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Green capsule phase microextraction employing hydrophobic monolithic sol-gel octadecyl siloxane platforms for the monitoring of organophosphorus pesticides in environmental water samples

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Abstract: In this study, a novel, facile and green capsule phase microextraction (CPME) method is presented for the extraction and preconcentration of organophosphorus pesticides (i.e., chlorpyrifos, disulfoton, ethoprophos, fenchlorphos, prothiofos, and parathion-methyl) from environmental water samples. Monolithic sol-gel octadecyl siloxane (sol-gel C_{18}) sorbent encapsulated within porous polypropylene capsules was synthesized, characterized, and evaluated for its efficiency towards the adsorption of the target organophosphorus pesticides. CPME was combined with gas

chromatography-mass spectrometry (GC-MS) for the monitoring of the target analytes. The method was optimized to ensure high method sensitivity and it was fully validated. The limits of detection of the CPME-GC-MS method for the OPPs were 0.02-0.15 ng mL^{-1}. The relative standard deviations were 1.5-8.7% for intra-day study and 5.4-9.6% for inter-day study, demonstrating satisfactory precision. Moreover, good method accuracy was obtained, since the relative recoveries were within the range 92.6-107.0% and 90.8-107.6% for intra-day and inter-day (c=5.00 and 20.0 ng mL^{-1}), respectively. The absence of interferences in the blank samples demonstrate that the proposed method is selective. The sol-gel C_{18} sorbent encapsulated CPME media could be reused for at least 25 adsorption/desorption cycles. In addition, the methodology presents advantageous features in comparison to existing methods. The final protocol was used for analyzing four different water sample types (i.e., lake water, river water, pond water and tap water sample).

Keywords: organophosphorus pesticides; water samples; capsule phase microextraction; GC-MS

1. Introduction

Organophosphorus pesticides (OPPs) comprise a big and diverse class of compounds used to control pests and increase the production of crops (Hu et al., 2013; Mangas et al., 2017). The exposure of humans to OPPs can cause serious health problems and may lead to distinct neurotoxic effects, depending on the type of pesticide, the dose and the frequency of exposure (Čadež et al., 2021). The mechanism of action of OPPs in the human body involves the de-activation of acetyl-cholinesterase that could cause accumulation of acetylcholine and acetylcholine receptors' disorder (Hu et al., 2013). Moreover, individual OPPs may exhibit carcinogenic, teratogenic, mutagenic and cytotoxic effects (Xie et al., 2013). These compounds are among the most widely used insecticides (Singh and Walker, 2006). The occurrence of OPPs in rivers, soil, air, plants and groundwater remains a concern for public health, because of their toxicity and their widespread use (Čadež et al., 2021). Particularly for environmental water systems, OPPs can enter to it through many sources, and serve as a threat both for animals and for humans (Gao and Pan, 2020). Thus, the development of sensitive and accurate methodologies for the monitoring of these pesticides in environmental samples is of paramount importance.

High-performance liquid chromatography (HPLC) (Harshit et al., 2017), capillary electrophoresis (Li et al., 2010), and gas chromatography (GC) (Hu et al., 2013; Lambropoulou et al., 2000) can be employed for monitoring the OPPs levels in environmental water samples. Among these instrumental techniques, GC coupled to various detection systems including nitrogen phosphorus detector (NPD) (Ballesteros and Parrado, 2004), electron capture detector (ECD) (Oliva et al., 2000), flame ionization detector (FID) (Amiri et al., 2019), flame thermionic detector (FTD) (Lambropoulou et al., 2000) and mass spectrometers (MS) (Lambropoulou et al., 2000) comprises the main analytical strategies for the monitoring of OPPs, due to their good performance. In order to enable the chromatographic determination of OPPs, sample preparation is necessary to provide sufficient clean up and preconcentration (Kaur et al., 2019). Solid-phase extraction (SPE) (Brito et al., 2002; Gillespie and Walters, 1991; Harshit et al., 2017) and liquid-liquid extraction (LLE) (Brito et al., 2002; Harshit et al., 2017) are between the most common methods used for the extraction of OPPs. However, LLE is considered to be a time-consuming technique and it requires high quantities of hazardous solvents. Similarly, SPE requires sample pretreatment and elution can be a tedious task, particularly with samples that have a high fraction of suspended matter (Ahmadi et al., 2006).

Following the development of Green Analytical Chemistry (GAC) principles that was an outcome of Green Chemistry, large efforts have been made by the scientific community to develop greener sample preparation methods (Anastas, 1999; Armenta et al., 2015). As a result, multiple miniaturized techniques have been proposed and successfully employed for the preconcentration and extraction of OPPs. Typical paradigms of these techniques include single drop microextraction (SDME) (Pinheiro et al., 2011), dispersive liquid–liquid microextraction (DLLME) (Cacho et al., 2018), pipette-tip solid phase extraction (Esrafili et al., 2020), solid-phase microextraction (SPME)(Delińska et al., 2022), dispersive solid-phase extraction (d-SPE) (Amiri et al., 2019), stir bar sorptive extraction (SBSE) (Hu et al., 2013), QuEChERS extraction (Alcântara et al., 2019), magnetic solid-phase extraction (MSPE) (Liu et al., 2020; Xie et al., 2013) and fabric phase sorptive extraction (FPSE) (Kaur et al., 2019). At the same time, various novel materials were introduced for the extraction of pollutants from complex samples (Li et al., 2021; Xu et al., 2022). In the above-mentioned sorbent-based extraction techniques, extraction takes place either by directly adding the sorbent in the sample (e.g., MSPE, d-SPE) or after the immobilization of the sorbent in suitable

substrates (e.g., FPSE). Undoubtedly, the exploration of novel extraction techniques and materials is critical for the miniaturization of the extraction of OPPs from water samples.

