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Novel extraction methods and compound-specific isotope analysis of methoxychlor in environmental water and aquifer slurry samples

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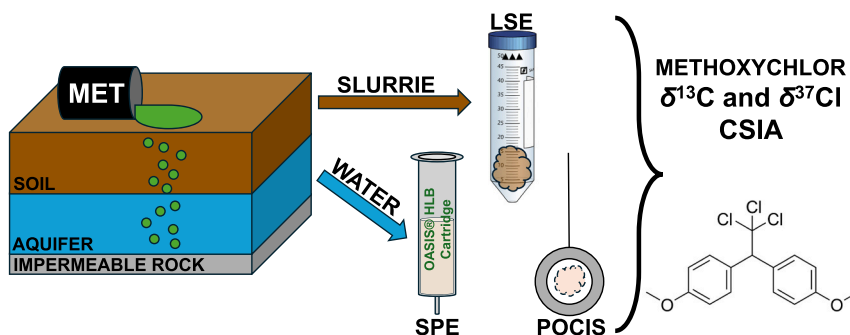
HIGHLIGHTS

High isotopic accuracy of methoxychlor and metabolite solid phase extraction from water

Methoxychlor liquid-solid extraction from slurry permits its stable isotope analysis. Methoxychlor uptake by PES membranes of POCIS may cause carbon isotopic effects.

Initial stride towards using ME-CSIA for elucidating methoxychlor sources and processes.

GRAPHICAL ABSTRACT



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ABSTRACT

Multi-element compound-specific stable isotope analysis (ME-CSIA) allows monitoring the environmental behavior and transformation of most common and persistent contaminants. Recent advancements in analytical techniques have extended the applicability of ME-CSIA to organic micropollutants, including pesticides. Nevertheless, the application of this methodology remains unexplored concerning harmful insecticides such as methoxychlor, a polar organochlorine pesticide usually detected in soil and groundwater. This study introduces methods for dual carbon and chlorine compound-specific stable isotope analysis ($\delta^{13}\text{C}$ -CSIA and $\delta^{37}\text{Cl}$ -CSIA) of both methoxychlor and its metabolite, methoxychlor olefin, with a sensitivity down to 10 and 100 mg/L, and a precision lower than 0.3 and 0.5 ‰ for carbon and chlorine CSIA, respectively. Additionally, three extraction and preconcentration techniques suitable for ME-CSIA of the target pesticides at environmentally relevant concentrations were also developed. Solid-phase extraction (SPE) and liquid-solid extraction (LSE) effectively extracted methoxychlor ($107 \pm 27\%$ and $87 \pm 13\%$, respectively) and its metabolite ($91 \pm 27\%$ and $106 \pm 14\%$, respectively) from water and aquifer slurry samples, respectively, with high accuracy ($\Delta\delta^{13}\text{C}$ and $\Delta\delta^{37}\text{Cl} \leq \pm 1\%$). Combining CSIA with polar organic chemical integrative samplers (POCISs) for the extraction of

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methoxychlor and methoxychlor olefin from water samples resulted in insignificant fractionation for POCIS-CSIA ($\Delta\delta^{13}\text{C} \leq \pm 1\text{‰}$). A relevant sorption of methoxychlor was detected within the polyethersulfones membranes of the POCISs resulting in temporary carbon isotope fractionation depending on the sorbed mass fraction during the first deployment days. This highlights the critical role of the interactions of polar analytes with POCIS sorbents and membranes in the performance of this method. Altogether, this study proposes a proof of concept for ME-CSIA of methoxychlor and its metabolites, opening the door for future investigations of their sources and transformation processes in contaminated sites.

1. Introduction

Organochlorine pesticides (OCPs) present a significant environmental concern owing to their enduring presence in the environment, considerable toxicity, and propensity for bioaccumulation within the food chain (Ntow, 2005; Swarczewicz and Gregorczyk, 2012; Xue et al., 2006). Among OCPs, the insecticide methoxychlor (MET) (2,2,2-trichloro-1,1-bis (4-methoxyphenyl) ethane) has been used mainly in agriculture, gardens and animal feeds of industrialized countries due to its high effectiveness against a wide variety of insects (Basavarajappa et al., 2011; Chen, 2014; Harris et al., 2002). There is a considerable concern about MET exposure due to its estrogenic activity (Frye et al., 2012; Staub et al., 2002) that may induce ovarian cancer cell to grow (Kim et al., 2014) and makes it highly toxic to aquatic invertebrates and fish, for which acute lethal concentrations are below 1 $\mu\text{g/L}$ and 10 $\mu\text{g/L}$, respectively (Anderson and DeFoe, 1980). MET has thus been restricted or banned in many countries since 2004, when it failed to be registered for the US Environmental Protection Agency (EPA) (Stuchal et al., 2006). Despite its ban, several sites are still highly polluted with this compound due to its high persistence in soils (Affum et al., 2018; Cruzeiro et al., 2016; Prajapati et al., 2022), mirroring its relatively low solubility (<0.05 mg/L at 24 °C in water) and high partition coefficient ($\log K_{ow} > 5$; Table S1). Even though most of this pollutant can be detected in soil, reaching concentrations up to 522 $\mu\text{g/g}$ (Thiombane et al., 2018), its monitoring in drinking water resources reveals concentrations up to 56 $\mu\text{g/L}$ (Oyekunle et al., 2022). Given the detrimental implications of MET on human health and ecosystems, it becomes paramount to comprehensively understand its environmental fate. Despite its high environmental persistence, MET degradation to methoxychlor olefin (MET-OLEF) has been reported via photochemical dechlorination (Zepp et al., 1976), oxidative dehydrochlorination (Hirai et al., 2004), and alkaline dehydrochlorination (Wolfe et al., 1977). MET-OLEF is also a high persistent compound with a high partition coefficient (Table S1). The monitoring of parent pesticide dissipation and detection of transformation products is often used to elucidate pesticide degradation (Fenner et al., 2013). However, concentration measurements of the parent compounds are often insufficient for discriminating between degradative processes involving molecular bond cleavage and other non-degradative processes, such as dilution or sorption, because all of them lead to a concentration decrease. In this context, compound-specific stable isotope analysis (CSIA) provides a complementary line of evidence to track pollutant degradation in environmental systems at different spatial and temporal scales (Elsner and Imfeld, 2016; Hofstetter et al., 2008, 2024; Hunkeler et al., 2008). Non-degradative processes (i.e., dilution, diffusion, sorption and volatilization) usually have much smaller effects on the isotope composition at natural abundance (Sun et al., 2021). In contrast, bond-cleavage reactions typically cause observable shifts in the isotope ratios (e.g., $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, $^{37}\text{Cl}/^{35}\text{Cl}$) at natural abundance. Therefore, CSIA has shown capacities for tracking the pathways and extent of degradation processes (Elsner, 2010; Elsner et al., 2012; Hofstetter and Berg, 2011). In particular, for improved precision in comprehending degradation mechanisms, concurrent monitoring of the signatures of two or more stable isotopes can be employed through multi-element compound-specific isotope analysis (ME-CSIA). ME-CSIA considers multiple isotope effects, effectively mitigating the potential masking of single-element

isotope fractionation that may result from rate-limiting steps other than bond cleavage (Elsner et al., 2012).

