a second-generation class of insecticides which were synthesized and used after the first-generation organochlorine insecticides had been banned.
The OPPs class includes compounds with very different structural characteristics, in which the common moiety can formally be considered the phosphoric acid ester group reported in Fig. 2, where X is a leaving group of variable structure, and R_1 and R_2 can be alkoxy, amino, thioalkyl, phenyl or other substituent groups [48,49].
OPPs are characterised by high acute toxicity for humans; however, they generally undergo rapid biodegradation in soil and water, thus being of minor environmental concern compared to OCPs. Nevertheless, some OPPs are currently banned (parathion, chlorfenvinphos, methidathion, triazophos) and the use of some of them (diazinon, dichlorvos, malathion, fenitrothion) is restricted in Europe [50].
Due to the wide use of OPPs for plant insect control, their analysis in soil is up to date and OPPs are very often included in the development of specific or multiresidue analytical methods [31,44,46,51,52].

Asensio-Ramos et al. [51] investigated the matrix effect and recovery in the extraction of ten OPPs (see Table 1) from three different soils, using a buffered QuEChERS procedure in which CH_3CN was added to the dried soil at a ratio of 2/1 v/w and a sonication step was introduced before clean-up. Moreover, a final solvent exchange from CH_3CN to cyclohexane was carried out prior to the GC-MS/MS analysis, probably in the aim of injecting a solvent with better gas-chromatographic performances than CH_3CN. With this method all the investigated soils showed a significant matrix effect and the MMC was therefore applied. The recoveries were mostly higher than 70%, except for fenitrothion, and above all malathion and malaoxon, the latter being a degradation product of the former. According to the authors, this result could mainly be ascribed to degradation phenomena rather than to soil retention.

Yang et al. [44] investigated the recovery of 13 OPPs using the previously described buffered multiresidue method (see Table 1), and obtained satisfactory recoveries, ranging from 77% to 102% for profenophos and phoxim respectively.

Fernandes et al., included three OPPs (diazinon, chlorpyrifos and malathion) in their optimized multiresidue method [46], described in the previous paragraph. As reported for OCPs, the sample re-hydration, the doubling of solvent/soil ratio and the introduction of the sonication-assisted extraction improved the recovery of OPPs as well. The recoveries, evaluated at four spike levels and on two different soils, were satisfactory for chlorpyrifos and above all diazinon, which were found in the ranges 70-83% and 88-103% respectively, depending on the soil and the spiked concentration investigated. Conversely, the recovery of malathion was in any case significantly higher than 100% (range: 129-150%), despite the use of the MMC approach. Even though the presence of a matrix effect was not highlighted by the authors, no other apparent reasons can be hypothesized for explaining the recovery data obtained for malathion.

Chlorpyrifos and its derivative chlorpyrifos-methyl, together with the chlorfenvinfos, were analyzed by Lesueur et al. [31] employing the original QuEChERS protocol (see Tab.1); recovery results were strongly dependent on the soil investigated, but they cannot be explained on the basis of the organic matter content, with the highest values (93-106%) obtained for Eurosoil 7 (organic matter content 11.52%) and the lowest (27-60%) for the corresponding subsoil SO26 (organic matter content 1.81%). However, as underlined above, the lack of soil re-hydration could have compromised the recovery; moreover, the absence of a study on matrix-effect is a further element of uncertainty in the evaluation of results.

Recently, Li et al. [52] applied an unbuffered QuEChERS procedure to the enantioselective LC-MS/MS analysis of nine enantiomeric pairs of pesticides belonging to various classes, including the OPPs isocarbophos and fenamiphos, which do not contain ionisable groups. Besides the peculiar chromatographic conditions adopted for chiral separation, the extraction method was validated on a sandy-loam soil at three different spike levels (5, 25 and 50 µg/kg), taking into account the matrix-induced signal suppression/enhancement; quantitative results (higher than 80%) were reported for all the investigated racemates.

Carbamate derivatives

Carbamic acid derivatives are a group of pesticides mainly used as insecticides, since they act as inhibitors of acetyl cholinesterase enzymes, similarly to OPPs [53]. Hence, they exhibit a significant acute toxicity towards human beings and some of them (e.g. carbofuran and carbaryl) have therefore been banned in Europe, whereas the use of this compound class is still permitted in United States.

Nine carbamate derivatives (i.e. carbaryl, carbofuran, isoprocarb, methiocarb, methomyl, phenmedipham, promecarb, propoxur and prosulfocarb) have been investigated on re-hydrated samples, using more or less modified QuEChERS methods [39,44,46,53,54]. These molecules do not contain ionisable groups and should not therefore be sensitive to pH for their extraction and clean-up. In accordance with this consideration, very good recoveries were obtained for various carbamic pesticides by Santalad et al. [53] (82-114% for propoxur and promecarb, respectively), who coupled an unbuffered sonication-assisted QuEChERS extraction to a clean-up based on the

use of C18 cartridges. In this paper [53] it is also remarkable that the instrumental analytical technique consisted of micellar electrokinetic chromatography with Pt-electrode amperometric detection.
According to Fernandes et al. [46], the use of sonication also improved the recovery of methiocarb; however, buffered QuEChERS approaches without sonication were adopted for the analysis of prosulfocarb [54], isoprocarb, carbofuran [44] using different solvent/soil ratios (see Table 1), in all cases obtaining recoveries higher than 75%.
A simplified QuEChERS procedure for the LC-MS/MS analysis in soil of phenmedipham, together with four other non-carbamate herbicides (i.e. atrazine, mefenacet, metholachlor and hexazinone) was introduced by Mei et al. [39]. The novelty of the method lies in the fact that the extraction and clean-up processes were completed in a single step by the sequential addition of the reagents in the same extraction tube. The method was validated with soil samples spiked at two fortification levels (4 and 40 μg/kg), using the MMC approach; recoveries were in the range of 75 %–95 % depending on the type of clean-up adsorbents used, as the best results were obtained with PSA/C18 mixture 1:1.
A QuEChERS approach modified for the use of ethyl acetate as extraction solvent in unbuffered media was found to be effective by Sahoo et al. [55] for the quantitative recovery of propamocarb, using GC-MS as instrumental detection equipment (see Table 1). The method was successfully employed for analysing both soil and vegetables, thus evidencing once again the versatility of the QuEChERS approach.

Pyrethroids

Pyrethroid pesticides (PPs) were developed as a synthetic version of pyrethrins, the naturally-occurring insecticide found in chrysanthemums and represent the third-generation insecticide class. As with pyrethrins, pyrethroids are characterized by much lower acute toxicity for mammals and birds than OPPs. For this reason an increase in their use, together with a declining utilization of OPPs, has been highlighted [56].
The QuEChERS approach has been adopted for pyrethroid analysis in a multiresidue environment, whereas methods specifically designed for pyrethroid extraction from soil, have not yet been reported in literature.
With the previously described multiresidue method, Yang et al. [44] analysed deltamethrin, cypermethrin, cyfluthrin and fenvalerate, obtaining very good recoveries for all the investigated PPs (ranging from 97% to 128% for cypermetrhin and fenvalerate respectively) with spike levels of 10, 50 and 100 ppt. Mantzos et al. [35], working with the same spiking level range and using an ultrasonic assisted QuEChERS method, obtained similar results for cypermetrhin (89-108%) (see Table 1). In this regard, Fernandes et al. demonstrated the crucial role of ultrasounds also for improving the recovery of deltametrin and bifentrin, thus obtaining good extraction yields for these two PPs from different soils [46].

Azole derivatives

Among the compounds belonging to this class, chemicals with pesticide functions are mainly triazole derivatives, which have been largely used as systemic fungicides due to their inhibition activity towards enzymes involved in the biosynthesis of steroid hormones. However, this mechanism is generally active in wildlife, including mammals; according to the elevated persistence of these compounds in the environment, most of them (namely: carbendazim, difeconazole, epoxiconazole, fenbuconazole, propiconazole, tebuconazole and triadimefon) are an environmental concern and are included on the EU endocrine disruptor list.
A number of azole derivative pesticides were investigated by different authors employing the QuEChERS extraction approach [31,36,38,39,44,46,52,54,57-59].
Fenbuconazole was firstly investigated by Li and co-workers on a sandy-loam soil using a conventional QuEChERS extraction and clean-up method, achieving recoveries around 90% [57]. Recoveries approximately equal to or higher than 80% were obtained by the same team [58], on the

same sandy-loam soil, for eight triazole fungicides, including fenbuconazole, using the previously described unbuffered QuEChERS method with C18 d-SPE clean-up. According to the pKa values [20] of these compounds, the lack of pH control should not influence the recovery in the pH range 3-12.

Caldas et al. [38] evaluated some crucial parameters of QuEChERS extraction and clean-up for the analysis of two triazole fungicides (i.e. propiconazole and tebuconazole), one pyrazolic insecticide (i.e. fipronil) and one isoxazolidinone herbicide (i.e. clomazone), evidencing a significant recovery increase of clomazone and above all fipronil in response to the addition of 0.1% acetic acid. The influence of acidity can be explained on the basis of an increase of pesticide stability, and seems to be more effective for fipronil due to the presence of the trihalomethylthio functional group in the target molecule, as mentioned in paragraph 1.2.1. It should however be noted that fipronil, together with propiconazole and triadimefon, were quantitatively recovered by Yang et al. [44] from an uncharacterized soil, using a conventional buffered QuEChERS method, without any further acid addition. According to Caldas and co-workers [38] a further significant positive effect on clomazone recovery arose from the elimination of sodium chloride, which caused a higher water content in the CH_3CN extract and a higher polarity of the organic phase; hence, polar compounds such as clomazone (log K_{OW}=2.5) should be more favourably partitioned in the organic solvent. The elimination of sodium chloride during the unbuffered extraction and partitioning phases was also adopted by Mei et al [39] to analyse mefenacet, a medium-polarity thiazole derivative (log K_{OW}=3.2), obtaining recoveries higher than 90%. However, this modification surely leads to a poor phase separation; moreover, other authors reported very effective recoveries for polar azole derivatives using the conventional salt addition ($MgSO_4$/NaCl 4/1), as in the case of Li et al. [52] for paclobutrazol (log K_{OW}=2.8). The d-SPE clean-up step was also evaluated by Caldas et al. [38], who took into account both PSA and a mixture of PSA and C18, leading to the conclusion that this step decreased recovery. Under the best experimental conditions reported in Table 1, Caldas and co-workers [38] obtained satisfactory recovery percentages varying from 71% (clomazone) to 120% (fipronil) in the spike range from 10 to 500 ppb. However, the conclusions drawn by Caldas et al. cannot be generalized since the need and the effect of a clean-up step are strongly dependent on the properties of the investigated soil, as well as the characteristics of target analytes and the analytical robustness of the instrumentation used. For example, Guan and Zhang [59] obtained a quantitative recovery from an uncharacterized soil for benazolin-ethyl, a polar benzothiazole derivative (log K_{OW}=1.9), using an unbuffered QuEChERS extraction followed by a d-SPE clean-up with a PSA-C18 mixture.

Fernandes et al. [46] adopted the previously discussed ultrasound-assisted QuEChERS procedure for the analysis of myclobutanil and tetraconazole. Surprisingly, despite the use of MMC, recoveries obtained for the latter triazole derivative were in the range 124-145%. As for the other pesticide classes investigated by Fernandes et al., the positive influence of sonication on the recovery was demonstrated for these two herbicides.