Capsule phase microextraction (CPME) is an extraction/preconcentration technique that aims to simplify the sample preparation procedure of complex food, biological and environmental samples. CPME utilizes specially designed capsules that include three parts: (a) a permeable microporous membrane from polypropylene, (b) a magnet with cylindrical shape and (c) a sol–gel sorbent (Manousi et al., 2022). Because of the inherent porosity of the membranes, the CPME devices integrate a filtration mechanism and, thus, this technique may be directly used for analyzing complex matrices without pretreatment. At the same time, the device integrates a stirring mechanism, resulting in rapid extraction kinetics. As a result, CPME overcomes potential losses of the target analytes during sample pretreatment as it eliminates further external steps of sample preparation, or potential sample contamination due to the addition of external magnets (Georgiadis et al., 2019). An advantageous feature of CPME is the utilization of a monolithic sol-gel sorbent. Sol–gel technology comprise an efficient vehicle for preparing advanced hybrid inorganic–organic polymer sorbents that are characterized by high chemical and thermal stability, remarkably high surface area as well as tunable selectivity and porosity (Lazaridou et al., 2020). Using sol-gel technology, a wide variety of sorptive phases including non-polar, polar, medium polar, negatively- or positively-charged, zwitterionic multi-mode sorbents can be prepared to fabricate coated microextraction capsules, resulting in increased selectivity towards a wide range of target analytes with diverse chemical properties (Samanidou et al., 2018). Until now, CPME has found to be a great analytical tool for the monitoring of various environmental pollutants, such as polycyclic aromatic hydrocarbons (N. Manousi et al., 2021b), basic and acidic compounds (Carles et al., 2020), and triazine herbicides in water (N. Manousi et al., 2021a).

The purpose of this work was to develop an efficient CPME method combined with GC-MS for the simultaneous extraction and preconcentration of six representative OPPs (chlorpyrifos, disulfoton, ethoprophos, fenchlorphos, parathion-methyl and prothiofos) from environmental water. Different coated CPME devices were evaluated for their performance to find the most efficient sorptive phase in order to find the best compromise for the studied OPPs. Subsequently, the main factors (i.e., extraction time, sample volume, salt content, stirring rate, eluent, mode of elution, volume of eluent and

desorption time) were optimized. Following method optimization and validation, the herein developed scheme was validated and used for analyzing tap, pond, lake, and river.

2. Experimental

2.1. Reagents, chemicals, and samples

LC-MS grade acetonitrile and methanol were obtained from Honeywell (Charlotte, North Carolina, USA), while HPLC grade acetone and GC-MS grade toluene were obtained from Merck (Darmstadt, Germany). Ultrapure water was provided by a Milli-Q system Plus purification system (Millipore, Bedford, MA, USA) and it was used throughout the study. Reagent grade NaCl was also obtained from Merck (Darmstadt, Germany). Chlorpyrifos (≥98.0%), disulfoton (≥98.0%), ethoprophos (≥95.0%), fenchlorphos (≥98.0%), parathion-methyl (≥98.0%) and prothiofos (≥98.0%) were from Supelco (Bellefonte, PA, USA). The chemical structures of the target analytes are shown in Figure S1. A stock solution of the each analyte (1000 mg L^{-1}) was made in hexane:acetone (9:1, v/v) and were kept at 4ºC. On a daily basis, working standards were made through serial dilutions in acetone at a concentration range of 0.05 and 1000 ng mL^{-1}.

Building blocks of the microextraction devices such as porous polypropylene capillary membranes (nominal pore size is 0.2 micrometer), Accurel® was obtained from 3M Inc. (St. Paul, MN, USA). Magnets of cylindrical shape (1/4″ x 1/16 ″) were obtained from K&G Magnetics Incorporated (Pipersville, PA, USA). Tetramethyl orthosilicate (TMOS), poly(tetrahydrofuran) (PTHF), and poly(ethylene glycol) 300 (PEG 300) were obtained from Sigma Aldrich (St. Louis, MO, USA). Isopropanol, methylene chloride, methanol, HCl and NH_4OH were purchased from Fisher Scientific (Milwaukee, WI, USA). Poly(dimethyl siloxane) (PDMS), poly(caprolactone)-poly(dimethylsiloxane)-poly(caprolactone) (PCAP-PDMS-PCAP) and octadecyl trimethoxysilane (C_{18}) were from Gelest, Inc. (Morrisville, PA, USA). A tabletop impulse heat sealer (Uline Corp, Pleasant Prairie, WI, USA) was used to heat seal both the ends of the CPME devices.

The CPME-GC-MS methodology was employed for the analysis of different water samples. All samples were collected from Vienna, Austria in amber-glass vials with no headspace. Until their analysis, all samples were stored at 4 °C (Roldán-Pijuán

et al., 2015; Zohrabi et al., 2016). No sample pre-treatment steps (e.g., filtration) were required prior to the microextraction procedure.

2.2. Instrumentation

A GC-2010 gas chromatograph and a QP2010 Plus mass spectrometer (MS) from Shimadzu (Kyoto, Japan) equipped with a Rtx-5MS (30 m × 0.25 mm, 0.25 μm) column (Restek Corporation, Bellefonte, PA, USA) was used in this study. The mobile phase used was helium (99.999%) and it was delivered at a constant gas flow rate of 1.05 mL min^{-1}. The injector was operated at 280°C. Splitless high pressure injection was performed at 300 kPa for 0.50 min using an injection volume of 3 μL. The oven temperature was: 80 °C initial temperature (hold time 2 min), raised to 280 °C at a ramp rate of 8 °C min^{-1} and raised to 350 °C at a ramp rate of 50 °C min^{-1}. The analysis time was 28.4 min and a solvent delay of 7 min was used. The ion source was operated at 220 °C and the interface was operated at 250 °C. The quantification was conducted in the selected ion monitoring (SIM) mode to ensure good sensitivity and selectivity. For this purpose, one target ion was used as quantifier and two reference ions were used as qualifiers for each analyte taking into consideration their abundance. The selected m/z values for the OPPs are presented in Table S1, along with their retention times.

A Philips XL30 Scanning Electron Microscope equipped with an EDAX detector, an Agilent Cary 670 FTIR Spectrometer, a RIGAKU diffractometer model SmartLab II, and a dynamic sorption surface area analyser Flowsorb III from Micrometrics Instrument Corporation were used for the characterization of the sol-gel C_{18} sorbent.

2.3. Preparation of microextraction capsules

CPME devices encapsulating sol-gel sorbents were created using an in-situ gelation of sol solutions where the microextraction capsules were kept submerged during the phase transition, from liquid sol to solid gel. The overall CPME device fabrication process involves several sequential steps: (a) preparing porous polypropylene capillary membranes for the device fabrication; (b) preparation and design of sol solutions; (c) in-situ creation of the coating on the porous polypropylene wall and the monolithic bed inside the lumen; and (d) aging/conditioning/cleaning of the CPME devices. Seven sorbents were prepared to study their efficiency towards the extraction of selected organophosphorus pesticides. The sol-gel sorbents include: (1)

sol-gel PTHF; (2) sol-gel sol-gel PDMS; (3) sol-gel poly(dimethyldiphenylsiloxane) (sol-gel PDMDPS); (4) sol-gel poly(caprolactone)-poly(dimethylsiloxane)-poly(caprolactone) (sol-gel PCAP-PDMS-PCAP); (5) sol-gel PEG 300; (6) sol-gel Carbowax 20 M (sol-gel CW 20M); and (7) sol-gel C_{18}.