Regarding ME-CSIA application to pesticides, recent reports have predominantly focused on analytical methodologies for carbon CSIA and its fractionation arising from diverse pesticide degradation processes (Drouin et al., 2021; Gilevska et al., 2022a; Junginger et al., 2022; Lihl et al., 2020; Masbou et al., 2023; Torrentó et al., 2021). Some of these studies have also fostered the development of analytical methods for chlorine CSIA (Ponsin et al., 2019; Renpenning et al., 2018) and their application to evaluate pesticides degradation (Liu et al., 2020a, 2021a, 2022; Torrentó et al., 2021). Even though CSIA has been applied for pesticides in some field studies (Alvarez-Zaldívar et al., 2018; Liu et al., 2017; Masbou et al., 2023; Melsbach et al., 2020), field applications remain scarce mainly due to the fact that a significant preconcentration of pesticides within the sub- $\mu\text{g/L}$ range is needed for precise and accurate measurement of stable isotope ratios (Elsner and Imfeld, 2016; ISO, I. S. O., 1994; Schmidt and Jochmann, 2012). In this preconcentration process, which must not alter the pesticide isotope ratios, matrix constituents also become enriched alongside the target compounds, thereby limiting chromatographic resolution and leading to less reliable measurement of the stable isotope ratio of the target compound (Blessing et al., 2008; Blessing and Baran, 2022; Elsner et al., 2012). The combination of extraction methods and ME-CSIA should therefore be validated for each target compound. In this sense, different methods (e.g., liquid-solid extraction, ultrasonic-assisted extraction, Soxhlet extraction) have been used to extract and preconcentrate pesticides from soil samples for $\delta^{13}\text{C}$ -CSIA (Droz et al., 2021; Ivdra et al., 2014; Masbou et al., 2018; Niu et al., 2016) and $\delta^{37}\text{Cl}$ -CSIA (Liu et al., 2020b, 2021b; Torrentó et al., 2021). Solid phase extraction (SPE) methods have been widely used to extract and preconcentrate pesticides from large-volume environmental water samples for ME-CSIA (C, N, Cl) (Ponsin et al., 2019; Schreglmann et al., 2013; Torrentó et al., 2019).

Polar organic chemical integrative samplers (POCISs) are recognized methods for monitoring pesticides in water, mainly surface water (Booij and Chen, 2018; Chepchirchir et al., 2020; Valenzuela et al., 2021), to limit the collection of large volumes of water samples, and reduce extraction costs and solvent use. POCISs, typically consisting in a sorbent enclosed between polyethersulfones (PES) membranes, have recently been demonstrated as valuable tools for the preconcentration of specific pesticides from environmental water samples, thus facilitating $\delta^{13}\text{C}$ -CSIA (Gilevska et al., 2022b). A recent study from Suchana et al. (2024) obtained promising results extending the combination of POCIS with ME-CSIA (C, N, H) for polar nitro- and amino-substituted chlorobenzenes, which show high affinity for both sorbent and PES membrane phases. Although insignificant for carbon (<0.5 ‰), this work reported significant nitrogen isotope shifts, likely associated with the sorption to the PES phase of the studied substituted chlorobenzenes, with relatively high partition coefficients ($\log K_{ow}$ between 2.3 and 3.1). This highlights the importance of considering the interactions between the target compound, the sorbent and the PES membranes, and the isotopic consequences they may cause. It has also not been validated yet the combination of POCIS with CSIA for low flow rates for covering a wider range of hydrological conditions, since this is a key parameter for pesticide uptake capacity of the POCIS (Alvarez et al., 2004; Gilevska et al., 2022a).

Notwithstanding the progress in analytical techniques, CSIA has not

been applied to MET and its derivatives so far. The purpose of this study was thus to validate robust extraction and preconcentration techniques for MET and MET-OLEF in order to establish a ME-CSIA approach for environmental samples. This study endeavors to devise methods for carbon and chlorine CSIA ($\delta^{13}\text{C}$ -CSIA and $\delta^{37}\text{Cl}$ -CSIA) of MET and, MET-OLEF. It also encompasses the development and validation of extraction and preconcentration approaches for these pesticides from environmental samples, including both water and slurry/soil, ensuring that these methods do not alter the stable isotope composition of the targeted compounds. Additionally, the study explores the feasibility of combining CSIA with POCISs for these compounds with high partition coefficients ($\log K_{ow} > 4$), paying special attention on their sorption to the PES membranes and the potential carbon isotopic effect, and on the effect of the hydrological conditions, offering a promising avenue for integrative sampling and monitoring of MET and MET-OLEF from contaminated water.

2. Materials and methods

2.1. Chemicals

Analytical standards MET (1-methoxy-4-[2,2,2-trichloro-1-(4-methoxyphenyl)ethyl]benzene; 72-43-5; Pestanal® quality) and MET-OLEF (1-[2,2-dichloro-1-(4-methoxyphenyl)ethenyl]-4-methoxybenzene; 2132-70-9; standard quality) were purchased from Supelco®. Phenanthrene and docosane, both with a minimum purity of 98 %, were sourced from Sigma-Aldrich® and employed as carbon isotope standards. The international isotope reference standard USGS72, consisting of eicosanoic acid methyl ester with a minimum purity of 99.5 %, was graciously provided by Dr. Arndt Schimmelmann's laboratory at Indiana University. Stock solutions were prepared in hexane at 1 mg/mL and stored at $-18\text{ }^{\circ}\text{C}$. Methoxychlor-d14 (100 $\mu\text{g}/\text{mL}$ in acetone, standard quality), used as surrogate, was purchased from Dr. Ehrenstorfer™. Extraction tests for validating the different extraction techniques were performed with MET and MET-OLEF intermediate solutions prepared in acetone and used as spiked solutions. The in-house reference standards for chlorine isotope analysis, trichloroethene and methyl chloride were purchased from Merck and Linde Gas AG, respectively. The solvents used for extraction, hexane, dichloromethane (DCM), and ethyl acetate (EtAc), in SupraSolv® quality, and acetone and methanol (MeOH), in EMPROVE® ESSENTIAL quality, were purchased from Merck.

2.2. Analytical methods

2.2.1. MET and MET-OLEF quantification

Concentration of MET and MET-OLEF was determined using a Shimadzu QP2010 single quadrupole Gas Chromatograph Mass Spectrometer (GC-MS). The mass spectrometer was operated in the electron ionization mode (70 eV). Selected-ion monitoring measurements were performed and each analyte was quantified based on peak area using one quantifier and three qualifier ions. The monitored m/z ratios and corresponding retention times are provided in Table S2. Typical concentrations range for analysis were from 10 $\mu\text{g}/\text{L}$ to 2000 $\mu\text{g}/\text{L}$. Additional instrumental and methodological details are provided in the Supporting Information section S2.1.