Very recently, the emerging insecticide cyantranilprole was analyzed by Sun et al. [60], obtaining quantitative recoveries (see Table 1).

Urea derivatives

Urea derivatives are pesticides widely employed for weed control (e.g. sulphonylureas and phenylureas) due to their capacity to interrupt the electron transport chain in photosynthesis, or as insect growth regulators (e.g. benzoylureas) since they inhibit the synthesis of chitin, a vital part of the insect exoskeleton during the moult stage. These mechanisms are responsible for toxic effects towards terrestrial and aquatic environments and some urea derivatives (i.e. methabenzthiazuron, metoxuron, monolinuron) have therefore been banned in Europe.

A group of nine phenylurea derivatives, together with one benzothiazolic urea have been investigated by Lesueur et al. [31] on three reference soils, using the method described above (see Tab.1). Recoveries differed greatly from one soil to another, but they cannot be explained on the

basis of their properties; moreover, they showed an erratic trend as a function of log K_{OW} of target analytes.
Wang et al. [61] investigated the diafenthiuron temporal decline under field application, using an unbuffered QuEChERS approach (see Table 1). This method was fully validated through the MMC approach and included the soil re-hydration and an ultrasonic-assisted extraction. This last procedure was demonstrated to be of paramount importance for the recovery of diafenthiuron, thus increasing the recovery percentage from 60% up to 95-100%. An analytical approach quite similar to that of Wang and co-workers, modified for the use of the vortex instead of ultrasounds, was performed by Zhao et al. [62] for the analysis of monosulfuron ester with satisfactory results (see Table 1). Unlike Zhao and co-workers, Wu et al. [63] observed that the use of PSA clean-up negatively influenced the recovery of rimsulfuron, a urea herbicide structurally related to monosulfuron; for this compound a recovery as high as 81% was obtained with the use of C18 d-SPE.

Triazine and diazine derivatives

A group of four structurally related triazine derivatives widely used as herbicides (atrazine, simazine, propazine, terbutylazine) and two metabolites (desethylatrazine, desisopropylatrazine) have been investigated by different authors using the QuEChERS sample treatment approach [31,39,44,54]. The application of a conventional QuEChERS method to the analysis of atrazine, simazine, desethylatrazine and desisopropylatrazine in three non-hydrated soil samples was investigated by Leuseur et al. [31], who found recoveries included between approximately 45% and 85%, depending on the soil and the analyte investigated. The comparison of atrazine recoveries obtained by Leuseur et al. [31] (58-82%), Mei et al. [39] (86-91%) and Yang et al. [44] (88-95%) suggested an important role of soil re-hydration for obtaining quantitative yields even for this compound, which is characterized by a log K_{OW}=2.63. Accordingly, quantitative recoveries were obtained by Nagel et al. [54] for propazine and terbutylazine using the soil re-hydration technique. This approach seems to be useful also for achieving a more effective extraction of polar triazinone herbicides, as hexazinone is recovered more efficiently on re-hydrated soils [39] than metamitron without this expedient [31]. Similar considerations can be drawn by comparing the recoveries obtained from agricultural soils for the insecticide buprofezin (a hydrophobic diazinone derivative with log K_{OW}=4.3) by Yang et al. [44] and Asensio-Ramos et al. [51]. Very good recoveries were also reported by Li et al. [52] and Yang et al. [44] for other diazinone derivatives (i.e. indoxacarb and pyridaben), using the soil hydration method.
As described above, for some azole derivatives, the recovery of azoxystrobin (a structurally complex pyrimidine derivative devoid of ionisable groups) was in the range of 74-119% and positively affected by the addition of 0.1% CH_3COOH and the absence of NaCl in the extraction mixture [38]. This molecule, together with other pirimidine derivatives (i.e. bupirimate, pyrimethanil, mepanipyrim and cyprodinil) was analysed by Fernandes et al. [46] using the optimized QuEChERS method, extensively described above, which allowed for obtaining quantitative extractions (97-121%).

Biochemical pesticides

According to the Environmental Protection Agency [64], biochemical pesticides (BPs) are naturally-occurring chemicals that are extracted from living organisms such as plants, bacteria or minerals. They are all able to control pests with non-toxic mechanisms and are therefore permitted in organic farming.
To the best of our knowledge, the application of QuEChERS methodology to the analysis of biochemical pesticides in soil has only been reported in two papers [65,66].
Drożdżyński and Kowalska [65] first investigated azadirachtin, rotenone, spinosyn A and spinosyn D (see Table 1) using a buffered QuEChERS extraction method with a PSA-C18 d-SPE clean-up and an elaborate solvent exchange procedure prior to the LC-MS/MS analysis. With this method no significant matrix effect was observed and recoveries higher than or equal to 83% were achieved.

Prestes and co-workers developed and validated an analytical procedure for the simultaneous determination in soil of 15 BPs (comprising the above-mentioned spinosyn A), including piperonyl butoxide (commonly used as synergists of certain pesticides such as carbamates, pyrethrins and pyrethroids), via buffered QuEChERS extraction, without any clean-up step [66]. The elimination of the clean-up step allowed for obtaining a higher throughput, but it was probably the origin of the significant matrix effect observed for some analytes that obliged the authors to adopt the MMC. Recoveries evaluated at spiking levels included in the range of 10-100 ppt, were in most cases higher than 75%, even though very low values were found for nicotine (34%) and sabadine (37%). As regards spinosyn A, a lower recovery was obtained by Prestes and co-workers [66] (68-91%) compared to the results of Drożdżyński and Kowalska [65] (98-104%). Even though no clear trend was observed for recoveries obtained by Prestes et al. as a function of log K_{OW} values, the linear regression between these two variables was statistically significant (R^2=0.60; *P*=0.0007) and the lowest recovery percentages were observed for the above-mentioned BPs, which are characterized by negative log K_{OW} and therefore poorly partitioned in organic solvents, compared to water.

Other pesticides

Many other pesticides, characterized by chemical structures differing from those previously discussed and belonging to the functional classes of insecticides, herbicides and fungicides, have been investigated using QuEChERS procedures [34,39,44,46,52,54,55,59,67-72].

Among these pesticides, procymidone, a medium-polarity dichloroanilide derivative (log K_{OW}=2.9) used as a fungicide, was successfully recovered (82-121%) from re-hydrated soils, using the conventional QuEChERS approach [67], as well as variously modified methods, such as buffer addition [44,46] or the use of ultrasounds during extraction [46]. The recovery of other dichloroanilide derivatives (i.e. iprodione, vinclozilin and fenhexamid), structurally similar to procymidone, were also investigated by Fernandes et al. [46], obtaining much higher values than 100%, despite the use of MMC.

The recovery of four dialkylanilide derivatives (i.e. acetochlor, butachlor, metolachlor and oxadixyl) was investigated by Yang et al. [44] achieving very good results in all cases. Metholachlor was also investigated by Mei et al. [39], confirming the very good performance of the QuEChERS approach for the extraction of these molecules from soil.

Pendimethalin and trifluralin, two hydrophobic dinitroaniline derivatives (log K_{OW}=5.20 and 4.56, respectively) used as herbicides, were quantitatively recovered by Nagel [54], who adopted the original method modified for sample re-hydration and buffer addition, obtaining quantitative recoveries. Based on data of Fernandes and co-workers [46], the addition of water to the sample and above-all, the use of the 2/1 CH_3CN/soil v/w ratio, was advantageous for the recovery of pendimethalin.

Other pesticide molecules, such as propisochlor (an important emergent chloroacetanilide herbicide) [70], metaflumizone [34,68], quizalofop-p-ethyl [46,52,59], quinchlorac [69], bispyribac [72], fluopicolide [55] and clethodim [71] have recently been extracted from soil samples by different authors using the QuEChERS approach; the very good recoveries obtained for these pesticides, irrespective of the soil and the various modifications to the original procedure (see Table 1), confirmed once again the versatility of this sample preparation approach.

Non-pesticide organic pollutants

Phenol derivatives

Phenol and a number of chlorophenols were determined in soaked peat in the study of Rouvière et al. (see the section “QuEChERS application to soil analysis”, “*Organochlorine*” paragraph) [47]; recoveries were affected by the ratio between soil amount and solvent volume, as with OCPs. The clean-up step also influenced the recovery, producing a significant decrease in phenolic compound concentrations in the final extract. Finally, CH_3CN produced less repeatable recoveries than CH_2Cl_2, often much higher than 100%, probably owing to an unfavourable solvent-matrix interaction and/or instrumental analytical artefacts.

Six of the eight chlorophenols studied by Rouvière et al. were also investigated by Padilla-Sanchez and co-workers [73] on re-hydrated agricultural soil samples, adopting a QuEChERS procedure devoid of clean-up, in which acidified CH_3CN was used as the extraction solvent. Moreover, the optimized procedure required the use of higher amounts of $MgSO_4$ in order to obtain the complete removal of water (see Table 1 for details); after derivatization at room temperature with acetic acid anhydride, the analytes were determined by GC-MS/MS. According to this procedure, all the investigated chlorophenols, as well as some alkyl and nitrophenols, were recovered very well (recovery range: 84-116%), even though in all cases a matrix effect was observed, thus making it necessary to adopt the MMC for quantification.

Perfluorinated compounds

The first application of the QuEChERS procedure to extract perfluoroalkyl substances (PFAS) from peat bogs was made by Dreyer et al. [74] in the aim of assessing whether ombrotrophic bogs are natural archives suitable to reconstruct historical atmospheric PFAS pollution. The authors performed an in-depth investigation of the extraction and clean-up steps employing different QuEChERS reagents, commercially available within protocols suggested by various manufacturers. The optimized method was based on a double ultrasonic extraction with CH_3CN, each one using a 2/7.5 sample/solvent ratio followed by the addition of the two QuEChERS component mixtures Macherey & Nagel, Mix I and Mix V (see Table 1). The use of labelled internal standards allowed for correcting the matrix effect, thus obtaining recoveries in the range of 83-111% for 21 out of the 24 compounds tested.

Chlorinated hydrocarbons

Rouvière et al. [47] provided the investigation of several chlorinated hydrocarbons, obtaining higher recoveries with CH_2Cl_2 than CH_3CN; as previously observed for other compounds, the better recoveries were found using a 1/7.5 soil/solvent ratio, while the results were weakly affected by the presence/absence of the clean-up step. The high volatility of some target analytes, such as dichloro- and trichloro-alkanes, and dichloro- and trichloro-alkenes, with 2-3 carbon atoms, also influenced the recovery which ranged from 72 to 79%, compared to 92-95% for trichlorobenzenes.
Trihalomethanes (THMs) were investigated by the same team in three different papers, using the same QuEChERS method with GC coupled to both electron-capture (ECD) [40,75] and MS detectors [41]. Due to the high volatility of these compounds, analytical procedures should entail the least possible sample manipulation; in order to fulfil this requisite, the authors avoided the clean-up step. Moreover, the use of GC techniques called for a change of extraction solvent from acetonitrile to ethyl acetate [40]. The use of ECD allows for obtaining high sensitivity and selectivity, thus reducing the matrix interference and providing recoveries included within the range of 62–93% for chloroform, 1,2-dichlorobenzene, and HCB; similar results were achieved by Martin et al. [75] for THMs (recoveries range: 65-94%). The same authors investigated THMs, benzene, toluene, ethylbenzene and xylenes by GC-MS equipped with a programmable temperature vaporizer and a liner packed with Tenax-TA [41]. This apparatus allows the injection of large volumes of sample, enhancing the method sensitivity without any concentration steps. The recoveries (ranging from about 68% to 75%) rose as the boiling point of the analytes increased, thus evidencing the importance of this physicochemical property for evaluating the potential analyte losses during the sample manipulation steps.