All CPME devices were built at three-centimeter-long size. Capsule phase microextraction devices were prepared for surface coating/creating monolithic bed, Accurel® S6/2 membranes were cut into 3-centimeter-long sections, followed by cleaning and drying. Two capillary membranes were impulse heat sealed using the tabletop impulse heat sealer. A magnet was then placed into one of the capillary membranes. Subsequently, the open ends of the two capillary membranes were impulses sealed and the CPME media are ready for the creation of monolithic bed/ sol-gel sorbent coating.

Design of the sol solution for the preparation of sol-gel coating and/or monolithic bed is the most important and challenging task in the CPME device fabrication process with a goal to have high efficiency and to minimize sample preparation time, with least possible sample handling. As such, the sol solution preparation process was streamlined utilizing the same molar ratio between the reagents for a different sol solutions. The molar ratio between TMOS, methyl trimethoxysilane, polymer, solvent, hydrochloric acid, and water were kept at 1:1:0.2:30:0.04:8, respectively. The reagents were sequentially added to a 50-milliliter reaction vessel with vortexing after adding each ingredient. Then, the sol solution remained for 12 hours at room temperature. to enable the sol-gel precursor(s)hydrolysis. Subsequently, 1 M ammonium hydroxide was added at a molar ratio at 1:0.18 (TMOS:ammonium hydroxide) under constant stirring. Twenty capsule units were then immersed in the solution that was sonicated and transformation of the solution into solid gel occured within an hour. During the phase transition, a solid network was formed in the pores of the walls of the capillary membrane, while a monolithic bed was created inside of the capillary membranes' lumen. The capsules were then aged and conditioned for 24 h at 50 °C. The capsules were washed with dichloromethane:methanol (50:50 v/v) for 30 min under ultrasonic irradiation. During the ultrasonic irradiation process, the sol-gel sorbent monolithic bed is crashed into micro particles, leading to significant expansion of the overall surface area. Prior to their use for analytical experiments, all capsules were dried for 2 h at 50°C.

2.4 CPME procedure

Prior to the microextraction procedure, sol-gel C_{18} CPME devices were placed in an Eppendorf tube that contained 2 mL of methanol for 5 min for the removal of potential residues of the sol-gel synthesis process and to activate the surface of the sorbent. Subsequently, the capsules were rinsed with H_2O for the removal of traces of organic solvents from the sorptive phase that could potentially hinder the adsorption of the OPPs.

Initially, twenty millilitres of sample was placed in a vial and extraction took place within 60 min under a stirring rate of 500 rpm. Then, the CPME device was isolated and cleaned with H_2O. Prior to the desorption of the adsorbed OPPs, the CPME device was wiped and dried thoroughly using tissue (lint free). Desorption of the target analytes took place in Eppendorf tubes by adding a volume of 250 μL acetone. No stirring was required during this step and complete elution was achieved in 1 min. The eluent was filtered using PTFE filters (0.22 μm) and analysed by GC-MS.

Washing of the used capsules was performed by immersion in 2 mL of methanol for 5 min. The clean sol-gel C_{18} CPME device was left to dry at room temperature, and they were placed in airtight sealed vials for storage until their next application. Figure S2 shows the main steps of the CPME-GC-MS method.

3. Results and discussion

3.1. Characterization of coated CPME devices

The sol-gel C_{18} sorbent was characterized using scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) adsorption isotherm, Fourier transform infrared spectroscopy (FT-IR), and X-Ray diffraction analysis (XRD). The characterization study was performed as a basis for understanding the composition and structure of the herein used sorbent. The preparation procedures, obtained results and characterization data regarding the other examined sorbents included in this study have been previously reported elsewhere (N. Manousi et al., 2021b, 2021a; Manousi et al., 2022).

3.1.1 Characterization of the sol-gel C_{18} by FT-IR

The functional composition of the sorbent and their building blocks were evaluated using FT-IR Spectrometry. Figure 1 shows the FT-IR spectrum of sol-gel C_{18} (up) and C_{18}-TMOS (bottom).

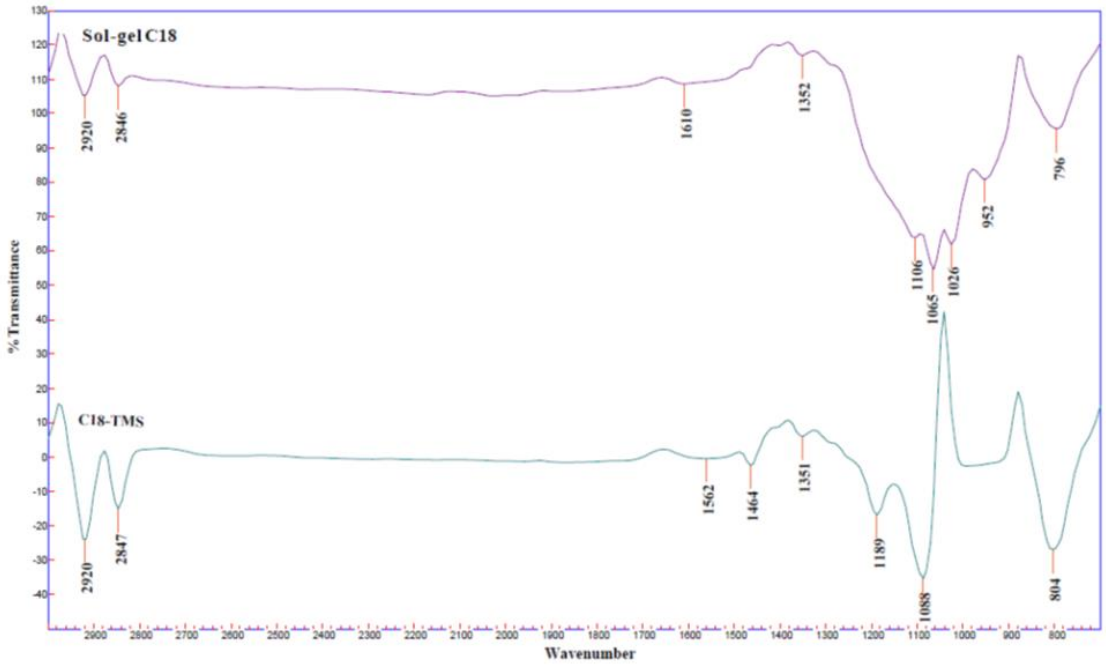

Figure 1. FT-IR spectra of sol-gel C_{18} (up) and C_{18}-TMOS (bottom)

The spectrum of C_{18}-TMOS (Figure 1, bottom) demonstrates characteristic bands at 2920 cm^{-1} and 2846 cm^{-1} that correspond to C-H stretching (Einati et al., 2009). The band at 1190 cm^{-1} corresponds to the asymmetric bending of C-H bonds. The band at 1075 cm^{-1} corresponds to Si-O-C bonds. Similar bands are also seen in the FT-IR spectrum that is shown in Supplementary Figure S3 as both C_{18}-TMOS and TMOS have the same base unit. The spectrum of sol-gel octadecyl siloxane reveals many features presented either in the spectrum of C_{18}-TMOS or that of TMOS or common to both, suggesting the integration of both the sol-gel precursors into the network of the sol-gel sorbent.