2.2.2. CSIA of MET and MET-OLEF

Carbon isotope measurements of MET and MET-OLEF were performed by gas chromatography coupled with isotope ratio mass spectrometry (GC-IRMS) using a Trace GC 1310 coupled to a MAT 253 Plus IRMS through a GC Isolink II and a Conflo IV interface (Thermo Fisher Scientific). Gas chromatography coupled with multiple-collector inductively coupled plasma mass spectrometry (GC-MC-ICPMS) was used for chlorine isotope analysis (Renpenning et al., 2018), since the ionization fragmentation pattern of MET (i.e., low relative peak intensities of fragments with chlorine atoms) hinders chlorine isotope

ratios determination by GC-qMS. A Trace 1310 GC coupled to a NEPTUNE MC-ICPMS (Thermo Fisher Scientific) via an AE2080 transferline (Aquitaine Electronique) was used. Further instrumental and methodological details are provided in Supporting Information S2.2 and S2.3.

C and Cl isotope values are reported in per mil (‰) using the delta notation (δ) relative to the international reference points Vienna PeeDee Belemnite (V-PDB) and Mean Ocean Chloride (SMOC), respectively:

$$\delta^h E (\text{‰}) = \left[\frac{R_E}{R_{E,\text{std}}} - 1 \right] \quad (1)$$

where E is the considered element (C or Cl), h is the atomic mass of the heavier isotope (13 for C and 37 for Cl), R_E and $R_{E,\text{std}}$ are the isotope ratios of the element E ($^{13}\text{C}/^{12}\text{C}$ for carbon and $^{37}\text{Cl}/^{35}\text{Cl}$ for chlorine) in the sample and the corresponding reference compound, respectively.

The carbon isotope ratios were calibrated using a laboratory standard gas (CO_2), which was introduced at the beginning and end of each run. $\delta^{13}\text{C}$ raw values were then calibrated against the VPDB standard using a 5-point linear calibration with the in-house standards of MET, MET-OLEF, phenanthrene, and docosane and the international reference material (USGS72) spread throughout the chromatograms diluted to a similar sample concentration and measured in duplicate. The carbon isotope ratios of the working standards were determined by EA-IRMS (Elemental Analyser Flash coupled to an IRMS DELTA V ADVANTAGE).

The chlorine isotope ratios were referenced using the in-house reference compound methyl chloride. The obtained raw $\delta^{37}\text{Cl}$ values were then normalized to the SMOC scale by applying a two-point calibration approach using the two in-house reference compounds of known isotope signatures: methyl chloride and trichloroethene. These reference compounds were offline characterized by dual inlet (DI)-IRMS (Renpenning et al., 2015). Further details may be found at the Supporting Information S2.2 and S2.3.

Linearity ranges of $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ measurements were assessed as a function of injected concentration, and limits of precise isotope analysis were then derived according to the moving mean procedure (Jochmann et al., 2006), using uncertainty intervals of ± 0.5 and ± 1 ‰, respectively.

2.3. Extraction methods

For all extraction methods, extraction efficiency and isotope fractionation were evaluated by using spiking solutions of the MET and MET-OLEF working standards of known carbon and chlorine isotope ratios.

2.3.1. MET and MET-OLEF extraction from small water volumes (10–500 mL)

The solid phase extraction (SPE) method was adapted from EPA METHOD 525.3 (Grimmett and Munch, 2013). Divinylbenzene N-vinylpyrrolidone copolymer cartridges (Oasis HLB 500 mg, Waters) were used. The cartridges were first rinsed with 5 mL EtAc, conditioned with 10 mL MeOH and finally rinsed again with 10 mL MilliQ water. Water samples (10 to 500 mL) spiked with methoxychlor-d14, used as a surrogate, were loaded on the cartridges at approximately 5 mL/min. The cartridges were then rinsed twice with 5 mL MilliQ water and dried under vacuum for 60 min. Elution was performed by adding 5 mL EtAc followed by 5 mL DCM. The eluates were then evaporated to dryness followed by reconstitution with an appropriate volume of hexane for GC-MS, GC-IRMS and GC-MC-ICPMS injections.

The efficiency of the SPE method was assessed regarding its ability to extract target compounds from a mixture under varying conditions, including different concentration levels (ranging from 0.025 $\mu\text{g}/\text{L}$ to 2.5 mg/L), water volumes (ranging from 10 to 500 mL), mass load (ranging from 0.002 to 2 μg), and different water matrices (comprising MilliQ water and pesticide-free groundwater). Detailed information about the

sampling and hydrochemical composition of the used pesticide-free groundwater can be found in **Supporting Information S2.4**. Finally, the entire SPE-CSIA procedure was validated for both MET and MET-OLEF with distilled water at two mass load levels (25 and 50 µg) by varying water volume (from 10 to 100 mL) and analyte concentration (from 0.25 to 5 µg/L). Those tests were performed in duplicate.

2.3.2. MET and MET-OLEF extraction from large water volumes (10–20L)

Large water volumes are required to perform SPE for routine ME-CSIA of MET and MET-OLEF at environmentally relevant concentrations (< 2 µg/L). To validate the use of this method for environmental samples, the method for small water volumes was upscaled and Oasis HLB 6 g cartridges (Waters) were used to retain more pesticide mass from a larger volume of water. The solvent volumes were also upscaled, and, therefore, the cartridges were first rinsed twice with 15 mL EtAc, conditioned four times with 15 mL MeOH and equilibrated four times with 15 mL MilliQ water. The cartridges were then attached to polytetrafluoroethylene (PTFE) sampling tubing using PTFE cap adapters and large-volume water samples (10–20 L) were pumped through the cartridges at 5 mL/min. A 20 L Nalgene™ heavy-duty vacuum carboy served as a water trap between the vacuum pump and the vacuum manifold (Fig. S4). Subsequently, the sorbent was rinsed with 15 mL Milli-Q water four times and dried under vacuum. The cartridges were eluted with three times 15 mL EtAc and three times 15 mL DCM. Eluates were then evaporated to dryness. The dry extracts were stored frozen until concentration and isotope analyses. Appropriate reconstitution volumes of hexane were used for GC-MS, GC-IRMS and GC-MC-ICPMS injections.

Extraction efficiency and isotope fractionation were evaluated for 10–20 L of distilled water and the pesticide-free groundwater described in the **Supporting Information S2.4** spiked with MET and MET-OLEF at a range of concentrations between 200 and 2000 ng/L.

2.3.3. Set up of the POCISs validation experiments for MET and MET-OLEF

Laboratory scale validation experiments were conducted to evaluate the performance of the whole POCIS-CSIA procedure. The experimental set-up was adapted from Gilevska et al. (2022b). For all the tests, 5-l tanks filled with deionized water, maintained at laboratory temperature (20 ± 1 °C) and covered with aluminium foil to prevent photo-degradation and algal development, were used.