Pharmaceutical compounds

The analysis of pharmaceutical compounds in soils was investigated in-depth by Salvia et al. [42,43] who developed a multiresidual method based on a QuEChERS extraction for the analysis of 11 steroids, 14 veterinary antibiotics and 5 human drugs by LC–MS/MS (see Table 1). The comparison of the two official QuEChERS protocols [18,19] showed better performances for the acetate-based extraction procedure [18], particularly for veterinary antibiotics such as sulphonamides, macrolids and beta-lactams.

According to Salvia et al. both PSA and PSA/C18 mixtures, as well as the use of non-conventional sorbents such as Florisil, silica, aluminium oxide and strong anion exchange phases like d-SPE sorbents, provided analyte losses or high signal suppression. Therefore, for these compounds, the clean-up step of the CH_3CN extract was performed with strong anion-exchange (to remove the matrix) and polymeric reversed phase (to retain the analyte of interest) cartridges in series; however, recoveries were strongly compound-dependent and in some cases (*i.e.* sulphonamide, erythtomycin, tylosin, roxithromycin, penicillin G, paracetamol, fluvoxamine and ibuprofen) unsatisfactory for the current standards of analytical chemistry. However, the clean-up step is essential for reducing the matrix effect that strongly affects recoveries, especially for steroids, which exhibit a suppressive matrix effect as high as 90% when no purification step is performed.
A dedicated QuEChERS method for the analysis of ibuprofen (IBP) and its metabolites in 16 different soils was developed by Braganca et al. [76], taking into consideration a number of parameters including soil characteristics, sample amount/solvent volume ratios, extraction solvent, pH of extraction mixtures, extraction technique (vortex/ultrasound) and QuEChERS salts. Each of these parameters was shown to affect extraction recovery, and therefore they must be optimized to obtain the highest method performance. The best results are summarised in Table 1; surprisingly, no clean-up procedure was attempted. The method used vortex and ultrasonic techniques in series for homogenising soil/QuEChERS salts and successive CH_3CN extraction, thus obtaining recoveries within 79 and 101%, for hydroxyIBP, carboxyIBP and IBP extracted from soils with different organic contents.

QuEChERS application to sediment analysis

Sediments represent the integration of biological, physical and chemical processes that occur in an aquatic ecosystem. Sediments may differ in form and composition and are considered to be pollutant accumulation compartments from the water column.
Extraction of compounds with environmental significance from sediments by QuEChERS methodology is a very recent approach. Experimental conditions for sediment analysis are illustrated in Table 2.

Organochlorine

The analysis of organochlorine insecticides was also applied for sediments [77,78] without sample re-hydration, using an unbuffered QuEChERS procedure. Although a direct comparison of the performance of the methods is hampered by the lack of the amount of acetonitrile used [78], better recoveries for α-endosulfan (119±1% vs 76±4%) and β-endosulfan (102±19% vs. 74±3%) were obtained by Quinete et al. [78] for comparable spiking levels of about 50 $\mu g\ kg^{-1}$. These differences can be ascribed to the fact that in one instance the QuEChERS procedure was applied to a dry sediment sample [77], whereas in the other case, water content ranged from 45 to 60%. These results are in agreement with previously discussions on soil.

Carbamate derivatives

Four carbamate derivatives (propamocarb hydrochloride, oxamyl, phenmedipham and molinate) were extracted from sediments using the QuEChERS method [79,80]. The use of unbuffered extraction solvent to dry sediment allowed for obtaining surprisingly high recoveries for oxamyl (81%), propamocarb (93%) and molinate (99%) [80] in view of the fact that the sample was not re-hydrated. Although Kvicalova et al. [79] compare several extraction conditions with varying pH, water and salt contents, recovery is not discussed in terms of these parameters. According to the data shown, phenmedipham can be extracted with a 60% recovery on a hydrated sediment using acidified acetonitrile and without a clean-up step. This value is considerably lower than that reported by Mei et al [39] (75%) and previously discussed despite being obtained on a re-hydrated soil. However, it should be noted that the matrix effect was not studied and that no MMC was reported. Moreover, the different procedure adopted (no pH control and d-SPE within the extraction

step), and the different physicochemical characteristics between soil and sediment must be taken into account.

Pyrethroids

Cypermethrin and etofenprox are the only two pyrethroid derivatives extracted to date from sediments [79,80]. As previously discussed for the carbamate derivatives, the conditions used by Kvicalova only provided a 51% recovery for cypermethrin, whereas good recoveries (97%) were obtained for etofenprox without the re-hydration step or the pH control. Similar recoveries were reported by Yang [44] with a buffered extraction on re-hydrated soils as discussed above.

Other pesticides

The aforementioned approaches were adopted for determining pesticides belonging to different classes, namely azole [77,79] biopesticide [80], hydrazine [80], carboxamide [79], nitroaniline [81], organophosphorus [80], urea [80], auxin [79], triazine [77], pyridazinone [79], imidazole [79], spiroketalamine [79], and piperidine [79] derivatives. The compounds belonging to the last four classes (chloridazon, carbendazim, spiroxamine and fenpropidin) were extracted in acetonitrile containing 1% NH_3, with recoveries higher than with the conventional QuEChERS approach. We found this behaviour to be in agreement with the lower solubility exhibited by all these compounds in basic conditions. Satisfactory recoveries were obtained for all the analytes except carboxin [79], probably not recovered due to its rapid decomposition in soil.
A different multiresidue QuEChERS approach, based on acetate buffered extraction, was very recently optimized by Berlioz-Barbier et al. [82] for the analysis of spinosad, pyriproxyfen, piperonyl butoxide and 3,4-dichloroaniline (a metabolite of the herbicide propanil), together with some pharmaceuticals (see Table 2) in sediment samples. The method was fully validated according to the International Conference on Harmonisation guidelines, by the use of MMC and provided for LOQ values comparable with literature data and recoveries ranging from 79 ± 10% for pyriproxyfen up to 90 ± 5% for piperonyl butoxide.

Other organic pollutants

The application of the QuEChERS approach to the determination of pharmaceutical compounds (i.e. ibuprofen and its hydroxy- and carboxy- metabolites) was firstly explored by Bragança et al. [76] using a method optimized on soil samples (see the paragraph "*Pharmaceutical compounds*" within the section "QuEChERS application to soil analysis"). Even though a detailed characterization of the eight sediment samples analysed was given, recovery data were provided only as an aggregate range (82-101%) including both soils and sediments, instead of individual values for each sediment, thus hampering any further critical consideration.
In the aforementioned study, Berlioz-Barbier et al. [82], reported very good recoveries for some pharmaceuticals and hormones (see Table 2). However, the method provided a poor recovery for ketoprofen, when a d-SPE clean-up step based on PSA-GCB and above-all PSA-C18 and PSA alone was employed. This finding must be ascribed to the anion-exchange interactions between the amino-group of the sorbent and ibuprofen, which is significantly present in the anionic form (pKa=4.23 [20]) at the extraction pH. In agreement with this consideration, Bragança and co-workers obtained a very good recovery for ibuprofen in absence of a clean-up treatment [76].

QuEChERS application to water analysis

The aquatic ecosystem has been adversely affected by human activities such as agricultural, urban and industrial practices. Despite the large amount of literature on extraction procedures of contaminants from water resources, extraction with the QuEChERS methodology is still a niche application, mostly limited to pesticide analysis.
When applied to water samples, the QuEChERS method differs from the conventional liquid-liquid extraction protocol, because the extraction solvent is initially water-soluble and the phase separation is induced by salt addition; moreover the extraction step is coupled with a d-SPE stage for the

removal of co-extracted compounds. This last purification step was omitted in some instances [70]. Extraction procedures applied to date to water samples are described in Table 2.

Pesticides

Organochloride pesticides (α-endosulfan and β-endosulfan) were extracted by a water:CH_3CN (1:1) mixture in the presence of salts [77] and clean-up with recoveries of 69% and 72% respectively, averaged on different levels of matrix spikes. Although no details are given about the evaluation of the recoveries (i.e. calibration procedure), the protocol shows lower performance for waters rather than sediments, both in terms of recoveries (see the paragraph "Organochlorine" within the section "QuEChERS application to sediment analysis") and RSD values which are below 5% for sediments and below 17% for waters.

It is interesting to note that despite the scarce data available, recoveries are not related to water solubility of the analyte. In fact, recovery for α-endosulfan and β-endosulfan (water solubility = $2.7 \cdot 10^{-6}$ M [20]) is about 70%, lower than for the more soluble atrazine (recovery = 94%, water solubility = $3.2 \cdot 10^{-4}$ M [20]) and also lower than the recovery of analytes with a similar solubility such as fipronil (recovery = 98%, water solubility = $1.9 \cdot 10^{-6}$ M [20]).

The above-mentioned experimental protocol was also applied to the extraction of several pesticides of different classes [80], namely carbamate (propamocarb hydrochloride, oxamyl, molinate) and phenylurea (linuron) derivatives, organophosphorus (malathion) and bisacydilhydrazine (tebufenozide) insecticides, pyrethroids (etofenprox) and biopesticides (piperonyl butoxide). According to the recovery data presented, we observed a positive linear correlation with log Kow values (R^2=0.68; *P*=0.02).

As previously mentioned [77], a generally better performance (*i.e.*: recovery and RSD) of the QuEChERS procedure was observed for sediments rather than waters [80]. Satisfactory recoveries were reported (89-97%), except for oxamyl (76%), in agreement with its low $\log K_{OW}$ value (-0.47 [20]).

Although the method was applied to the analysis of thirty lake water samples, no details are given about the evaluation of the recoveries (i.e. calibration procedure), and not even about the matrix effect.

Chloroacetanilide herbicide (propisochlor) was extracted from waters by the QuEChERS method [70], increasing the amount of acetonitrile, without the clean-up step, and analyzed by UPLC-MS/MS. Since the same procedure was also used to extract propisochlor from several matrices including soil, it is interesting to note that the highest matrix effect in reducing the signals was observed for waters rather than for soil. The method requires external MMC and has a similar performance for waters (recovery=84%, RSD=7%) and soil (recovery =83%, RSD=6%).

Other organic pollutants

The only application of the QuEChERS method to the extraction of non-pesticides compounds from waters is to date limited to polychlorinated biphenyls (PCBs) [83]. Even if banned since the late 1970s, PCBs still pose a risk due to their environmental persistence.

The QuEChERS approach was applied to extract eleven PCBs congeners (see Table 2) from municipal water samples at different stages of treatment plant, and commercial drinking-water samples. The extraction was performed under buffered conditions, even if the pH control appears unjustified due to the characteristics of the analytes. By using a GC-MS/MS (triple quadrupole analyzer), and an external calibration in hexane, MICRE was observed (recoveries included within 184%-284% for a 40 μg L^{-1} spike level). Although MICRE was avoided through MMC (recoveries in the range 66%-83%), the final calibration procedure was obtained by extracting all the spiked calibration levels with the QuEChERS method. Even though this system allowed to obtain recoveries in the range of 97%-102%, RSD% are in the range 6%-15%.