3.1.2 Characterization of the sol-gel C_{18} by SEM

The SEM images of porous polypropylene capillary membrane surface, before and after the sol-gel sorbent coating, are presented in Figure 2, both at ×1,000 magnification.

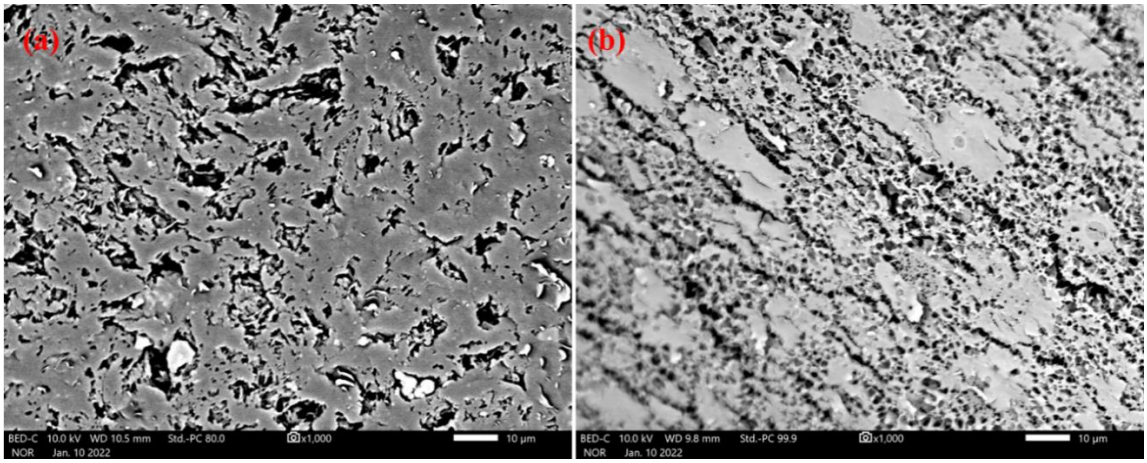

Figure 2. Scanning electron microscope images at ×1,000 magnification of the surface of porous polypropylene capillary membrane before coating (a) and after coating (b).

The polypropylene capillary membranes are porous with a 0.2 μm nominal pore size. The SEM image of surface before the coating procedure shows the opening of the pores almost evenly distributed on the surface. The SEM image representing sol-gel C_{18} coated capillary membrane surface is very different from that of the uncoated one, with a distinct layer of the sorbent coating. However, the pores on the surface remain intact, although the pore opening seems to be reduced. The polypropylene capillary membrane has thick walls of 450 μm. The sol solution can permeate without any difficulty through the walls during the coating process and transform into a polymeric gel within the porous channels. Consequently, the thick walls of the CPME device behaves like a solid-phase extraction disk.

3.1.3 X-ray diffraction analysis (XRD)

The XRD pattern of sol-gel C_{18} is presented in Figure S4. The sample was run at 40 mA, 40 KV, 2 degrees/min, 0.02 step size. A broad peak at theta ~22.5° in the diffraction pattern represents a signature marker of amorphous solid that have been reported in the XRD patterns of amorphous silica obtained from several studies (Liu et al., 2008; Tanev and Pinnavaia, 1995).

3.1.4 Brunauer-Emmett-Teller adsorption isotherm

The average pore width, the pore volume and the specific surface area of sol-gel C_{18} were carried out. For the comparison purpose, the same characterizations were performed on a commercial C_{18} sorbent. The BET nitrogen adsorption isotherm data

obtained for sol-gel C_{18} and commercial C_{18} are distinctly different. Sol-gel C_{18} has a specific surface area of ~650 cm^2/g, whereas the specific surface area for commercial C_{18} sorbent is ~346 cm^2/g. Sol-gel C_{18} sorbent was created by the polycondensation of hydrolysed TMOS with hydrolysed octadecyl trimethoxysilane. The sol-gel synthesis process allows changing the molar ratio between the functional precursor (C_{18}-TMS) and the networking precursor (TMOS) that may be exploited to achieve higher carbon loading in the synthesized sorbent. As the commercial C_{18} sorbents utilize spherical silica particles as the substate to bind C_{18} moieties on their surfaces, carbon loadings on commercial C_{18} sorbents are limited and primarily determined by the size of substrate silica particle. The pore volume of sol-gel C_{18} was found as 0.43 cm^3/g compared to 0.72 cm^3/g for commercial C_{18}. The average pore width for sol-gel C_{18} was calculated as 26.9 Å whereas the average pore width for the commercial C_{18} was 83.7 Å.

3.2 Optimization of the CPME procedure

The effect of the experimental parameters that may affect the CPME method were thoroughly investigated and optimized. Initially, different CPME devices (i.e., different sol-gel sorbents and different dimensions) were tested for the extraction of the OPPs from the environmental water samples. Subsequently, the adsorption and desorption steps were individually studied by means of the one-variable-at-a-time (OVAT) approach. As such, all variables that could have an influence on the performance of the CPME method were independently examined, and the other parameters remained constant.

3.2.1 Selection of the sol-gel coated CPME device

Firstly, the seven sol-gel sorbent encapsulated CPME devices (see section 2.3) were evaluated. The length of the capsules was 3 cm. These capsules were initially tested under the following experimental conditions: salt content: 0% w/v NaCl, extraction time: 30 min, sample volume: 20 mL, stirring rate: 500 rpm, eluent: acetone, volume of eluent: 1 mL, desorption time: 5 min. Table S2 presents the results of the investigation of the different sol-gel sorbents. Sol-gel C_{18} exhibited the best adsorption performance taking into consideration all the examined analytes. C_{18} is a powerful sorbent for the extraction of OPPs from water samples (Ballesteros and Parrado, 2004; Harshit et al., 2017; Xie et al., 2013).