By modifying the size and the speed of magnetic stir bar used for stirring, various flow velocities were simulated. The stirring speed (rpm) was determined through Reynolds number calculations to attain the desired flow rate:

$$rpm = \frac{v \cdot L \cdot \mu}{u \cdot D^2 \cdot \rho} \quad (2)$$

where v (m/s) is the flow speed, L (m) is the diameter of the beaker, μ (g/cm·min) is the dynamic viscosity, u (m²/s) is the kinematic viscosity, D (cm) is the length of the stirring bar, and ρ (g/cm³) is the density.

POCISs were prepared using 280 mg of HyperSep™ Retain (Thermo Scientific) sorbent (equivalent to Oasis HLB sorbent). The sorbent was placed between two microporous polyethersulfone (PES) membranes (0.1 µm pore size, 90 mm outside diameter, Pall Corporation) and tightly fixed to two stainless-steel rings (90 mm outside diameter, AFFINISEP) with five screws (Fig. S5).

Two set of experiments were performed; on one hand, four tanks (tanks A-D) were used for assessing the compatibility of POCIS with CSIA for MET and MET-OLEF under different scenarios. These tanks were equipped with eight POCISs each and spiked with the MET and MET-OLEF working standards at two distinct concentrations (2 and 10 µg/L). The tanks were stirred at two different flows: 2.5 cm/s (100 rpm) or 15 cm/s (600 rpm) to cover different hydrological conditions (Fig. 1). Water was changed in each tank every 3–4 days in order to maintain a constant concentration along the experiment. Concurrently, water samples (100 mL) were collected 15 min following the spiking event in every water change to determine initial pesticide concentrations. Pairs of POCIS samples were collected for each treatment on Days 20, 25, 30, and 35.

On the other hand, complementary tests were performed for assessing MET and MET-OLEF losses by other processes rather than retention into the POCIS sorbent, and for evaluating pesticide sorption to the PES membrane and its potential carbon isotopic effect (tanks E and F). Both tanks were stirred at 600 rpm (15 cm/s) during 7 days and 100 mL water samples were collected on Days 0, 1, 2, 3, 6 and 7 to quantify MET and MET-OLEF in water. Tank E contained 8 sorbent-free POCISs (i.e., without sorbent) and was spiked with the working standards of MET and MET-OLEF at 10 µg/L to quantify the sorption of MET and MET-OLEF on the PES membrane, the stainless-steel rings, and the tank walls, and potential losses by other factors (Fig. 1). On Days 2, 3, 6 and 7, two sorbent-free POCISs were collected for pesticides extraction from the PES membranes and the stainless-steel rings. Tank F was spiked with MET and MET-OLEF at approximately 15 µg/L and 5 µg/L, respectively, and no POCISs were introduced to assess if other factors affected pesticides concentrations over time. At the end of the experimental period, the walls of tanks E and F were cleaned with EtAc for pesticide concentration measurements. A fluorescein diacetate (FDA)-assay to discard microbial activity was performed with water samples of both tanks (E and F) at the beginning and the end of the complementary tests. More information about the protocol, adapted from Adam and Duncan (2001), can be found in **Supporting Information S2.4**.

2.3.4. MET and MET-OLEF extraction procedures from POCIS validation experiments

The 100 mL water samples were extracted and preconcentrated with Oasis HLB 200 mg cartridges using an AutoTrace 280 SPE system (Dionex® 160), using the same SPE procedure as described in Section 2.3.1 for small water volumes. Extracts were reconstituted in appropriate hexane volumes for GC-MS injections for determining pesticide concentrations, expressed as time-weighted average concentrations in

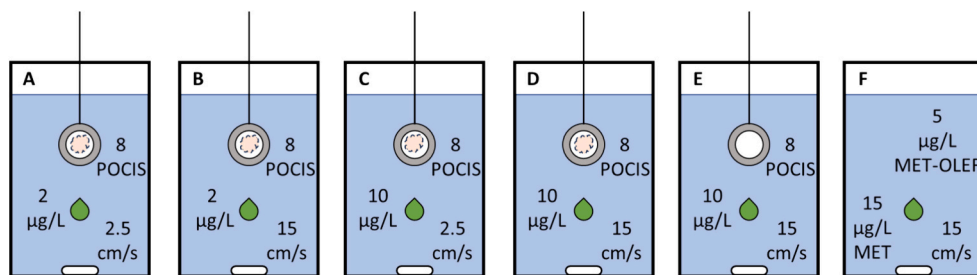


Fig. 1. Schemes of the POCIS validation experiments for MET and MET-OLEF. **Tanks A-D:** POCIS experiments with two MET and MET-OLEF concentrations and two flow rates. **Tanks E-F:** Complementary POCIS tests for assessing MET and MET-OLEF losses by other processes rather than retention into the POCIS sorbent, and for evaluating pesticide sorption to the PES membrane and its potential carbon isotopic effect. Tank E was performed with sorbent-free POCIS, whereas in Tank F no POCISs were introduced.

water (C_w).

Each POCIS was carefully opened to transfer the sorbent into an empty 6 cc SPE cartridge and covered from both sides with HDPE frits (Thermo Scientific). Samples were dried under a gentle stream of nitrogen for 30 min and eluted using the SPE procedure explained in Section 2.3.1. Once the extracts were evaporated to dryness under a gentle stream of nitrogen, they were reconstituted in appropriate hexane volumes for GC-MS and GC-IRMS injections.

The pollutant concentration in a POCIS (C_{POCIS}) ($\mu\text{g/g}$) is calculated dividing the pollutant amount in a POCIS (N_{POCIS}) (μg) by the sorbent mass (M_{POCIS}) (g):

$$C_{POCIS} = \frac{N_{POCIS}}{M_{POCIS}} \quad (3)$$

To extract the pesticides from the PES membrane, the method was adapted from Suchana et al., 2024. Briefly, the PES membranes were air-dried inside a fume hood for 5 h, cut into small pieces, and extracted using 20 mL of EtAc on an orbital shaker at 250 rpm for 48 h. Once the elute was collected, the container was cleaned with 10 mL of EtAc. The 30 mL were then filtered using a 0.22- μm PTFE syringe filter, and evaporated in a 2 mL vial for its further resuspension in appropriate volumes of hexane for GC-MS and GC-IRMS injections. To evaluate possible interferences, a blank PES membrane was extracted using the same protocol. To clean the stainless-steel rings and the tank walls, EtAc was used, recovered and evaporated into a 2 mL vial for resuspension in appropriate hexane volumes for GC-MS injections.

2.3.5. MET and MET-OLEF extraction from slurries

The liquid-solid extraction (LSE) method for aquifer slurries was adapted from Fuentes et al., 2014. Slurry samples were centrifuged (9000 rcf, 5 min, 4 °C) to separate the solid from the aqueous phase. The solid phases were then stored in the dark at -20 °C until extraction. Portions of 1 g of solid slurry were transferred to polypropylene centrifuge tubes and combined with 4 mL of Milli-Q water, 3 mL of methanol, and 15 mL of hexane to facilitate the extraction of pesticides from the slurry into the organic phase. The tubes were hermetically sealed and vortexed for 10 min. Finally, the tubes were centrifuged (9000 rcf, 10 min, 4 °C) for separating organic and aqueous phases. The organic phases were removed using a pipette and transferred to glass vials. Finally, the organic phases were evaporated to dryness under a gentle stream of nitrogen. The residues were resuspended in hexane for GC-MS, GC-IRMS and GC-MC-ICPMS injection.