Although few examples of QuEChERS extractions from water samples are available to date, it is reasonable to expect that the QuEChERS approach will be used to a larger extent since easier and faster than other approaches (*i.e.* SPE) and maintains good analytical performance.

Comparison among QuEChERS and other extraction methods

Several authors have compared the efficiency of QuEChERS with other extraction methods for soils [31,47,66,73,74] and sediments [79].
The results presented by Rouvière et al. [47] for the analysis of 34 organochlorines on peat samples (see Fig. 3) highlighted much better performances of the QuEChERS procedure in comparison with accelerated solvent extraction (ASE), particularly for compounds with high vapour pressure (e.g. dichloro- and trichloro-alkanes, and dichloro- and trichloro-alkenes with 2-3 carbon atoms), which were not recovered by ASE. The better performance of QuEChERS is also demonstrated by the limits of quantitation achieved with the two approaches that were greatly lower for QuEChERS (7-640 $\mu g\ kg^{-1}$) than ASE (194-9000 $\mu g\ kg^{-1}$).
Lesueur et al. [31] clearly highlighted the great velocity and simplicity of QuEChERS compared to ASE, ultrasonic solvent extraction (USE) and liquid/solid extraction (LSE) (European Norm Din 12393), above all considering that the last three methods need an additional clean-up step. Moreover, the QuEChERS method provided for better "apparent recoveries" of the majority of compounds tested, which belonged to different structural and functional pesticide classes, with very different physico-chemical properties. It should be however highlighted that USE, LSE and ASE, provided for limits of quantitation slightly lower than QuEChERS.
Even better performances of the QuEChERS protocol were observed by Prestes et al. [66] for the analysis of numerous biopesticides, in comparison with the other extraction methods mentioned above (Fig. 3).
Padilla-Sanchez et al. [73] evaluated QuEChERS, ASE, USE, Soxhlet extraction (SE) and LSE with a high-speed homogeneizer technique for the recovery of phenol derivatives from soil, evidencing that only the QuEChERS method was suitable for the quantitative analysis of this compound class (see Fig. 3). However, the use of matrix standards in the context of the method comparison is not undoubtedly stated and therefore it is not clear if the comparison data referred to "apparent recoveries" or recoveries.
Finally, further evidence of the greater performances of QuEChERS was provided by Dreyer et al. [74], who compared different extraction methods (ASE, USE, SE and fluidized bed extraction) and cleaning procedures (SPE and d-SPE with different sorbents) with an ultrasonic-assisted QuEChERS protocol, for the analysis of PFAS.
A different picture seems to derive from the evaluation of the results of Kvicalova et al. [79] in a sediment mixture; in fact, better recovery data were generally achieved using an alkaline extraction method or the Luke method (both performed with water addition to the sample), compared to QuEChERS. However, in this paper no study of the matrix effect on quantitative accuracy has been reported, thus making strongly questionable the aforementioned results.

Soil and analyte characteristics as tools for recovery and matrix effect interpretation

The complex collection of data presented above could be better understood if a statistical approach to their interpretation had been systematically performed, in order to evaluate the role played by soil parameters and analyte physicochemical properties on the extent of recovery and the matrix effect.
Based on the literature overview, only Salvia and co-workers [43] attempted the statistical interpretation of their results, by applying the Pearson correlation, the analysis of variance and the least square regression as a function of several soil properties to the recovery and matrix effect data of a number of pharmaceutical compounds. The results highlighted that clay and organic carbon contents, as well as cation exchange capacity, were inversely related to the recovery. The role of organic carbon in enhancing the retention properties of soils towards organic compounds, thus reducing their recovery during the QuEChERS extraction, can be also deduced from the data presented by Bragança et al. [76]. In fact, recoveries of ibuprofen and its hydroxy- and carboxy-metabolite were found to be much lower in the soil containing the highest organic carbon content, compared to those with lower amounts of organic matter.

In addition, as highlighted by Salvia and co-workers [43], high contents of organic carbon increase the matrix effect.
It should however be noted that these relations were only observed for certain analytes and that soil parameters are interdependent variables; hence, recoveries and matrix effects are strictly soil specific and should always be accurately evaluated.
A contribution of physicochemical properties of target analytes in describing the trend of recovery is also expected; however, to the best of our knowledge, no comprehensive evaluation of recovery as a function of physicochemical characteristics has yet been performed. Hence, we used the recovery data reported by Salvia et al. [43] for 11 different soils, as dependent variables in a partial least square (PLS) regression where water solubility, vapour pressure and log K_{OW} were chosen as independent variables. We selected these properties owing to their influence on partition and evaporation processes during the extraction and clean-up steps. The values of these parameters were taken from SciFinder® [20] by selecting those referring to the extraction pH adopted by Salvia et al. (pH=5). PLS regression analysis was performed using the algorithm PLS of the software VPARVUS [84], obtaining statistically significant regression models for all the investigated soils, according to the Fisher test ($P \leq 0.05$); some illustrative PLS results, obtained for soils labelled as "B", "G" and "K" by Salvia and co-workers, are illustrated in Table 3. The PLS models showed limited predictive powers, since the cross-validated explaining variance of original data, as evaluated by the leave-one-out method, was included between approximately 30 and 40%, according to the soil examined. Therefore, the PLS approach discussed herein cannot be used for quantitative evaluation purposes, even though some information can be obtained. As general findings of this regression analysis, the closed forms of the models were characterized by negative correlation of recoveries with water solubility and vapour pressure, whereas log K_{OW} was positively or negatively correlated with recoveries, depending on the soil investigated. The inverse correlation of recoveries with vapour pressure and water solubility is in agreement with their role in partition and evaporation phenomena occurring during extraction. Log K_{OW} does not have an univocal effect, since higher values contribute to a higher analyte partition into the organic phase and a lower PSA sorption, but at the same time they are related to a higher soil retention; therefore, the positive or negative relations found within these PLS regressions suggest a different contribution of this parameter as a function of the different soil properties. Among the original predictive variables, the major contribution to the regression model was generally observed for water solubility, thus confirming the importance of partition phenomena in the extraction phase.
As clearly evidenced by the values of the parameters reported in Table 3, there was only a limited agreement between the experimental recoveries and those computed and predicted by the models. In particular, as shown in the example of Fig. 4 that concerns the same above-mentioned soils, the model failed mainly in the interpretation of the low recoveries obtained for roxithromycin and progesterone; it should however be noted that according to Salvia et al. [42] the recoveries observed for some target analytes, including roxithromycin and progesterone, are affected by a quite large variability (RSD=28 % and 21 % for roxithromycin and progesterone, respectively), that obviously contributes to the uncertainty of the model.

Conclusive remarks

QuEChERS represents a flexible analytical approach, characterized by such a wide applicability as to be commercially available from some companies. This technique exhibits better analytical performances, when compared to other common extraction approaches such as ASE, USE, SE and LSE for the soil analysis of chloroalkanes, phenol derivatives, BPs and PFAS. However, an appropriate method optimization is necessary, depending on the analyte and matrix investigated. Even though it is not possible to draw conclusive remarks on the "best" methodological expedients to be adopted for the QuEChERS extraction from environmental samples, especially in the case of multiresidue applications based on the discussion reported above, the use of the QuEChERS methods seems to be valid, especially when the following precautions are adopted: (i) dried samples

are re-hydrated before extraction; (ii) an excess of solvent compared to the soil is used (commonly 2/1 ratio); (iii) extraction is assisted by sonication; (iv) the clean-up step is accurately evaluated in relation to the target analytes, as PSA is not suitable for polar compounds; (v) the MMC is used. The use of statistical tools may contribute to a better understanding of the influence of physicochemical properties of target analytes and soil characteristics on recovery and matrix effect. As a future development of the QuEChERS technique, the introduction of an automated, on-line clean-up/preconcentration step prior the LC-MS/MS analysis would be advantageous, in agreement with the current needs of minimum sample manipulation and high analytical throughput [85,86]; for instance, an on-line purification of CH_3CN extract, compatible with a QuEChERS automated procedure was reported by [87].

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Table 1 QuEChERS extraction of different compounds from soil

Analytes	Extraction procedure	Clean-up procedure[a)]	Analytical method	% Recovery (% RSD)	Ref.
Atrazine, Desethylatrazine, Desisopropylatrazine, Carbendazim, Chlorfenvinphos, Chloroxuron, Chlorpyrifos, Chlorpyrifos-methyl, Deltamethrin, Dieldrin, Diuron, Flufenoxuron, Isoproturon, Lindane, Linuron, Metamitron, Methabenzthiazuron, Metobromuron, Metoxuron, Monolinuron, Pencycuron, Simazine, Trifluraline, Vinclozoline	10 g of soil with 20 ml CH_3CN, followed by a salting-out step with 4 g $MgSO_4$, 1 g NaCl, 1 g sodium citrate dihydrate and 0.5 g di-sodium hydrogen citrate sesquihydrate.	150 mg PSA and 950 mg $MgSO_4$. Filtration (0.45 µm) and transfer of 1.5 ml of the extract for analysis	GC-MS and HPLC-MS. Triphenylphosphate was used as internal standard and spiked before the extraction.	27.3-120.9 (18)	[31]
α-, β-, λ-, δ-, hexachlorocyclohexanes (HCH), hexachlorobenzene (HCB), o,p'-DDT ([1,1,1 trichloro-2,2-bis-(p-chlorophenyl)ethane]), p,p'-DDE ([2,2-bis(p-chlorophenyl)-1,1-dichloroethylene]), p,p'-DDD (dichlorodiphenyldichloro-ethane), aldrin, dieldrin, endrin, α-endosulfan, β-endosulfan, methoxychlor	5 g of dried sieved soil added with internal standard (4,4'-dichlorobenzophenone) and allowed to sit for 1 h is placed in the tube and 3 mL H_2O and 7 mL CH_3CN are added. The tubes are shaken to ensure that the solvent interact with the entire samples. Afterwards, 6 g $MgSO_4$, 1.5 g NaCl, 0.75 g Na_2HCit sesquihydrate and 1.5 g ($Na_3Cit\ 2H_2O$) dihydrate were added and shaken. Next, the mixture was sonicated (50/60 Hz, 100 W, 1 min) and samples centrifuged (4500 rpm, 10 min)	A 1.5 mL aliquot of the supernatant was transferred to the clean-up tube containing 50 mg of PSA, 150 mg $MgSO_4$ and 50 mg of C18. The tubes were shaken and centrifuged (4500 rpm, 5 min). After concentration of 1 mL of the supernatant to dryness (by N_2), the residue was reconstituted in 1.0 mL of *n*-hexane	GC-ECD	65-132 (<16)	[32]
HCB, α-HCH, β-HCH, γ-HCH, heptachlor, heptachlor epoxide (trans), aldrin, dieldrin, chlordane (trans), chlordane (cis), oxychlordane, α-endosulfan, β-endosulfan, endosulfan sulfate, endrin, p,p'-DDT, o,p'-DDT, p,p'-DDD and p,p'-DDE	After hydration of 5 g soil sample with 10 ml H_2O (30 min), an aliquot (10 ml) of CH_3CN + CH_3COOH mixture (99:1, v/v) was added to the centrifuge tube containing the sample. After 30 s vortex, 4 g anhydrous $MgSO_4$ and 1.7 g $CH_3COONa{\cdot}3H_2O$ were added and the tube shaken and centrifuged (5000 rpm, 5min)	Liquid-liquid back-extraction and clean-up: 8 ml of the CH_3CN layer were concentrated to 1 ml (N_2 on a dry block, 30 °C), mixed with 1 ml H_2O and 5 ml n-hexane and swirled on a vortex mixer (15 s). 4 ml of the upper n-hexane layer was transferred into another glass tube. After addition of the internal standard, the extract was concentrated to near dryness (N_2 on a dry block, 30 °C and made up to 1 ml volume with n-hexane, prior to analysis	GC–MS/MS	70-100 (<20)	[33]
Metaflumizone	5 g of grinded soil (40 mesh) was added to 20 mL CH_3CN. An ultrasonic extraction step (30 min) was coupled before centrifugation (3 min, 4500 rpm).	An aliquot of 2.0 mL is transferred to a centrifuge tube containing 150 mg anhydrous $MgSO_4$, 50 mg PSA. After shaking on vortex for 30 s, the tube was centrifuged (9000 rpm, 2 min) and the supernatant diluted with 0.1 % formic acid in water 4:6 and filtered (0.22 µm) before analysis	LC-ESI-MS/MS	77.4 (8)	[34]
Metazachlor, oxyfluorfen, quizalofop-p-ethyl, quinmerac, α(±)-cypermethrin	10 g of soil mixed with 5 mL of water and shaken (1 min with a vortex device). After that 10 mL of ACN was added (acidified with acetic acid 1%, v/v for quinmerac analysis) and the mixture was shaken (1 min with a vortex device). 4 g $MgSO_4$, 1 g NaCl, 1 g Na_3-citrate·2 H_2O and 0.5 g Na_2Hcitrate·1.5 H_2O were added, and the mixture was shaken (30 s), sonicated (5 min) in an ultrasonic bath and centrifuged (5 min, 4000 rpm)	7.5 mL of supernatant were transferred to a 15 mL tube that contained 1.125 g of $MgSO_4$ and 0.225 g of C18, hand-shaken for 30 s, sonicated for 1 min and centrifuged (5 min, 4000 rpm). The extract (5 mL) was evaporated to 0.5 mL under a gentle stream of N_2	GC-MS and LC-MS/MS	70-110 (1.6-19)	[35]
Chlorantraniliprole	10 g soil were added with 40 ml CH_3CN, extracted in an ultrasonic water bath (30 min, room temperature) and centrifuged (8000 rpm, 3 min).	2.0 mL of the extract were transferred to a centrifuge tube with 150 mg anhydrous $MgSO_4$, 50 mg PSA, 50 mg. After shaking on vortex (30 s), the tube was centrifuged (10000 rpm, 2 min). The supernatant was diluted with 0.1% HCOOH in water in 1:4	LC–ESI–MS/MS	76.9–82.4(<15)	[36]