Subsequently, two different dimensions of sol-gel C_{18} encapsulated CPME devices (i.e., 1 cm and 3 cm) were evaluated (Figure S5). The 3 cm microextraction capsules showed higher extraction performance, due to the higher sorbent loading. Thus, further experiments were conducted using of sol-gel C_{18} encapsulated CPME devices of 3 cm.

3.2.2 Optimization of adsorption conditions

The parameters that can affect the adsorption step were optimized. The optimization of the adsorption conditions was conducted starting from the following experimental conditions: sol-gel sorbent: C_{18}, length of microextraction capsules: 3 cm, salt content: 0% w/v NaCl, extraction time: 30 min, sample volume: 20 mL, stirring rate: 500 rpm, eluent: acetone, volume of eluent: 1 mL, elution time: 5 min.

In equilibrium-based microextraction techniques, the implementation of external stimuli (e.g., stirring, shaking or sonication) can enhance the diffusion of the target analytes and result in lower extraction time and enhanced recovery (N. Manousi et al., 2021a). CPME integrates a stirring mechanism, since it contains a magnetic rod and, thus, sample stirring can be employed to assist the adsorption step. Four different stirring rates between 0 and 1000 rpm were investigated. Figure 3 shows the effect of stirring rate on the extraction recovery. It is noteworthy that without constant stirring, negligible extraction recoveries were obtained for all the target analytes.

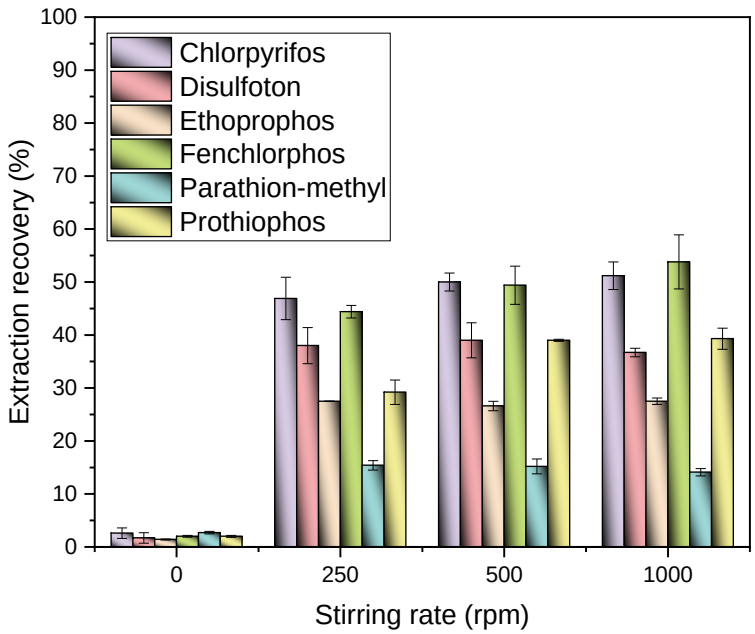

Figure 3. Evaluation of the effect of different stirring rates.

An increase of stirring rate up to 500 rpm had a positive impact on the CPME procedure. Moreover, the extraction recoveries of all analytes remained constant up to a stirring rate of 1000 rpm. Thus, extraction was conducted using a stirring rate of 500 rpm.

Subsequently, sample volume was examined in the range of 10-50mL. Higher recoveries were obtained when 10 mL of water sample were utilized (Figure S6). However, regarding sample enrichment the operation of higher sample amount (e.g., 20 mL or 50 mL) could result in higher PFs and, thus, enhanced method sensitivity. Therefore, as a compromise between ER% and PF values, further experiments were performed using 20 mL of sample.

Extraction time is a factor that is important for the performance of equilibrium-based techniques like CPME, since it is necessary to find a time span sufficient for all analytes to reach equilibrium (N. Manousi et al., 2021a). During the investigation of the extraction time, five different time spans between 15 and 75 min were examined. As shown in Figure S7, most analytes reached an equilibrium at 60 min. Only for parathion-methyl the recovery was enhanced for an extraction time up to 75 min. However, since adequate sensitivity was obtained for all analytes and in order to avoid prolonging of the extraction time and to ensure method rapidity, an extraction time of 60 min was chosen.

Finally, the impact of the ionic strength of the water sample was investigated. Therefore, different amounts of sodium chloride between 0 and 20% w/v) were evaluated. Salt addition may have either a positive effect (i.e., by decreasing the target analytes' solubility and thus favoring their interaction with the adsorbent, known as salting-out effect) or a negative effect (i.e., by increasing the density of the aqueous sample and lowering the mass transfer of the target analytes) in the microextraction process (N. Manousi et al., 2021b). An increase of the ionic strength up to 5% w/v did not have an impact on the efficiency of extraction for the target analytes (Figure S8). However, an enhancement of the NaCl content up to 10% w/v had a negative impact for chlorpyrifos, fenchlorphos and prothiophos. Moreover, at 20% w/v NaCl the extraction performance for most analytes was significantly reduced. As a compromise for all OPPs, further experiments were carried out with no salt addition.

3.2.3 Optimization of desorption conditions

Following the optimization of the adsorption step, the effect of the main parameters affecting the elution (i.e., eluent, mode of elution, eluent amount and desorption time) were studied. Adsorption optimization was conducted using the following initial experimental conditions: sol-gel sorbent: C_{18}, dimensions of microextraction capsules: 3 cm, stirring rate: 500 rpm, extraction time: 60 min, sample volume: 20 mL, salt content: 0% w/v NaCl, eluent: acetone, volume of eluent: 1 mL, desorption time: 5 min.

The effect of eluent was examined by evaluating the performance of four different solvents, i.e., acetone, methanol, acetonitrile, and toluene for the desorption of the adsorbed OPPs. An appropriate eluent must provide effective desorption of the analytes with enhanced recovery (Kaur et al., 2019). As shown in Figure S9, similar results were obtained for most analytes using acetone, methanol, and acetonitrile. However, acetone exhibited better performance compared to the other solvents for prothiophos, while it also characterized by low toxicity. Thus, acetone was chosen as eluent.

Accordingly, the elution mode was investigated. Since the CPME device contain a magnetic rod, the device can spin when a magnetic stirrer is employed. The need for stirring during the elution process was studied to ensure sufficient desorption of the analytes and two different modes of elution (i.e., with and without stirring) were evaluated. As it can be observed from Figure S10, stirring was not required during the elution of the target analytes. This is probably because of the sponge-like morphology and the inherent porosity and of sol-gel sorbents that enables the diffusion of the eluent during the desorption process, thus overcoming the need for any external energetic stimulus during this step (Kabir and Samanidou, 2021). Therefore, elution of the OPPs from the sol-gel C_{18} coated CPME device was carried out without stirring.