Efficiency and method performance of the slurry extraction method was evaluated with pesticide-free aquifer slurry samples spiked with different concentrations of the working standards of MET (from 0.01 to 100 $\mu\text{g/g}$) and MET-OLEF (from 0.001 to 100 $\mu\text{g/g}$). The slurry samples were collected from the bottom of the same non-contaminated well where the groundwater samples used in this study were sampled. The sampled pesticide-free slurry showed an organic carbon content of 1.1 ± 0.1 %, determined by elemental analysis (Kennedy et al., 2005). Slurries were spiked with 1 mL of corresponding pesticide stock solutions in acetone, and vortexed during 1 min to ensure homogenization. Slurry samples were incubated for 24 h in the dark at room temperature until complete acetone evaporation before extraction.

3. Results and discussion

3.1. Analytical methods validation

3.1.1. Validation of C-CSIA by GC-IRMS

$\delta^{13}\text{C}$ values of the MET and MET-OLEF working standards measured by GC-IRMS were reproducible throughout the analysis period ($\sigma \leq 0.4$ ‰, 1 month). Good precision (expressed as $\pm \sigma$) of ± 0.3 and ± 0.2 ‰ was achieved for $\delta^{13}\text{C}$ ($n = 31$) analysis of MET and MET-OLEF, respectively. The accuracy for $\delta^{13}\text{C}$ ($\Delta\delta^{13}\text{C}$, expressed as the deviation from the EA-IRMS values) was for both compounds within $\leq \pm 0.2$ ‰

(Table S4). Instrumental detection limits of 10 mg/L were determined for both MET and MET-OLEF. Notably, there was no observed concentration dependence on the precision and accuracy within the tested range above the instrumental limit, spanning from 10 to 100 mg/L (from 10 to 100 ng of compound on column, i.e., 6–56 ng C) (Fig. S6).

A 2-min reactor oxidation before each analysis was found to be crucial for maintaining optimal measurement conditions in terms of precision, accuracy, and instrument response (m/z 44 amplitude, $\sigma = \pm 0.3$ ‰ and 0.3 ‰ for MET and MET-OLEF, respectively). More information and the comparison with no oxidation or oxidation of the reactor every 5 runs may be found in Supporting Information S3.1.

3.1.2. Validation of Cl-CSIA by GC-MC-ICPMS

The $\delta^{37}\text{Cl}$ values of the MET and MET-OLEF working standards measured by GC-MC-ICPMS were reproducible ($\sigma \leq 0.4$ ‰) for independent sequences measured at different days, and showed a good precision (expressed as $\pm \sigma$) of ± 0.5 ‰ for MET ($n = 48$) and ± 0.4 ‰ for MET-OLEF ($n = 11$) (Table S5). In line with Renpenning et al. (2018), an overall excellent accuracy for the two in-house reference compounds with known isotope signatures was achieved, with $\Delta\delta^{37}\text{Cl}$ values of $\leq \pm 0.03$ ‰ (expressed as the deviation from the DI-IRMS values) for both compounds. Corresponding precision ($\pm \sigma$) was ± 0.1 ‰ for $\delta^{37}\text{Cl}$ of methyl chloride ($n = 28$) and trichloroethene ($n = 28$) (Table S5). Instrumental detection limits of approximately 100 mg/L in solvent before injection were achieved for both MET and MET-OLEF. Precision was concentration-dependent for MET, whereas no concentration dependence on the precision was observed for MET-OLEF within the tested range above the instrumental limit, spanning from 100 to 1100 mg/L (from 100 to 1100 ng of compound on column, i.e., 31–339 ng Cl) (Fig. S6).

3.2. Validation of MET and MET-OLEF extraction methods

3.2.1. Validation of the SPE-ME-CSIA method for small water volumes (10–500 mL)

The 500 mg Oasis HLB cartridges extract a high MET proportion (recoveries >90 %) from small volume distilled water samples (10 to 500 mL) with mass loads between 0.01 and 2 μg (Table S6), corresponding to concentration levels between 0.05 and 200 $\mu\text{g/L}$ (Fig. S9). High recoveries (>90 %) were also obtained for MET-OLEF, with the exception of concentrations below 0.2 $\mu\text{g/L}$ when employing 100 mL (72 ± 18 %); nevertheless, high recoveries (>80 %) were achieved with extraction volume of 500 mL (Fig. S9). Extraction efficiencies and repeatability, expressed as relative standard deviation (RSD), are detailed in the Supporting Information S4.1.

Subsequent extraction tests were conducted at elevated concentrations of MET and MET-OLEF to detect any isotope fractionation introduced by SPE when processing distilled water samples with varying analyte mass loads (25 and 50 μg). Extractions from 50 and 100-mL samples resulted in high recoveries for both MET (91–105 %, with RSDs 0.2–22 %) and MET-OLEF (92–113 %, with RSDs 4–26 %) at all concentration levels (Fig. S10). Decreasing the volume to 10 mL resulted in lower recoveries, especially for the highest concentration of 5 mg/L (63 ± 9 % for MET and 57 ± 3 % for MET-OLEF), indicating that further optimization of the flow rate may be required since a slower flow rate may allow a higher sorption of the analytes to the sorbent.

Independently of the recovery, the accuracy of the entire SPE-ME-CSIA method for the small volume samples (10–100 mL) with high mass loads for both compounds (25 and 50 μg) was within the interval of ± 1 ‰ for both carbon and chlorine, except for the $\Delta\delta^{37}\text{Cl}$ -MET value of the sample with the lowest volume (10 mL) and mass (25 μg), with $\Delta\delta^{37}\text{Cl} = 1.3 \pm 0.3$ ‰ (Fig. 2). Briefly, extraction of MET resulted in $\Delta\delta^{13}\text{C}$ values ≤ 0.3 ‰ for 50 and 100-mL samples, whereas higher shifts were observed for 10-mL samples ($\leq \pm 0.6$ ‰). For MET-OLEF, no effect in $\delta^{13}\text{C}$ values was detected ($\Delta\delta^{13}\text{C}$, i.e., GC-IRMS vs. EA-IRMS: ± 0.1 ‰) in any case (Fig. 2). Higher shifts were observed for $\delta^{37}\text{Cl}$, but still within