		ratio and filtered (0.22 μm) before analysis			
Oxadiargyl	10 g soil into 15 mL CH_3CN in the presence of 4 g $MgSO_4$, 1 g NaCl. After shaking, the tube was centrifuged (5 min, 2000 rpm) and the supernatant was concentrated to near dryness and re-dissolved in ethyl acetate for further analysis	No clean-up	GC-ECD	112 (2.8)	[37]
Fipronil, propiconazole, azoxystrobin, clomazone and tebuconazole	was the following: 10 g dried soil added with 100 μL CH_3COOH and 10 mL of CH_3CN were shaken for 1 min. Subsequently, 4 g of anhydrous $MgSO_4$ and 1 g NaCl were added.	No clean-up	LC-APCI-MS/MS	70-120 (18)	[38]
Atrazine, phenmedipham, mefenacet, metholachlor, hexazinone	1.0 g of soil sample was added with 0.5 mL H_2O and let to stand for 20 min. 4 mL CH_3CN was added to the extraction tube and the mixture shaken (2 min). 0.1 g of anhydrous $MgSO_4$ were added, and the tube shaken (20 s). 0.1 g PSA + 0.1 g C18 adsorbent were adde, and the extraction tube was shaken (2 min) and centrifuged (10000 rpm, 3 min). The supernatant was filtered before analysis	Within the extraction step	UPLC-MS/MS	75-98 (12)	[39]
Chloroform, 1,2-dichlorobenzene, and hexachlorobenzene	2.5 g soil sample added with 1.5 mL H_2O was shaken (1 min); 2.5 mL ethyl acetate was added and the mixture was shaken (1 min). Then 1 g $MgSO_4$ was added, shaking it (1 min) as quick as possible to prevent conglomerates. The tube was finally centrifuged (5000 rpm, 5 min)	No clean-up	GC-ECD	62–93 (<3.5)	[40]
THMs and BTEX (benzene, toluene, ethylbenzene and xylenes)	As [75]	No-clean-up	GC-MS	68-75 (<7.3)	[41]
Veterinary antibiotics-Sulfonamides: Sulfanilamide, Sulfadiazine, Sulfathiazole, Sulfameter, Trimethoprim, Sulfadimidine, Sulfabenzamide, Sulfadimethoxine; *Antiparasitic*: Dicyclanil; *Macrolids*: Erythromycin, Tylosin, Roxithromycin; *β-Lactam*: Penicillin G; *Phenicol*: Florfenicol *Hormonal steroid-Progestagens*: Nore, G, Levono, P; *Androgens*: AE, T; *Oestrogens*: E3, E2, α-E2, EE2, E1 *Human drugs*: Paracetamol, Sulfamethoxazole, Fluvoxamine, Carbamazepine, Ibuprofen; *Plasticizer*: Bisphenol A	5 g soil was added with 10 ml H_2O water and 15 mL CH_3CN. The tube was shaken with a vortex device. Acetate buffer, pH 4.8, (1.5 g CH_3COONa and 6 g of $MgSO_4$) was then added, and the tube was shaken (30 s) and swirled on a vortex mixer (30 s) and shaken (750 rpm, 3 min) After centrifugation (5000 rpm, 2 min), 10 mL CH_3CN layer was transferred into a 12 mL glass tube and evaporated to dryness (N_2, 40 °C)	SPE (SAX and Strata-X)	LC-MS/MS	40-110 (<20)	[42]
Androstenedione, testosterone, progesterone, norethindrone, gestodene, levonorgestrel, sulphanilamide, sulphadiazine, sulphathiazole, sulphameter, sulphadimidin, sulphabenzamide, sulphadimethoxine, sulphamethoxazole, trimethoprim, erythromycin, tylosin, roxithromycin, penicillin G, dicyclanil, paracetamol, fluvoxamine and carbamazepine	As [42]	As [42]		1-89 (not given)	[43]
Phoxim, Isoprocarb, Dichlorvos, Carbofuran, Fenaminosulf, Ethoprophos, Phorate, Dimethoate, Atrazine, Chlorothalonil, Iprobenfos, Acetochlor, Malathion, Metolachlor, Dicofol, Chlorpyrifos, Isocarbophos, Triadimefon, Isofenphosmethyl, Quinalphos, Fipronil, Procymidone, Methidiathion, Butachlor, Isoprothiolane, Profenofos, Buprofezin, Endosulfan (I,) Endosulfan (II,) Chlorfenaphy, Oxadixyl, Triazophos, Propiconazol, Propargite, Pyridaben, Cypermethrin, Cyfluthrin, Fenvalerate, Deltamethrin	Freeze-dried soil/sediment samples (10 g) was added with 4 mL of water and after 30 min, 20 mL CH_3CN were added to the tube containing the sample. After shaking (1 min), to induce phase separation and pesticide partitioning, 8 g anhydrous $MgSO_4$, 2 g NaCl, 1 g $Na_2HCitrate$ sesquihydrate, and 2 g $Na_3Citrate$ dihydrate were added to the suspension derived from the first extraction. The tube was hand-shaken (1 min), and centrifuged (2500 rpm, 3 min).	10 mL of the CH_3CN phase was transferred into a centrifuge tube containing 1.5 g of $MgSO_4$ and 250 mg PSA and IS in CH_3OH were added and centrifuged (1500 rpm, 3 min). The extracts were dried and the residue was re-dissolved with 1 mL CH_3CN	GC-MS	>70 (<21)	[44]

HCH, HCB, HCH, Lindan, HCH, Aldrin, End I, Dieldrin, *p,p'*-DDE, Endrin, End II, *p,p'*-DDD, *o,p'*-DDT, Methoxychlor, Azoxystrobin, Bifentrin, Bupirimate, Chlorpyrifos, Cyprodinil, Deltametrin, Diazinon, Fenhexamid, Fluazifop-P-butyl, Fludioxinil, Iprodione, Malathion, Mepanipyrim, Methiocarb, Myclobutanil, Pendimetaline, Procymidone, Pyrimethanil, Quizalofop-P-ethyl, Tetraconazole,Tolylfluanid, Vinclozolin	10 mL CH_3CN and 3 mL H_2O to soil (5 g), vortexing, and adding 4 g anhydrous $MgSO_4$, 1 g NaCl, 1 g $Na_3Citrate.2H_2O$, 0.5 g $Na_2Citrate.1.5H_2O$. After vortexing, the tube was sonicated (5 min, at 50/60 Hz, 100 W) and centrifuged (5 min, 3000 rpm)	Disposable pipette-extraction: 150 mg $MgSO_4$, 50 mg C18, 50 mg PSA	GC-MS/MS	70–120 (RSD< 15) for 26 pesticides;	[46]
1,2-Dichloroethylene-cis, 1,2-Dichloroethane, 1,2-Dichloropropane, Trichloroethylene, Tetrachloroethylene, Chorobenzene, 1,1,2,2-Tetrachloroethane, Cumene, Phenol, 2-Chlorophenol, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 1,2-Dichlorobenzene, Hexachloroethane, 1,3,5-Trichlorobenzene, 2,4-Dichlorophenol, 4-Chlorophenol, 1,2,4-trichlorobenzene, 2,6-Dichlorophenol, Hexachlorobutadiene, 1,2,3-Trichlorobenzene, 1,2,3,5-Tetrachlorobenzene, 1,2,4,5-Tetrachlorobenzene, 2,4,6-Trichlorophenol, 2,4,5-Tricholorophenol, 1,2,3,4-Tetrachlorobenzene, Pentachlorobenzene, 2,3,4,6-Tetrachlorophenol, α-HCH, Hexachlorobenzene, β-HCH, Lindane, Pentachlorophenol, δ-HCH	2 g of soaked soil was extracted with 15 mL CH_2Cl_2. After shaking, 4 g $MgSO_4$, 1 g NaCl, 1 g $Na_3Citrate.2H_2O$, 0.5 g $Na_2Citrate.1.5H_2O$ were added and the mixture was vortexed (1 min). After centrifugation (5000 rpm, 2 min), the upper layer was transferred in a vial for analysis	No-clean-up	GC-MS	70-100 (<25) <70 for 1,2-dichloroethylene cis, tetrachloroethylene, chlorobenzene	[47]
Ethoprofos, dimethoate, diazinon, malaoxon, chlorpyrifos–methyl, fenitrothion, malathion, chlorpyrifos, fenamiphos, phosmet, buprofezin	A 10-g portion was added with the internal standard (triphenylphosphate) and evaporated with a gentle stream of nitrogen. 20 mL CH_3CN were added and the sample was shaken (1 min). Next, 4 g of $MgSO_4 \cdot H_2O$, 1 g of NaCl, 1 g of sodium citrate tribasic dihydrate and 0.5 g of sodium hydrogencitrate sesquihydrate were added. The mixture was vigorously shaken for 10 s, sonicated (5 min at 50/60 Hz and 100 W), and centrifuged (4000 rpm, 8 min)	The supernatant (approximately 10 mL) was placed in contact with1.5 g $MgSO_4 \cdot H_2O$ and 0.250 g PSA, shaking for a few seconds, sonicating (1 min), and centrifuging (4400 rpm, 10 min). The supernatant-cleaned extract was evaporated to dryness (40 °C, 200 mbar) using a Rotavapor. The dry residue was then redissolved in 1 mL of cyclohexane, with a very small amount of anhydrous Na_2SO_4. The supernatant was filtered (polytetrafluoroethylene filters before analysis.	GC-NPD	Forestal soil: 60- 96 (<10), Malathion and malaoxon, not extracted. Ornamental soil: 45-87 (<15). For malathion and malaoxon, recoveries were in the range 9–29%). Agricultural soil: 62-96 (<10)	[51]
Racemic indoxacarb, benalaxyl, carfentrazone-ethyl, quizalofop-ethyl, isocarbophos, fenamiphos, simeconazole, napropamide, paclobutrazol	10.0 g of soil were mixed with 5 mL water and 10 mL ACN and shaken for 30 min in a water bath. Subsequently, 4 g MgSO4 and 1 g NaCl were added. The tubes were capped and vortexed vigorously for 3 min and then centrifuged for 5 min. Afterward, for 1 min and centrifuged at 2077 × g RCF for 5 min.	1.5 mL of the ACN layer was transferred into a single-use 2 mL centrifuge tube containing 150 mg anhydrous MgSO4 and 50 mg C18. The samples were vortexed The supernatant was filtered (0.22 μm) for chromatographic injection.	Chiral UPLC-MS/MS	80-106 (13)	[52]
Methomyl, carbaryl, carbofuran, propoxur, isoprocarb, promecarb,	3mL H_2O was added to 5 g of the soil sample and sonicated (1 min). 5 mL CH_3CN was added and the soil sample was sonicated (1 min). Subsequently, 2 g $MgSO_4$ and 0.5 g NaCl were added with vigorous mixing to prevent the formation of $MgSO_4$ conglomerates. The extracted solution was filtered and CH_3CN was evaporated (N_2) until dryness. The resulting solid was	SPE	MEKC	82-114 (10)	[53]