The desorption time is another important factor that must be investigated during the optimization of the CPME protocol to find the optimum time span that is required for elution system to exhaustively scavenge the adsorbed analytes and to ensure high sample throughput (Kabir and Samanidou, 2021). In this study, the desorption time was investigated in the range of 1-15 min. As it can be observed in Figure S11, 1 min was sufficient for the desorption of most of the adsorbed OPPs and it was chosen for further experiments. Only for chlorpyrifos, a slight increase of the extraction efficiency was observed by increasing the desorption time at 5 min. However, in order have increased

sample throughput and a rapid sample preparation protocol a desorption time of 1 min was finally chosen.

Finally, the amount of acetone was investigated. For this purpose, aliquots (250-1500 μL) were used during the elution step. The amount of the desorption solvent is associated with the enriching ability of the method and thus the utilization of small amounts of eluent can provide enhanced method sensitivity. Moreover, the use of low solvent amount complies with GAC regarding the reduction of the consumption of hazardous chemicals. In this case, sufficient recovery was obtained using small amount of acetone (Figure S12). Only for chlorpyrifos, the ER% was improved by using a higher solvent amount (1500 μL). However, taking into consideration the requirements of GAC , the elution of the OPPs was conducted using 250 μL of eluent.

3.3. Figures of merit

Method validation is thoroughly described in the Supplementary Material. The figures of merit of the proposed method are presented in Table 1. Good linearity was achieved for the OPPs and the coefficients of determination were 0.9912-0.9996. The LODs of the CPME-GC-MS methodology for the target analytes were 0.02-0.15 ng mL^{-1} and the LOQs were 0.05-0.50 ng mL^{-1}. The PF of the proposed method was 80 for all OPPs taking into consideration that the initial volume of sample was 20 mL and the final volume after elution was 250 μL. Moreover, the EF values for the target analytes ranged between 15 and 47, while the ER% values were 19-59%.

Table 1. Figures of merit for the CPME-GC-MS protocol.

OPP	Regression Analysis	R^2	Linear range (ng mL^{-1})	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	ER%	EF
Chlorpyrifos	y = 11696x + 5981.8	0.9982	0.20-100.0	0.06	0.20	59	47
Disulfoton	y = 32847x – 41670	0.9912	0.05-50.0	0.02	0.05	48	39
Ethoprophos	y = 8734.8x + 9309.8	0.9985	0.20-50.0	0.06	0.20	34	27
enchlorphos	y = 23013x + 14285	0.9969	0.05-50.0	0.02	0.05	57	46
Parathion-methyl	y = 5819.1x – 1159.3	0.9996	0.50-100.0	0.15	0.50	19	15
rothiophos	y = 9119.1x + 33918	0.9982	0.20-100.0	0.06	0.20	53	42

The results for the evaluation of method precision and accuracy are presented in Table S3. The RR% for the target analytes ranged between 92.6% and 107.0% for the intra-day study and between 90.8% and 107.6% for the inter-day study, indicating good method trueness. Furthermore, the RSDs were 1.5-8.7% and 5.4-9.6% for the intra-day and inter-day study, respectively. Thus, the method exhibits good precision. At a final step, the capsule-to-capsule reproducibility was examined utilizing six (n=6) different sol-gel C_{18} encapsulated microextraction capsules. The CPME media were used for the extraction of OPPs (c=5.00 ng mL^{-1}) from standard solutions prepared in deionized water. As shown in Table S3, the RSDs were better than 3.2%, indicating good capsule-to-capsule reproducibility.

3.4. Reusability of the sol-gel C_{18} capsules

During the evaluation of the performance of the sol-gel C_{18} encapsulated microextraction capsules, their potential reusability was examined. For this purpose, a single CPME device was used in 25 continuous adsorption/elution cycles of the target analytes from tap water. The reusability was evaluated taking into consideration the RR% value derived from the initial performance of the sol-gel C_{18} coated capsule and the performance after consecutive microextraction cycles. As such, a threshold of ≥ 10% of performance loss was set. The results are summarized in Figure S13. Since no important performance's reduction was seen after continuous adsorption/elution cycles, it can be concluded that the capsules are reusable for at least 25 times.

3.5. Comparison with other studies

A comparison of the herein proposed CPME-GC-MS method with other studies published in the literature is shown in Table 2.

Table 2. Comparison with other studies

Extraction	OPPs	Instrumentation	Sample volume (mL)	RSD%	Relative Recoveries %	Enhancement factors	LODs (ng mL^{-1})	Ref.
MSPE	Chlorpyrifos methyl, diazinon, malathion, parathion, parathion-methyl, pirimiphos-methyl	GC-MS	10	≤ 10.7 %.	NA[1]	NA	1.8-5.0	(Xie et al., 2013)
DLLME	Parathion-methyl, phoxim	HPLC-UV	10	2.5-2.7	88.2-103.6	50	0.17-0.29	(Zhou et al., 2008)
PT-SPE	Malathion, parathion	GC-MS	2	≤ 6.37	89.37-101.22	42.7-47.3	0.10	(Esrafili et al., 2020)
Continuous SPE	Diazinon, dimethoate, fenthion, fenthion sulfoxide, malathion, methidathion, parathion ethyl, parathion methyl	GC-NPD	10	2.9-4.3	93.8-104.5	95.0-98.6	0.05-0.13	(Ballesteros and Parrado, 2004)
SPME	Bromophos ethyl, bromophos methyl, dichlofen- thion, ethion, fenamiphos, fenitrothion,	GC-MS and GC-FTD	2-5	7-14 (for GC-MS) 3-10 (for GC-FTD)	86.2-119.7	NA	0.01-0.05 (for GC-MS)	(Lambropoulou et al., 2000)

Extraction	OPPs	Instrumentation	Sample volume (mL)	RSD%	Relative Recoveries %	Enhancement factors	LODs (ng mL^{-1})	Ref.
	fenthion, malathion, parathion-ethyl, parathion-methyl						0.01-0.02 (for GC-FTD)	
d-SPE	Diazinon, fenitrothion, fenthion, phosalone, profenofos	GC-FID	20	4.9-8.5 (intra-day) 5.9-8.8 (inter-day)	91.9-99.5	803-914	0.03-0.21	(Amiri et al., 2019)
CPME	Chlorpyrifos, disulfoton, ethoprophos, fenchlorphos, parathion-methyl and prothiofos	GC-MS	20	1.5-8.7 (intra-day) 5.4-9.6 (inter-day)	92.6-107.0 (intra-day) 90.8-107.6 (inter-day)	15-47	0.02-0.15	This study