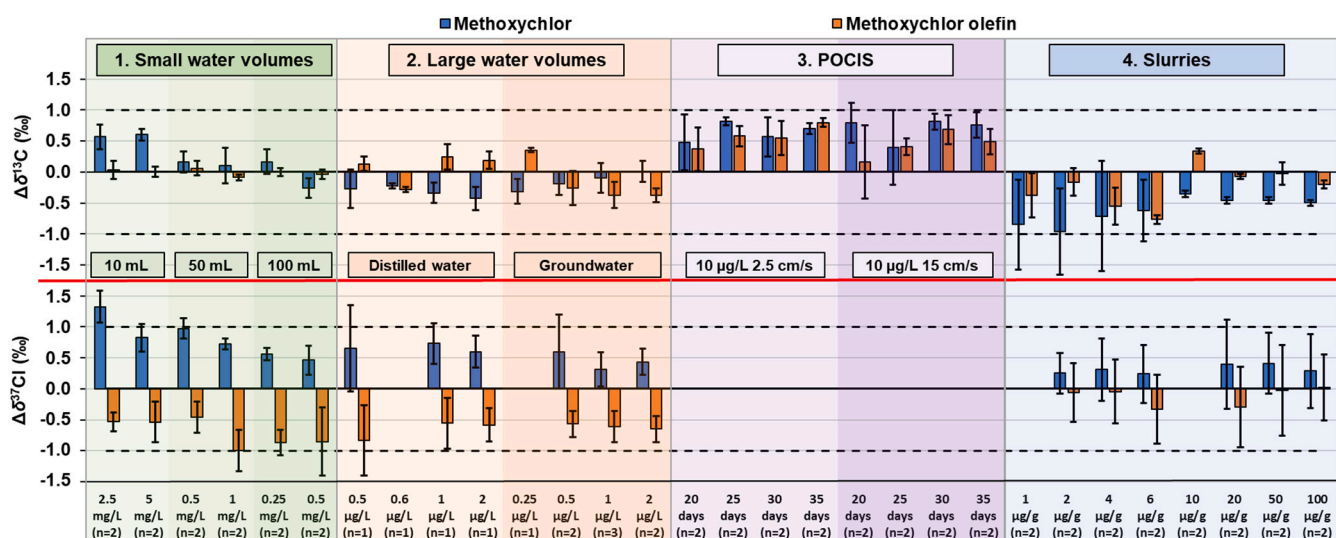


Fig. 2. Carbon (upper part) and chlorine (lower part) isotope fractionation associated with 1) SPE of small water volumes: Oasis HLB 500 mg cartridges extractions (green panel); 2) SPE of large water volumes: Oasis HLB 6 g cartridge extractions (orange panel); 3) POCIS validation experiments: POCISs extractions (purple panel); and 4) LSE of slurries: pesticide-free slurry samples extraction (blue panel), all spiked with MET and MET-OLEF. Accuracy ($\Delta\delta^{13}\text{C}$ and $\Delta\delta^{37}\text{Cl}$) of the whole SPE-, POCIS- and LSE-CSIA methods is reported as the shift of $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values of the GC-IRMS and GC-MC-ICPMS measurements compared to the values of the spiked standards measured by EA-IRMS and GC-MC-ICPMS, respectively. The black lines stand for $\Delta\delta^{13}\text{C}$ and $\Delta\delta^{37}\text{Cl} = 0$ ‰, respectively and the dashed lines represent a ± 1 ‰ uncertainty. Error bars represent the total uncertainty for the $\Delta\delta^{13}\text{C}$ and $\Delta\delta^{37}\text{Cl}$ values, calculated via error propagation based on the standard deviation of mean $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values from duplicate GC-IRMS and triplicate GC-MC-ICPMS measurements for each sample, respectively, and for replicate (n) extraction tests.

the ± 1 ‰ interval, except for the above-mentioned case (Fig. 2). Considering all the cases, a significant but low and constant average change in Cl stable isotope ratios associated with the extraction was observed for MET ($\Delta\delta^{37}\text{Cl} = 0.7 \pm 0.2$ ‰) and MET-OLEF ($\Delta\delta^{37}\text{Cl} = -0.7 \pm 0.2$ ‰) (Table S6).

3.2.2. SPE-ME-CSIA method scale-up to large water volumes (10–20 L) and validation

Extraction tests of large volume water samples (10 and 20 L) at environmentally relevant concentrations (0.2 to 2 $\mu\text{g/L}$) resulted in high recoveries for both compounds using distilled water (Fig. S11). Briefly, recoveries were 93 ± 8 % for MET and 60 ± 1 % for MET-OLEF for the 10 L extractions spiked with 200 ng/L ($n = 2$), and between 79 % and 141 % for MET and between 73 % and 124 % for MET-OLEF for the 20 L extractions spiked with 0.2 to 2 $\mu\text{g/L}$ ($n = 1$ for each concentration level). Similar recoveries were obtained for MET (between 77 and 106 %) for the 20 L extraction tests with spiked groundwater whereas the matrix effect resulted in lower recoveries for MET-OLEF (between 40 and 84 %) (Fig. S11). These lower recoveries obtained for the groundwater samples have also been observed in large water volume SPE of similar compounds such as butachlor, S-metolachlor, atrazine, acetochlor, S-metolachlor, metalaxyl and alachlor (Gilevska et al., 2022a; Schreglmann et al., 2013).

Independently of the recovery, the accuracy of the SPE-ME-CSIA method for the large water volumes was within the interval of ± 1 ‰ for both carbon and chlorine (Fig. 2). Indeed, similar carbon accuracy ($\Delta\delta^{13}\text{C}$) for MET and MET-OLEF was obtained whether distilled water (-0.3 ± 0.1 ‰ for MET; 0.1 ± 0.1 ‰ for MET-OLEF) or pesticide-free groundwater (-0.1 ± 0.1 ‰ for MET; -0.2 ± 0.1 ‰ for MET-OLEF) were used for the extraction tests (Fig. 2). Higher shifts were observed for $\delta^{37}\text{Cl}$ but also with similar accuracy ($\Delta\delta^{37}\text{Cl}$) for MET and MET-OLEF whether the extraction tests were performed with distilled water (0.7 ± 0.1 ‰ for MET; -0.7 ± 0.2 ‰ for MET-OLEF) or pesticide-free groundwater (0.5 ± 0.1 ‰ for MET; -0.6 ± 0.1 ‰ for MET-OLEF). Detailed results can be found in Table S6.

Therefore, after proving SPE to be a functional method for ME-CSIA of MET and MET-OLEF at environmental relevant concentrations under low and large water volume scenarios, POCISs were tested to assess the

feasibility of this methodology to reduce extraction costs and solvent use.

3.2.3. Validation of the POCIS-CSIA method

All the POCISs collected from the four POCIS validation experiments (tanks A-D) showed sorbent mass recoveries ranging from 72 to 92 % (Table S7). Although uptake and accumulation of the target pesticides occurred at the two tested concentrations (2 and 10 $\mu\text{g/L}$), the final concentration in POCISs collected from the two 2 $\mu\text{g/L}$ tanks was too low to enable reliable CSIA (Fig. S12). Pesticide sorption to the POCISs in the 10 $\mu\text{g/L}$ tanks exhibited a gradual and exponential pattern over the course of 35 days (Fig. S12), resulting in final retention levels of 71 $\mu\text{g/g}$ and 59 $\mu\text{g/g}$ for MET, and 22 $\mu\text{g/g}$ and 29 $\mu\text{g/g}$ for MET-OLEF at 2.5 and 15 cm/s, respectively (Table S6). These findings suggest that the flow rate exerts minimal influence on the uptake of the target analytes by the POCISs, indicating that this tool may also be effective for MET and MET-OLEF extraction in water bodies with low flow, such as groundwater or lakes, although further tests should be performed to confirm it. These results contrast with those obtained for other pesticides, such as atrazine (Gilevska et al., 2022b), where the water flow (6 vs. 14 cm/s) had a significant effect on the amount of pesticide accumulated on the sorbent. This effect may be related with the higher octanol – water partition coefficient ($\log K_{ow}$) for methoxychlor (5.08, Karickhoff et al., 1979) compared to atrazine (2.61, Paschke et al., 2004).