	redissolved in 10 mL H_2O before subjection to SPE				
Trifluralin, propazine, terbutylazine, prosulfocarb, flufonacot, pendimethalin, diflufenican, difenoconazol	20 g soil (spiked with 200 µL CH_3CN solution of the desired pesticides and allowed to react for 1 h) is added with 12 mL H_2O, and shaken for 4 h. Subsequently, 20 mL CH_3CN is added and the tube is shaken (1 min). The supernatant is transferred quantitatively to a centrifuge tube containing 6 g $MgSO_4$, 1.5 g NaCl, 1.5 g Na_3Citrate dihydrate and 750 mg Na_2HCitrate sesquihydrate. After 1 min-shaking, and centrifugation (3000 rpm, 5 min), the tube is cooled down with ice water.	6 mL of the extracted supernatant is transferred into a centrifuge tube containing 150 mg PSA and 900 mg $MgSO_4$. After 30 sec shaking the sample is centrifuged (3000 rpm, 5 min)	GC/MS(n) or LC/MS(n)	87.4 (difenoconazol)-116 (trifluralin) (<8%), at 100 µg/kg spiked level	[54]
Fluopicolide, Propamocarb	A 15-g was added with H_2O (to get a moisture content of 80 %) and with 30 mL ethyl acetate and mixed (3 min, 15,000 rpm). 10 g NaCl was added and the sample was centrifuged (3,000 rpm, 3 min).	15 mL ethyl acetate layer was transferred over 10 g anhydrous Na_2SO_4 in a test tube. The ethyl acetate extract (6 mL) ethyl acetate was taken in a test tube containing 0.15 g PSA, 0.9 g anhydrous $MgSO_4$, and 0.05 g GCB, shaken (1 min), and centrifuged (3,000 rpm, 3 min). 4 ml was evaporated to near dryness until complete evaporation of ethyl acetate residues. The sample was reconstituted by adding distilled hexane.	GC-ECD, GC-MS	85-92 (4)	[55]
Fenbuconazole, (R,S)4-(4-chlorophenyl)-2-phenyl-2-(1H-1,2,4-triazol-1-ylmethyl)) butyronitrile, and its two major metabolites (diastereomers RH-9129 and RH-9130)	10 g soil samples were added with 5 mL H_2O and 10 mL CH_3CN, and the mixtures were shaken (30 min, 25 ◦C) in a water bath shaker) and 4 g anhydrous $MgSO_4$ and 1 g NaCl were added. The tubes were vortexed, centrifuged.	1 mL of the CH_3CN layer was transferred into a centrifuge tube, and 150 mg anhydrous $MgSO_4$ and 50 mg PSA were added. The samples were vortexed and centrifuged. The supernatant was filtered (0.22 µm nylon syringe filter) before analysis	Chiral LC-MS/MS	87-92 (<10.4)	[57]
Tetraconazole, epoxiconazole, fenbuconazole , diniconazole, hexaconazole, triadimefon, paclobutrazol, and myclobutaniltended	As [57]	1.5 ml of the CH_3CN layer was transferred into a centrifuge tube, and 150 mg anhydrous $MgSO_4$ and 50 mg C18 were added. The samples were vortexed and centrifuged (2077 rpm, 5 min). The supernatant was filtered (0.22 µm nylon syringe filter) before analysis	Chiral LC-MS/MS	76.4–108.1 (<14.1)	[58]
Quizalofop-p-ethyl, benazolin-ethyl	10.0 g of soil were mixed with 5mL water, 10mL acetonitrile and then 3.0 g NaCl were added into the tube which was vortically extracted for 2 min and centrifuged (5 min)	1mL of supernatant acetonitrile layer was transferred into a 2mL centrifuge tube containing 200mg PSA and 50 mg C18 and then vortexed for 1 min. The extract was centrifuged (5 min). The upper layer was filtered (0.22 µm)	HPLC-MS/MS	96-97 (3)	[59]
Cyantraniliprole, J9Z38	Homogenized soil samples (10 g) were added with 10 mL CH_3CN. The centrifuge tube was shaken (30 min) and 6 g anhydrous $MgSO_4$ and 1.5 g sodium acetate were added. The sample was mixed and centrifuged (8 min, 5,000 rpm).	2 mL of acetonitrile layer was transferred into a tube containing 50 mg PSA and 150 mg anhydrous $MgSO_4$. The sample was mixed and centrifuged (5 min, 5,000 rpm). CH_3CN layer was filtered through a 0.22 µm filter membrane for UPLC–MS/MS analysis.	UPLC-MS/MS	92-94 (6.3)	[60]
Diafenthiuron	10 g soil sample mixed with 2 ml H_2O were added with 10 ml CH_3CN. Shaking with vortex mixer (1 min). Next 1 g NaCl and 4 g anhydrous $MgSO_4$ were added and vortexed (30 sec). The sample was extracted in an ultrasonic bath for 2min. The extracts	1 ml CH_3CN layer was placed into a micro-centrifuge vial containing 50 mg PSA and 150 mg $MgSO_4$. The sample was vortexed (1 min) and centrifuged (6000	HPLC-MS	95.2 (7.3)	[61]

	were centrifuged (3800 rpm, 5 min).	rpm, 5 min).The extract was filtered (0.45 µm) before analysis			
Monosulfuron-ester	10 g of soil was added with 10 mL CH_3CN. The sample tubes were shaken (0.5 h). 4 g of NaCl were added and the sample was vortexed (1 min) and centrifuged (5 min, 1776 rpm).	1 mL of the upper layer added with 25 mg PSA. Then, the samples were vortexed (1 min) and centrifuged (5 min, 5550 rpm). The resulting supernatant was filtered (0.22 µm)	LC-MS/MS	86 (8)	[62]
Rimsulfuron	10 g soil sample added with 10 mL CH_3CN. The tubes were vortexed (4 min). Then 4 g anhydrous $MgSO_4$ and 2 g NaCl were added. The tubes were vortexed(1 min) and centrifuged (5 min, 2,077rpm).	1.5 mL of the supernatant was transferred into a 2.0 mL tube containing 50 mg C18 and 150 mg anhydrous $MgSO_4$. The tubes were vortexed (1 min). The tubes were centrifuged (5 min, 2,077rpm) and filtered (0.22 µm)	UPLC-MS/MS	81 (11)	[63]
Azadyrachtin, spinosyn A, spinosyn D and rotenone	5 g soil placed in a centrifuge tube and 5 mL water, 50 µL internal standard solution (150 µg/mL isoproturon-D6), 100 µL acetic acid and 10 mL CH_3CN were added. After shaking (5 min), 0.5 g $Na_2HCitrate$ sesquihydrate, 1 g $Na_3Citrate$ dihydrate, 4 g anhydrous $MgSO_4$, and 1 g NaCl were added. The mixture was hand-shaken (1 min) and centrifuged (4,500 rpm, 2.5 min).	5 mL of the extracted supernatant were transferred into a polypropylene centrifuge tube containing 900 mg $MgSO_4$, 150 mg PSA, and 150 mg C-18. After vortexing (1 min) and centrifugation (4500 rpm, 2.5 min), a 2 mL aliquot of the supernatant was transferred into a glass test tube and evaporated to dryness by nitrogen and the residue was re-dissolved in 0.25 mL of 0.1% ammonium acetate in methanol using ultrasonic bath followed by an addition of 0.25 mL of 0.1% ammonium acetate in water, then vortexed	UPLC-MS/MS	83-104 (<9)	[65]
Nicotine, sabadine, veratridine, rotenone, azadirachtin, cevadine, deguelin, spynosad A, pyrethrin I, pyrethrin II, cinerin I, cinerin II, jasmolin I, jasmolin II and piperonyl butoxide	5 g of homogenized sample were added with 2.5 mL H_2O (30 min soaking). Subsequently, 5 mL 1% CH_3COOH in CH_3CN solution were added, and the tubes were shaken (1min). 4.0 g anhydrous $MgSO_4$, 4.0 g NaCl, 0.5 g $Na_2Citrate.1.5H_2O$ and 1.0 g $Na_3Citrate.2H_2O$ were added and the tubes were shaken (5 min, 5000 rpm). The supernatant was filtered before analysis.	No clean-up	UHPLC-MS/MS	70-110 (<25) except for nicotine and sabadine (about 30%)	[66]
Procymidone	10 g homogenized sample was mixed by vortexing (1min) with 10 ml CH_3CN and 3 ml H_2O. After addition of 2 g NaCl,the sample was mixed by vortexing (1 min) and centrifuged (3800 rpm, 5 min)	1 ml CH_3CN layer was transferred into a 2ml micro-centrifuge tube containing 50 mg PSA and 250 mg anhydrous $MgSO_4$.The sample was mixed by vortexing (1 min) and centrifuged (6000 rpm, 2 min). The acetonitrile layer was filtered (0.45 µm)	GC-MS	82.5 (7.0)	[67]
Metaflumizone	10 g sieved soil sample was added with 5 mL H_2O and 10 mL CH_3CN. After shakins (30 min, 25°C in a water bath shaker), then 4 g anhydrous $MgSO_4$ and 1 g NaCl were added. The tubes were vortexed (2 min) and centrifuged (2077 rpm, 5 min)	1mL of the CH_3CN layer was transferred into a centrifuge tube containing 200 mg anhydrous $MgSO_4$ and 30 mg PSA. The samples were vortexed (1 min) and centrifuged (2077 rpm, 5min). The supernatant was filtered (0.22 µm Nylon syringe filters) before analysis	UPLC-MS/MS	78 (5)	[68]
Quinclorac	5 g soil samples were added with 2 mL water and 10 mL CH_3CN (1% acetic acid). The centrifuge tube was shaken (2 min) and 3 g anhydrous $MgSO_4$and 0.9 g sodium acetate were added. The sample was mixed and centrifuged (5 min, 5,000 rpm).	9 mL of supernatant was filtered through a Na_2SO_4 column, dried under N_2 and redissolved in 1 mL CH_3OH.	HPLC-UV	74-106 (16)	[69]
Propisochlor	10 g soil sample was added with 20 mL of CH_3CN. The tubes	1.5 mL of supernatant was transferred into	UPLC-MS/MS	83 (<9)	[70]