[1] N.A.: Not available

As it can be observed, the developed approach permitted the utilization of higher amount of sample compared to those in literature (Ballesteros and Parrado, 2004; Esrafili et al., 2020; Lambropoulou et al., 2000; Xie et al., 2013; Zhou et al., 2008). In addition, the accuracy (in terms of RR% values) and the precision (in terms of RSD% values) of the proposed method is satisfactory, compared to other studies. The enhancement factors of the proposed method were similar to those of ref. (Esrafili et al., 2020; Zhou et al., 2008) but lower to those of ref. (Amiri et al., 2019; Ballesteros and Parrado, 2004). The LODs for the OPPs were better than those reported in ref. (Esrafili et al., 2020; Xie et al., 2013; Zhou et al., 2008) and comparable to those in refs. (Amiri et al., 2019; Ballesteros and Parrado, 2004; Lambropoulou et al., 2000). In case that further enhancement of method sensitivity is required, the herein developed microextraction protocol can be combined with more sensitive systems (e.g., GC-MS/MS instruments).

Besides the analytical performance parameters, the green nature of the selected procedures was also compared by application of ComplexGAPI (Płotka-Wasylka and Wojnowski, 2021). This tool enables the evaluation of the different analytical methods according to the principles of GAC. ComplexGAPI index takes into consideration the procedures, reagents, and instrumentation that are employed in an analytical method, while it also considers all the processes before the analysis (Płotka-Wasylka and Wojnowski, 2021). A green colour indicates the compliance with the respective requirements. From the GAPI pictogram in Figure 4, it can be concluded that the synthesis of the capsules shows high process yield and reduced waste generation, while it also shows a low E-factor, supporting green economy. Moreover, reduced consumption of chemicals and reduced waste generation can be also considered among the benefits of the technique since microextraction is used. As it can be seen, the proposed CPME-GC-MS method shows a greener character compared to previously reported protocols.

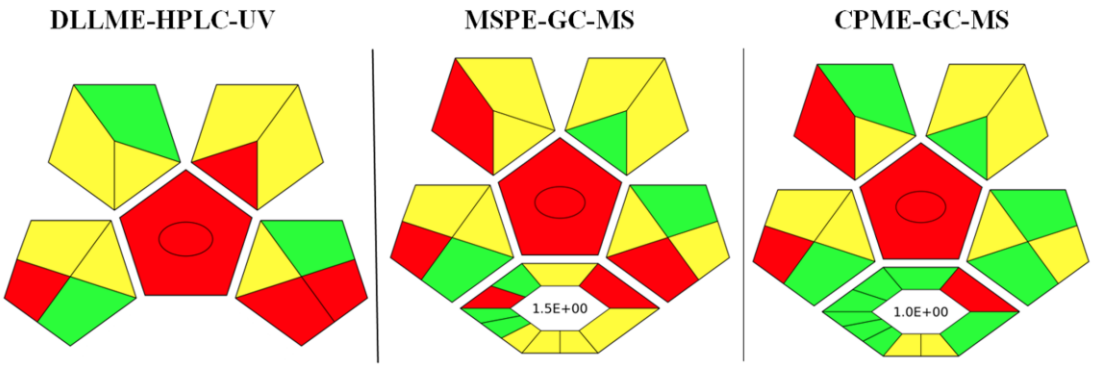

Figure 4. ComplexGAPI pictograms obtained for procedures based on DLLME-HPLC-UV (Zhou et al., 2008), MSPE-GC-MS (Xie et al., 2013), and CPME-GC-MS (this study)

Considering other advantages, CPME offers the benefits of fast and easy isolation of the sorptive phase, since the CPME device can be easily handled by using tweezers resulting in ease in isolation from the sample solution. On the contrary, the separation of the adsorbent in d-SPE (or MSPE) processes can be a time-consuming step and it may require additional instrumentation (e.g., centrifugation).

Additionally, in comparison with conventional SPE and LLE approaches, CPME offers the ability to use reduced amount of organic solvents and to simplify the overall procedure. When compared to a procedure based on HPLC-UV (Zhou et al., 2008), the same conclusion can be made, meaning, reduction of the solvent consumption and production of waste. Considering MSPE-GC-MS method (Xie et al., 2013) in which also additional processes are required prior to analysis, it is visible at first glance that the CPME-GC-MS method is greener, mainly in terms of the conditions used for the synthesis of required elements (sorbents, devices).

All features considered, CPME is a powerful technique for the monitoring of OPPs in environmental water samples.

3.6. Analysis of real samples

The CPME-GC-MS protocol was finally employed for the determination of OPPs in real water samples. Chromatograms of a spiked and a blank water sample are shown in Figure 5.