The pesticide mass in the extracts was insufficient to conduct both carbon and chlorine CSIA. Consequently, only GC-IRMS measurements were performed (Table S6). For both compounds, a consistent and reproducible change in the carbon isotope ratios compared to the EA-IRMS values was observed throughout the deployment period for MET (average $\Delta\delta^{13}\text{C} = 0.6 \pm 0.2$ ‰ and 0.7 ± 0.2 ‰) and MET-OLEF (average $\Delta\delta^{13}\text{C} = 0.5 \pm 0.1$ ‰ and 0.4 ± 0.3 ‰) at 2.5 (tank C) and 15 cm/s (tank D), respectively (Fig. 2). This slight reproducible inverse isotope effect (i.e., enrichment in the heavier isotope in the sorbed phase) is consistent with the work of Suchana et al., 2024 with substituted chlorobenzenes with relatively high partition coefficients ($\log K_{ow} = 2.3$ to 3.1) and containing chloride substituents. Therefore, in accordance with previous results for other pesticides and substituted chlorobenzenes (Gilevska et al., 2022a; Suchana et al., 2024), the POCIS

approach for MET and MET-OLEF showed high carbon isotopic accuracy and precision ($\Delta\delta^{13}\text{C} < 0.7\text{‰}$), even at lower flow rates than those reported so far. Further tests are required to assess the feasibility of this approach for $\delta^{37}\text{Cl}$ -CSIA.

The test using sorbent-free POCISs (i.e., without sorbent material) (tank E) showed a rapid decrease in the concentration of both MET and MET-OLEF in the water within the initial day, dropping from 10 $\mu\text{g/L}$ and 7 $\mu\text{g/L}$, respectively, to 1 $\mu\text{g/L}$ in both cases (Table S8). This aligns with an increase in the pesticide mass adhering to the POCIS, primarily occurring on the PES membranes: by the end of the test (7 days), 72 % of the MET mass and 45 % of the MET-OLEF mass had adhered to the PES membranes, while only 8 % and 32 % were adhered to the stainless-steel rings, respectively. Even though the proportion of MET and MET-OLEF mass adhered to the PES membranes and the stainless-steel rings fluctuated over time (Fig. S13), MET presented a greater affinity for PES membranes and a lesser affinity for stainless-steel rings in comparison to MET-OLEF. Minimal losses occurred through sorption into the tank walls, amounting to 1 % of the mass for MET and 3 % for MET-OLEF. When considering all compartments (water, PES membranes, stainless-steel rings, and tank walls), the recoveries of both MET and MET-OLEF from the entire test were 101 % and 91 % of the total mass, respectively (Figs. 3 and S14).

The concentration of MET and MET-OLEF in the water of the tank without POCISs (tank F) remained constant throughout the test period ($16.4 \pm 0.7\text{ }\mu\text{g/L}$ and $4.0 \pm 0.5\text{ }\mu\text{g/L}$, respectively). Only a minor mass was found on the tank walls by the end of the test (2 % and 8 % of the mass of MET and MET-OLEF, respectively). No microbial activity was detected by the FDA-Assay in any tank at any point. Therefore, losses by other processes, such as volatilization or biodegradation, can be discarded, demonstrating a significant pesticide sorption to the PES membranes and stainless-steel rings, but not to the tank walls. Previous studies have documented the affinity of various compounds to PES membranes (Bope et al., 2018; Endo and Matsuura, 2018; Schäfer et al., 2011; Suchana et al., 2024). However, to the best of our knowledge, adherence of any compound to POCISs stainless-steel rings has not been reported before. Based on the findings of the current study, future POCIS tests should encompass not only the sorption of the target compounds to the sorbent material but also to both the PES membranes and the stainless-steel rings.

Carbon isotope characterization of the MET extracted from the PES membranes from the test with sorbent-free POCISs (tank E) is shown in Fig. 3. As occurred with the conventional POCIS configuration (tanks C-D), an inverse isotope effect was observed (i.e., enrichment in the heavier isotope in the sorbed phase), but in this case, with a high

deviation from the $\delta^{13}\text{C}$ value of the spiked MET after 2 days ($\Delta\delta^{13}\text{C} = 6.3 \pm 0.1\text{‰}$). Detailed results can be found in Table S9. Interestingly, a linear correlation ($r^2 = 0.96$; $p\text{-value} = 0.02$) between the $\delta^{13}\text{C}$ values and the fraction of MET mass sorbed onto the PES membrane was observed. The more the MET mass was sorbed onto the PES membrane, the closer the $\delta^{13}\text{C}$ value gets to the one of the spiked MET. This might indicate that the PES membrane phase of POCIS, contrary to what occurred with the sorbent phase, shows lower ability to preserve the stable isotope ratios of the retained MET, although this effect is only occurring during the first deployment days. The temporary nature of this effect is corroborated with the results of the experiments with conventional POCIS configuration (tanks C-D), where an insignificant shift ($< 0.8\text{‰}$) was observed after 20 days of deployment under both flow rates (Table S6). Therefore, as Suchana et al. (2024) suggests, this effect might be avoided within the longer deployment time required for environmental water bodies (Alvarez, 2010). In any case, given the observed linear correlation, a correction may be applied if needed. Additional research is required to evaluate the effects on stable isotope ratios of pesticide mass retained by the PES membranes of POCISs deployed at environmental sites for extended periods, since biofilm is often formed (Alvarez et al., 2004; Harman et al., 2009; Rosen et al., 2018; Suchana et al., 2024). This is crucial as stable isotope ratios may shift due to biodegradation processes.

3.2.4. Slurry MET and MET-OLEF extraction validation

The recoveries obtained from the LSE method for 1 g-aquifer slurries spiked at 0.001 to 100 $\mu\text{g/g}$ ranged from 67 to 126 % (RSDs 0–18 %) for MET, and from 80 to 138 % (RSDs 1–13 %) for MET-OLEF. Detailed data are shown in Fig. S15 and Table S6. These high recoveries are in accordance with previous studies for MET (Fuentes et al., 2014) and for the similar compound hexachlorocyclohexane (Quintero et al., 2005).