	were vortexed (4 min) and 4 g $MgSO_4$ and 2 g NaCl were added. The tubes were vortexed (1 min) and centrifuged (5 min, 2077 rpm).	the d-SPE tubes containing 25 mg PSA and 150 mg $MgSO_4$. The tubes were vortexed (1 min) and centrifuged (5 min, 2077 rpm). The supernatant was filtered (0.22 µm)			
Clethodim, clethodim sulfoxide, clethodim sulphone	10 g of soil sample was mixed (by vortexing, 1.5 min) with 20 mL CH_3CN. After addition of 3 g anhydrous $MgSO_4$ and 1 g NaCl, the samples were shaken (1 min) and centrifuged (5 min, 3800 rpm).	1 ml of supernatant was transferred into a vial containing 50 mg PSA. The sample was mixed (on a vortex mixer, 1 min) and centrifuged (2 min, 6000 rpm). The supernatant was filtered (0.22 µm).	LC–MS/MS	79-104 (<9)	[71]
Bispyribac	10 g of soil samples was added with 5 ml H2O and 15 ml CH_3CN. The sample was shaken (0.5 min), then 2 g anhydrous NaCl was added and samples were oscillated (1 h, 200 rpm). The extracts were centrifuged (5 min, 3,800 rpm).	1ml of the upper layer was added with 50 mg PSA. The sample was vortexed (0.5 min), centrifuged (3 min, 14,000 rpm). The upper extract was filtered (0.22-µm)	LC–MS/MS	93 (9)	[72]
2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 2,4-dimethylphenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 4-n-nonylphenol, 4-chloro-3-methylphenol, 4-tert-octylphenol, pentachlorophenol	10 g of sample were added with 10 mL CH_3CN (1% v/v acetic acid) and 5 mL H_2O. The mixture was shaken (1 h) in a rotary shaker. Afterwards, 1.7 g CH_3COONa, 6 g $MgSO_4$ and 4 g NaCl were added and the tubes were shaken (1 min). After centrifugation (5000 rpm, 5 min), 1.5 mL of the CH_3CN layer was added with 0.75 g $MgSO_4$ in order to remove residual water. The analytes extracted were subsequently derivatized (room temperature with acetic acid anhydride) for analysis	No clean-up	GC–QqQ–MS/MS	70-110 (<20)	[73]
Perfluoro-n-butane sulfonate, perfluoro-n-hexane sulfonate, perfluoro-n-heptane sulfonate, perfluoro-n-octane sulfonate, perfluoro-n-decane sulfonate, perfluoro-n-butanoate, perfluoro-n-pentanoate, perfluoro-n-hexanoate, perfluoro-n-heptanoate, perfluoro-n-octanoate, perfluoro-n-nonanoate, perfluoro-n-decanoate, perfluoro-n-undecanoate, perfluoro-n-dodecanoate, perfluoro-n-tridecanoate, perfluoro-n-tetradecanoate, perfluoro-n-hexadecanoate, perfluoro-n-octadecanoate , perfluoro-1-octane sulfonamide ,N-Methyl perfluoro-1-octane sulfonamide, N-Ethyl perfluoro-1-octane sulfonamide, 2-(N-Methyl perfluoro-1-octane sulfonamido)-ethanol, 2-(N-Ethyl perfluoro-1-octane sulfonamido)-ethanol, N-Methyl perfluoro-1-butane sulfonamide, 2-(N-Methyl perfluoro-1-butane sulfonamido)-ethanol	2 g samples were ultrasonic-extracted with 7.5 mL CH_3CN (15 min) and centrifuged (5000 rpm, 5 min). The extraction procedure was repeated once, and corresponding supernatants were combined. Sampling volume was reduced to 5 mL using rotary evaporators and samples were transferred to tubes containing 5 mL H_2O adding 4 g of $MgSO_4$, 1 g of NaCl, 0.5 g of $Na_2Hcitrate{\cdot}1.5\ H_2O$, 1 g of Na_3-citrate$\cdot 2\ H_2O$. The tubes were shaken vigorously (1 min) and centrifuged (5000 rpm, 5 min) afterward.	The supernatant CH_3CN phases were transferred to new tubes. Glacial CH_3COOH (400 µL) and 0.15 g of CHROMABOND Diamino with 0.9 g $MgSO_4$ and 45 mg of carbon were added. The tubes were shaken vigorously (1 min), centrifuged (5000 rpm, 5 min), and contents were transferred to 10-mL glass vials. 5 ml CH_3CN was again added and the tubes were softly shaken and centrifuged as described above.	HPLC-MS/MS	98 (17)	[74]
THMs: chloroform, bromodichloromethane, dibromochloromethane, bromoform	5 g of soil sample was weighed in a 15mL glass centrifuge tube (tube kept closed during the greater part of the sample preparation process) adding 3mL of H_2O and shaken (1 min) with a vortex device. Then, 2.5mL of ethyl acetate was added shaking (1 min) by a vortex mixer. 2 g $MgSO_4$ were added, and the tube was vortex mixed (1 min). Then, the tube was centrifuged (5000 rpm, 5 min). Finally, the organic layer was transferred for analysis	No clean-up	FGC-µECD	65-94 (<8)	[75]
Ibuprofen and metabolites (hydroxyibuprofen, carboxyibuprofen)	5 g of soil sample was hydrated with 3 mL H_2O (pH 2.5 for HCl) and hand-shaken. 4 g of $MgSO_4$, 1 g of NaCl, 0.5 g of $Na_2Hcitrate{\cdot}1.5\ H_2O$, 1 g of Na_3-citrate$\cdot 2\ H_2O$ were added and the tubes were shaken by vortex (4 min). The tubes were posed in a ultrasonic bath (4 min) and 7 mL CH_3CN were added. After vortexing (4 min), and the use of an ultrasonic bath (4 min) and	No clean-up	LC-FLD	79-101 (3)	[76]

	centrifugation (4000 rpm, 10 min), the extract was filtered (0.2 μm) and transferred for analysis.				
Pyraclostrobin	10 g of homogenized soil sample placed in contact with 10 ml CH_3CN and shaken (30 min). Addition of 4 g $MgSO_4$ and 1 g NaCl, vortexing (1 min) and centrifugation (3800 rpm, 5 min).	1 ml CH_3CN transferred into a tube containing 100 mg PSA and 150 mg anhydrous $MgSO_4$. The sample was mixed, centrifuged (6000 rpm, 2 min). The acetonitrile layer was filtered (0.22 μm filter) before analysis	LC–MS/MS	108 (5)	[88]
Penconazole	10 g of soil was extracted using ethyl acetate (25 mL) by shaking (3 h). The ethyl acetate layer was separated and dried over 4 g of anhydrous MgSO4.	No clean-up	HPLC-UV	92 (9.5)	[89]

[a] If not differently specified, the clean-up step must be intended to be performed in the dispersive –SPE (d-SPE) mode.
MEKC: micellar electrokinetic chromatography
GC–QqQ–MS/MS: gas chromatography–triple quadrupole-mass spectrometry/mass spectrometry.
FGC: fast gas chromatography
FLD: fluorescence detection
FTD: flame thermoionic detector
THMs: trihalomethanes
SAX: strong anion-exchange
Strata-X is a polymeric reversed phase

Table 2 QuEChERS extraction of different compounds from sediment and waters

Analytes	Extraction procedure	Clean-up procedure[a)]	Analytical method	% Recovery (% RSD)	Ref.
Propisochlor	Water sample (10 g) was added with 20 mL of CH_3CN. The tubes were vortexed (4 min) and 5 g NaCl were added. The tubes were vortexed (1 min) and centrifuged (5 min, 2077 rpm).Then, the samples were filtered (0.22 µm)	-	UPLC-MS/MS	84 (<14)	[70]
Ibuprofen and metabolites (hydroxyibuprofen, carboxyibuprofen)	5 g of soil sample was hydrated with 3 mL H_2O (pH 2.5 for HCl) and hand-shaken. 4 g of $MgSO_4$, 1 g of NaCl, 0.5 g of $Na_2Hcitrate{\cdot}1.5\ H_2O$, 1 g of Na_3-citrate$\cdot 2\ H_2O$ were added and the tubes were shaken by vortex (4 min). The tubes were posed in a ultrasonic bath (4 min) and 7 mL CH_3CN were added. After vortexing (4 min), and the use of an ultrasonic bath (4 min) and centrifugation (4000 rpm, 10 min), the extract was filtered (0.2 µm) and transferred for analysis.	No clean-up	LC-FLD	Not available	[76]
Atrazine, fipronil and endosulfan	10 g of water or dry sediment added with 10 mL CH_3CN, 4 g $MgSO_4$ and 1 g NaCl. Centrifuged (3000 rpm , 1 min)	SPE cartridge containing 330 mg PSA, 330 mg C18 and a 1 cm layer $MgSO_4$ activated with CH_3CN. The extracted collected and analyzed	GC-MS	63-116 (12)	[77]
α-Endosulfan, β-Endosulfan, Endosulfan sulfate	20 g of sediment[b)] homogenized with 10 mL H_2O in a grinder with IS (β-endosulfan d4), vortexed 1 min and transferred into QuEChERS tubes ($MgSO_4$, NaCl). Vortexed for 1 min and centrifuged (4000 rpm, 5 min).	PSA, C18, $MgSO_4$. Vortexed for 1 min and centrifuged (4000 rpm, 5 min)	HPLC-MS/MS	52-135 (20)	[78]
Fluroxypyr, carboxin, chloridazon, carbendazim, cypermethrin, clomazon, spiroxamine, phenmedipham, fenpropidin	4 g of sediment (water 0-20 mL) hand-shaked and soaked for 1 h. 10 mL CH_3CN 1% additive (CH_3COOH or NH_3) 2 g salt mixture (NaCl, $MgSO_4$ or CH_3CCONa, $MgSO_4$) shaked and centrifuged (2500 rpm, 10 min)	2 g $MgSO_4$	LC-MS/MS	20-95 (7-22%)	[79]
Malathion, etofenprox, molinate, oxamyl, propamocarb hydrochloride, tebufenozide, linuron, piperonyl butoxide)	As [77]	5 mL of the CH_3CN extract was added with 900 mg MgSO4, 150 mg PSA, 150 mg activated C18 and SPE	GC-MS	76-98 (<18)	[80]
Trifuralin	10 g of sediment added with 20 mL CH_3CN. Vortexed 1 min. Salting with 4 mg $MgSO_4$, 1 g NaCl, 1g Na_4-citrate$\cdot 2\ H_2O$ 0.5 g $Na_2Hcitrate{\cdot}1.5\ H_2O$. Vortexed 1 min and centrifuged (4500 rpm, 10 min)	150 mg PSA, 900 mg $MgSO_4$. Centrifuged (4500 rpm, 8 min)	GC-ECD after solvent changing	87.2-93.9 (3.2)	[81]
Pharmaceuticals: carbamazepine, tamoxifen, triclosan, econazole, ketoprofen *Hormones:* norethindrone, estrone *Pesticides:* spinosad, pyriproxyfen Synergists: piperonyl butoxide *Propanil metabolite:* 3,4- Dichloroaniline *Alkylphenols:* 3,5-di-terbutylphenol, 2,6-di-ter-butylphenol *UV filter*: 4-methybenzylidene camphor *Plasticiser:* bisphenol A	Freeze-dried sediment (2 g) was added with 10 mL H_2O and vortexed (30 s). Then 10 mL CH_3CN and acetate buffer were added. The mixture was shaken, vortexed (30 s) and centrifuged (5000 rpm, 5 min).	6 mL of the CH_3CN phase was transferred into a tube containing PSA/GCB. The tube was shaken, vortexed (30 s) and centrifuged (5000 rpm, 5 min). 5 mL of the extract was evaporated (40 °C under a nitrogen stream) and reconstituted with 500 µL of CH_3CN spiked with Nore-d6. A 100-µL aliquot was diluted ten-fold using 89/11 H_2O/CH_3CN solution for LC-MS/MS analysis	LC-MS/MS	37-98(<16)	[82]
PCBs congeners (PCB28, PCB30, PCB52, PCB73, PCB101, PCB118, PCB138, PCB153, PCB155, PCB180 and PCB204)	10.0mL water sample with 15.0 mL CH_3CN. The mixture is shaken (1.0 min). Further, 0.5 g $Na_2Hcitrate{\cdot}1.5\ H_2O$, 1.0 g Na_3-citrate$\cdot 2\ H_2O$, 4.0 g anhydrous $MgSO_4$, and 1.0 g NaCl were added; the mixture was hand-shaken (1.0 min) then centrifuged (6500 rpm, 5.0 min).	12.5 mL of the supernatant was transferred to a centrifuge tube containing 0.95 g anhydrous $MgSO_4$ and 0.125 g PSA, vortexed (0.5 min) and centrifuged (6500 rpm, 5.0 min). A 10.0-mL aliquot of the	GC-MS/MS	90-109 (<15)	[83]