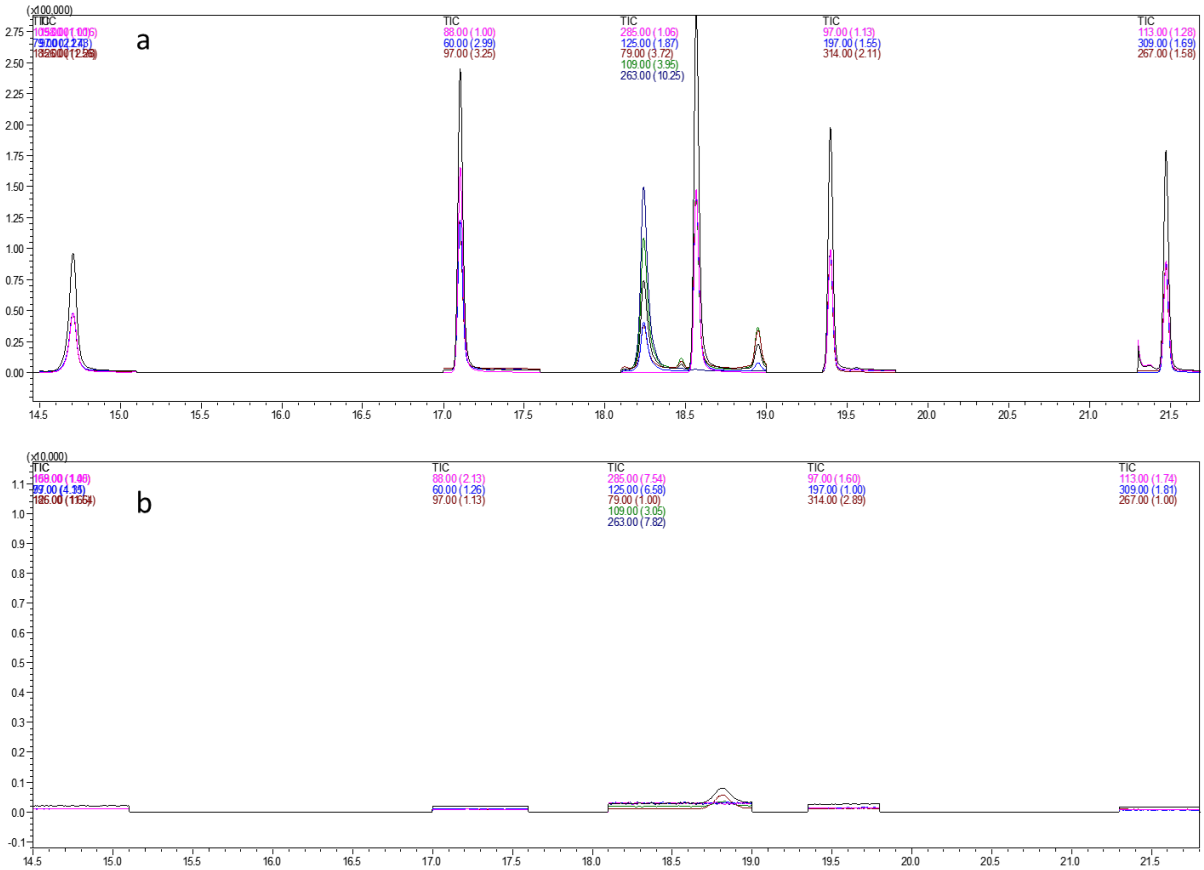

Figure 5. Chromatograms of (a) spiked river water sample (c=2.00 ng mL^{-1}) and (b) blank river water.

For the assessment of the potential method applicability in different types of water samples, spiked sample solutions (c=5.00 and 20.0 ng mL^{-1}) were prepared and analysed. Table 3 presents the obtained results for the real samples.

Table 3. Determination of OPPs by CPME-GC-MS in real water samples (n=2)

Analyte	Added (ng mL^{-1})	Lake water		Pond water		River water		Tap water	
		Found (ng mL^{-1})	Relative Recovery (%)	Found (ng mL^{-1})	Relative Recovery (%)	Found (ng mL^{-1})	Relative Recovery (%)	Found (ng mL^{-1})	Relative Recovery (%)
Chlorpyrifos	0	<LOD	-	<LOD	-	<LOD	-	<LOD	-
	5.00	5.58±0.49	111.6	5.73±0.40	114.6	5.18±0.39	103.6	4.77±0.20	95.4
	20.0	18.2±1.2	91.0	20.4±1.2	102.0	17.6±1.4	88.0	20.4±0.1	102.0
Disulfoton	0	<LOD	-	<LOD	-	<LOD	-	<LOD	-
	5.00	5.18±0.34	103.6	5.34±0.30	106.8	5.32±0.45	106.4	5.20±0.29	104.0
	20.0	20.4±0.9	102.0	19.0±0.1	95.0	19.0±0.8	95.0	18.0±1.6	90.0
Ethoprophos	0	<LOD	-	<LOD	-	<LOD	-	<LOD	-
	5.00	4.87±0.33	97.4	5.05±0.36	101.0	5.32±0.45	106.4	5.71±0.31	114.2
	20.0	20.5±1.5	102.5	19.3±0.2	96.5	18.9±0.4	94.5	18.5±1.3	92.5
Fenchlorphos	0	<LOD	-	<LOD	-	<LOD	-	<LOD	-
	5.00	4.54±0.19	90.8	5.02±0.18	100.4	5.71±0.21	114.2	4.32±0.15	86.4
	20.0	21.3±0.3	106.5	20.6±1.0	103.0	20.5±0.7	102.5	18.1 ± 0.2	90.5
Parathion-methyl	0	<LOD	-	<LOD	-	<LOD	-	<LOD	-
	5.00	4.27±0.15	85.4	4.49±0.34	89.8	5.11±0.08	102.2	4.08±0.09	81.6

Analyte	Added (ng mL^{-1})	Lake water		Pond water		River water		Tap water	
		Found (ng mL^{-1})	Relative Recovery (%)	Found (ng mL^{-1})	Relative Recovery (%)	Found (ng mL^{-1})	Relative Recovery (%)	Found (ng mL^{-1})	Relative Recovery (%)
	20.0	21.8±1.0	109.0	21.4±1.4	107.0	19.8±0.2	99.0	20.9±0.4	104.5
	0	<LOD	-	<LOD	-	<LOD	-	<LOD	-
Prothiophos	5.00	5.27±0.51	105.4	4.69±0.37	93.8	4.75±0.41	95.0	4.82±0.25	96.4
	20.0	19.3±0.9	96.5	17.6±1.5	88.0	19.2±1.4	96.0	18.8±1.0	94.0

The OPPs were not detected in the real samples. Thus, either there were no residues of these compounds in the samples, or their concentrations were lower compared to their respective LOD values. The RR% values for all analytes were found to be 81.6-114.6%. The average value 99.0% demonstrates that no significant matrix effect exists between the examined matrices. Thus, the proposed analytical scheme can be used for the analysis of lake, river, pond and tap water samples with good accuracy. Finally, the absence of interferences in the real samples confirm method selectivity.

4. Conclusions

A simple and efficient CPME-GC-MS protocol was developed for the monitoring of OPPs in environmental water samples. Sol-gel C_{18} encapsulated microextraction media were proved to be the most efficient CPME device for extracting and preconcentrating the target analytes. The analytical scheme exhibited good linearity, accuracy, sensitivity, and precision. The sol-gel C_{18} coated CPME devices were able to extract the target analytes from water samples for at least 25 continuous adsorption/desorption cycles. Moreover, the proposed method showed a greener character compared to previously reported protocols. A disadvantage of this methodology is that extraction was not *in situ* performed. However, by utilizing CPME and portable magnetic stirring, extraction can be carried out directly in the field aiming to reduce sample transport/storage costs. All features considered, CPME is an efficient and simple novel sample preparation which can be utilized for monitoring pollutants in environmental water. Future directions towards the utilization of CPME for OPPs extraction include its application for the sample preparation of other complex samples (e.g., food samples) and the expansion of its application for the extraction of multi-class of pesticides.

Declaration of Competing Interest

The authors declare no conflict of interest

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