Slurry extraction tests spiked at 1 to 100 $\mu\text{g/g}$ resulted in $\delta^{13}\text{C}$ deviations from the EA-IRMS values of the spiked standards within $\pm 1.0\text{‰}$ for MET and $\pm 0.8\text{‰}$ for MET-OLEF (Fig. 2). The magnitude and reproducibility of this carbon isotope fractionation is clearly dependent on pesticide mass. An accuracy ($\Delta\delta^{13}\text{C}$) within a $\pm 0.5\text{‰}$ interval for both compounds was only achieved for pesticide contents equal to or higher than 6 $\mu\text{g/g}$. These results point to a relevant matrix effect, leading to a background generated by the co-extraction of concurrent organic matter (Fig. S16). Regarding chlorine isotope results, no significant isotopic fractionation is detected for MET ($\Delta\delta^{37}\text{Cl} = 0.3 \pm 0.1\text{‰}$) nor MET-OLEF ($\Delta\delta^{37}\text{Cl} = -0.1 \pm 0.2\text{‰}$). Detailed results can be found in Table S6. Therefore, high accuracy (within $\pm 1\text{‰}$) of the whole method coupling LSE slurry extraction and ME-CSIA ($\Delta\delta^{13}\text{C}$ and $\Delta\delta^{37}\text{Cl}$)

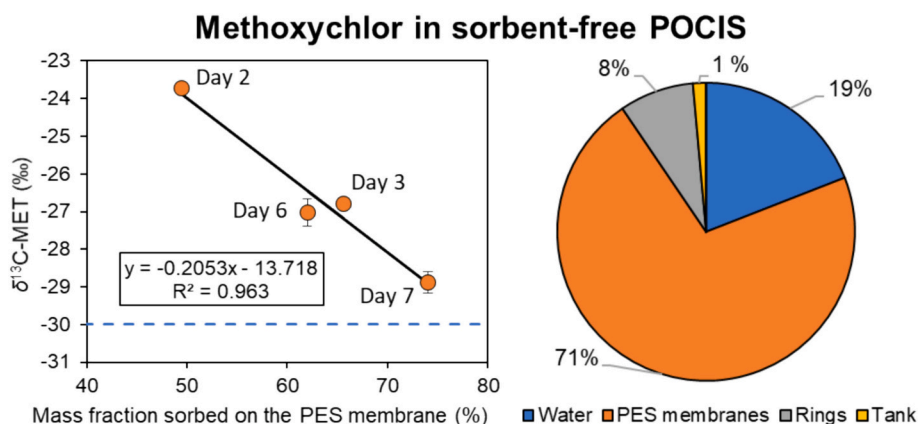


Fig. 3. Isotope results and MET mass distribution in the sorbent-free POCIS complementary experiment (Tank E). The left plot shows the carbon isotope fractionation associated to MET extracted from the PES membranes at days 2, 3, 6 and 7. The blue dashed line indicates the $\delta^{13}\text{C}$ values measured by EA-IRMS of the MET working standard used for spiking this complementary POCIS test. The error bars show the standard deviation (\pm sd) of the duplicate GC-IRMS measurements. In some cases, error bars are smaller than the symbols. The right panel shows the total mass distribution of MET at the end (day 7) of the complementary test in all the compartments.

was obtained for both MET and MET-OLEF at environmentally relevant contents (1 to 100 µg/g). If concentrations fall below 1 µg/g, a larger quantity of slurry may be needed to be extracted to conduct ME-CSIA.

4. Conclusions

This study presents the first multi-element compound-specific isotope (ME-CSIA) measurements of MET and MET-OLEF at environmentally relevant concentrations in water and slurry samples. The SPE-CSIA method was validated for a wide range of concentration (0.25–5000 µg/L) and under low and large water volume scenarios with both distilled and environmental water. The LSE-CSIA method was validated for environmental aquifer slurry samples spiked at field-relevant pesticide concentrations (1–100 µg/g). The accuracy ($\Delta\delta^{13}\text{C}$ and $\Delta\delta^{37}\text{Cl}$) of both SPE- and LSE-CSIA methods consistently remained within the range of $\pm 1\%$ for both MET and MET-OLEF across all tested conditions. For both SPE- and LSE-CSIA methods, the matrix effect is particularly relevant due to the coextraction of concurrent organic matter, leading to analytical interferences. Compound-specific matrix clean-up methods can be further explored to reduce this effect, such as molecularly imprinted polymers (Bakkour et al., 2018) and chromatographic HPLC separation (Schreglmann et al., 2013), or using an additional sorbent like as primary secondary amine (PSA) or graphitized carbon black (Anastassiades et al., 2003; Wilkowska and Biziuk, 2011), among others, for purification of extracts from water samples, and Florisil® column (EPA, 2007) and sulfuric acid (EPA, 1996) methods (Ivdrá et al., 2014), among others, for soil samples.

Promising outcomes were obtained from POCIS tests, demonstrating high carbon isotopic accuracy and precision ($\Delta\delta^{13}\text{C}$ within $\pm 1\%$) for deionized water containing 10 µg/L of the target contaminants, independently of the tested flow rate (2.5 and 15 cm/s). This validates the method as a valuable approach for the preconcentration and extraction of MET and MET-OLEF from water bodies at different hydrological conditions, followed by carbon CSIA. A substantial amount of pesticide was retained by the PES membranes of the POCISs, resulting on transitory carbon isotope fractionation depending on the sorbed mass fraction, highlighting the critical role of polar analyte-sorbent-membrane interactions in the performance of this approach. For the widespread implementation of the combined POCIS-CSIA approach into environmental sites, additional testing is imperative to optimize the method. This includes establishing validation criteria, defining concentration limits, POCIS deployment durations and water flow rates, and assessing the potential influence of environmental water matrices, especially for $\delta^{37}\text{Cl}$ -CSIA, which was not feasible in the current experiments. The use of extract clean-up approaches and/or alternative cyclodextrin polymers as highly selective sorbents (Glöckler et al., 2023) can also be considered. Additional tests are also necessary to explore the isotopic behavior of MET and MET-OLEF during sorption onto PES membranes and stainless-steel rings, especially in environmental conditions and long deployment times, where biofilm may grow, potentially leading to isotope fractionation.

Hence, the pesticide extraction techniques for water and slurry samples outlined in this study represent a significant initial stride towards assessing (multi-element) isotope ratios related to the insecticide MET and its derivatives in environmental samples. While further investigations are essential, it is also envisaged that POCIS may serve as an enhanced approach for monitoring pesticide isotope ratios in groundwater. This may collectively facilitate the tracing of pesticide transformation processes and origins, enabling the implementation of improved strategies for managing contaminated sites and advancing effective groundwater and soil/sediments remediation solutions.

CRedit authorship contribution statement

Martí Vinyes-Nadal: Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Formal analysis, Data

curation, Conceptualization. **Jérémy Masbou:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Steffen Kümmel:** Writing – review & editing, Methodology, Formal analysis. **Matthias Gehre:** Writing – review & editing, Resources. **Gwenaëlf Imfeld:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization. **Neus Otero:** Writing – review & editing, Resources, Project administration, Funding acquisition. **Clara Torrentó:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.172858>.

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