	supernatant was evaporated to near dryness (by N_2), and the residue was re-dissolved in 1.0 mL n-hexane prior to analysis

[a] If not differently specified, the clean-up step must be intended to be performed in the dispersive –SPE (d-SPE) mode.
[b] The same extraction protocol can be applied to 10 g of fish, 2g freeze dried algae

Table 3 Results of PLS regression analysis of recoveries found in the soils labelled as "B", "G" and "K" by Salvia et al. [43] for 21 pharmaceutical compounds, as a function of their water solubility, vapour pressure and log K_{OW} values.

Soil	**EV**	**MEC**	**SDEC**	**CVEV**	**MEP**	**SDEP**	***P*-value**
B	47.1	10.4	14.7	40.3	11.9	16.8	0.010
G	52.6	10.9	14.9	38.4	13.9	18.8	0.003
K	43.7	11.5	15.1	28.8	14.5	18.8	0.011
Variables	**Model Coefficients**				**Contribution to the model (%)**		
	Soil B	*Soil G*	*Soil K*		*Soil B*	*Soil G*	*Soil K*
Water Solubility (M)	-22.1	-43.6	-35.3		53.0	72.2	64.2
Vapour Pressure (torr)	$-2.7 \cdot 10^{6}$	$-2.6 \cdot 10^{6}$	$-7.3 \cdot 10^{5}$		36.9	2.5	7.6
Log K_{OW}	1.17	-4.25	-4.28		10.1	25.3	28.1
Constant	58.7	66.3	61.7		-	-	-

EV (%) = percentage of explained variance; MEC = mean error in calculation; SDEC = standard deviation error in calculation; CVEV (%) = cross-validated percentage of explained variance; MEP = mean error in prediction; SDEP = standard deviation error in prediction.

Fig. 1 The effects of soil re-hydration and solvent:soil ratio on the recovery of OCPs

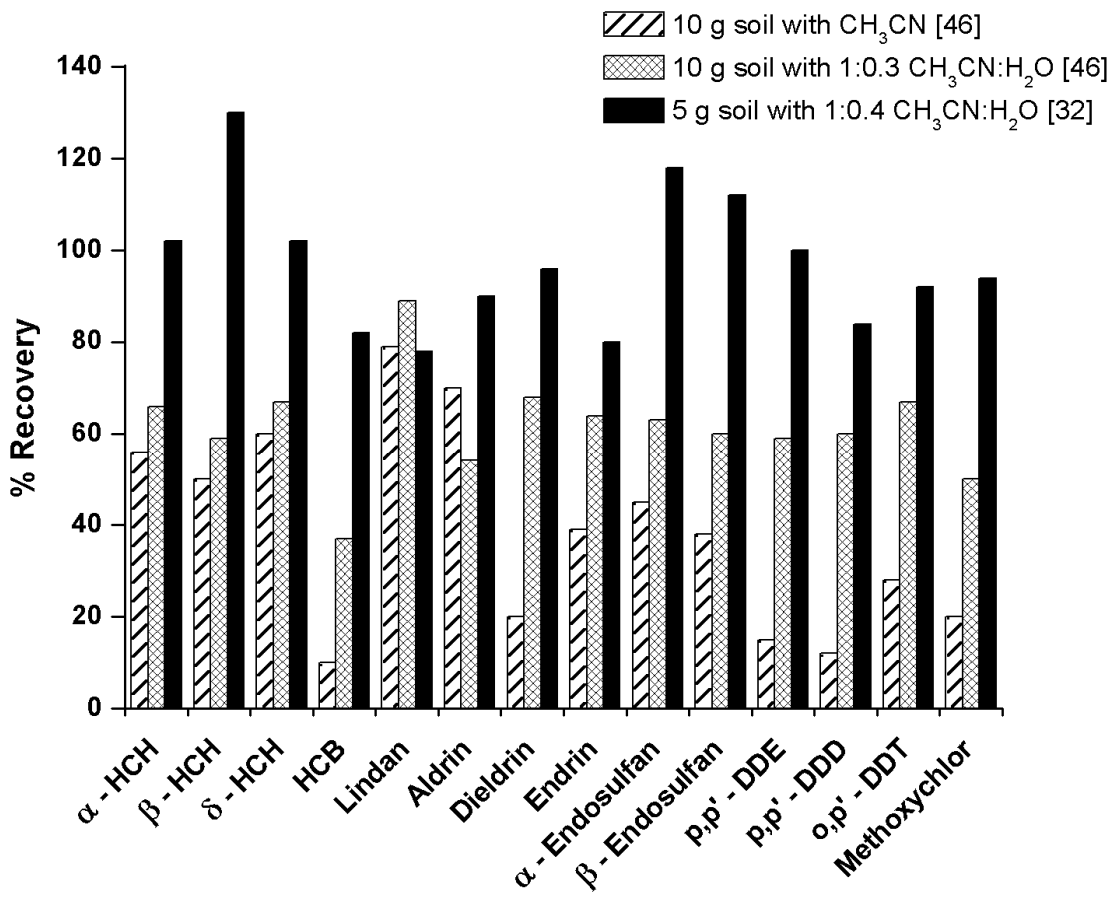

Fig. 2 Chemical structure of the OPPs compounds

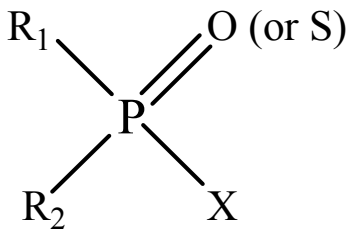

Fig. 3 Comparison of the performance of the QuEChERS approach with other extraction methods (ASE: accelerated solvent extraction; USE: ultrasonic solvent extraction; LSE: liquid/solid extraction) for selected classes of compounds according to data shown by references [47,66,73]. Inside each class of compounds, recoveries are expressed as average of the recovery data of all analytes. For each extraction method, bars representing the standard deviation from the average recovery value are also shown.
Extraction conditions: QuEChERS extraction was performed on re-hydrated soil samples and acetonitrile and dichloromethane as solvents; ASE, USE, LSE were tested on dried samples with solvents at wide polarity range

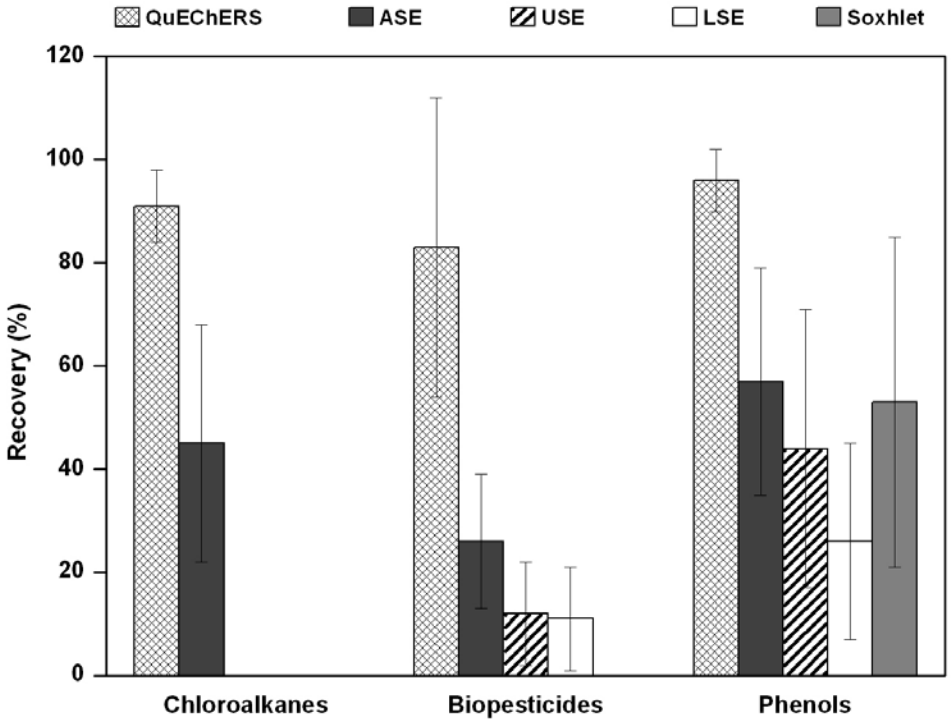

Fig. 4 Plots of experimental recovery values as a function of computed or predicted (leave one out cross-validation method) results obtained by PLS regression for soils labelled as "B", "G" and "K" by Salvia et al [43]. Black circles and triangles indicated progesterone and roxithromycin, respectively. The straight line represents the equation y=x.