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Analysis of chlordecone and its transformation products in environmental waters by a new SPME-GC-MS method and comparison with LLE-GC-MS/MS and LLE-LC-MS/MS: A case study in the French West Indies

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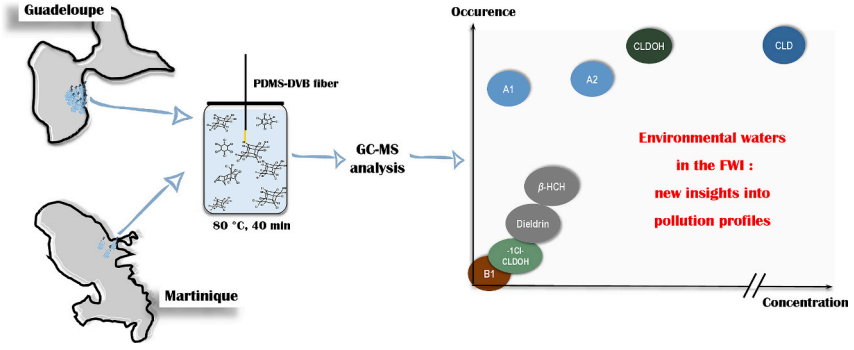
HIGHLIGHTS

- A SPME-GC-SIM/MS method for chlordecone and its main transformation products
- Five transformation products detected at least once in environmental waters
- Suspected overestimation of chlordecone levels with one of the routine protocols
- Suspected underestimation of chlordecol levels with one of the routine protocols

GRAPHICAL ABSTRACT



Abbreviations: CLD, chlordecone; CLDOH-d, chlordecol-deuterated; CLDOH, chlordecol; DCM, dichloromethane; DI, direct immersion; DM, dry matter; DVB, divinylbenzene; ECD, electron capture detector; EI, electron ionization; FS, full scan; FWI, French West Indies; GC, gas chromatography; HCB, hexachlorobenzene; HCBD, hexachlorobutadiene; HCH, hexachlorocyclohexane; HS, headspace; IPA, isopropanol; IS, internal standard; LC, liquid chromatography; LLE, liquid-liquid extraction; LOD, limit of detection; LOQ, limit of quantification; MeCN, acetonitrile; MeOH, methanol; MS, mass spectrometry; OC, organochlorine; OCP, organochlorine pesticide; PCB, polychlorobiphenyl; PCBz, pentachlorobenzene; PCE, perchloroethylene; PDMS, polydimethylsiloxane; POP, persistent organic pollutant; PTV, programmable temperature vaporization; RSD, relative standard deviation; SIM, selected ion monitoring; SPME, solid-phase microextraction; TCE, trichloroethylene; TIC, total ion current; TP, transformation product.

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ABSTRACT

Among the numerous organochlorines (OCs) applied in the French West Indies (FWI), chlordecone (hydrated form $C_{10}Cl_{10}O_2H_2$; CLD) still causes major environmental pollution nowadays. A recent report revealed the unexpected presence in FWI environment of transformation products (TPs) of CLD not routinely monitored due to a lack of commercial standards. Here, we present a method for surface waters and groundwaters to analyze CLD, its main TPs (hydroCLDs, chlordecol (CLDOH), 10-monohydroCLDOH and polychloroindenes) and other OCs. We developed an SPME-GC-SIM/MS method with a PDMS-DVB fiber. Since CLDOH-d commonly used as internal standard (IS) proved unsuitable, we synthesized several IS candidates, and finally identified 10-monohydro-5-methyl-chlordecol as a satisfactory IS for CLDOH and 10-monohydroCLDOH avoiding the use of ^{13}C-labelled analogue. LODs for CLD and its TPs varied from 0.3 to 10 ng/L, equal to or below LODs of the two laboratories, BRGM (the French geological survey) and LDA26 (one of the French Departmental Analytical Laboratories), requested in FWI pollution monitoring that used liquid-liquid extractions and advanced facilities (LLE-GC-MS/MS and LLE-LC-MS/MS methods, respectively). Then, we extended the multi-residue method to 30 OCs (CLD and its TPs, mirex, β-HCH, lindane, dieldrin, aldrin, HCB, hexachlorobutadiene, TCE, PCE) and applied it to 30 surface and ground waters from FWI. While CLD, 8- and 10-monohydroCLD, CLDOH, 10-monohydroCLDOH, dieldrin, and β-HCH were detected and quantified, pentachloroindene, another CLD TP, was sporadically found in trace levels. A comparison with BRGM and LDA26 confirmed the interest of the SPME method. Results suggested an underestimation of CLDOH and an overestimation of high CLD concentrations with one of the currently used routine protocol. In light of these findings, previous temporal monitoring of environmental waters in FWI were re-examined and revealed some atypical values, which may indeed be due to analytical bias. These discrepancies call for intensified efforts to reliably quantify CLD and its TPs.

1. Introduction

Before being progressively banned since the 1970s, organochlorine pesticides (OCPs) have been largely used worldwide since the 1940s for pest control in crops. In the French West Indies (FWI), the tropical climate has led to the use of several OCPs such as hexachlorocyclohexanes (HCHs), aldrin, dieldrin, and chlordecone (Bonvallot and Dor, 2004). From 1972 until 1993, chlordecone (hydrated form $C_{10}Cl_{10}O_2H_2$; CLD) has been applied extensively in banana plantations, causing massive environmental pollution predicted to last for 50 to 700 years depending on the models (Cabidoche et al., 2009; Comte et al., 2022; Saaidi et al., 2023). CLD concentrations above 1 mg/kg of DM (dry matter) can still be detected in several polluted fields nowadays (Desprats, 2021; Comte et al., 2022). Among the diverse pesticides detected, CLD turned out to be, by far, the most frequent one for waters in FWI, with maximum levels ranging from about 0.1 to 5 μg/L for the most polluted rivers (Cattan et al., 2019; Mottes et al., 2020; Rochette et al., 2020; Voltz et al., 2023) and from about 1 to 50 μg/L for the most polluted aquifers (Gourcy et al., 2009; Arnaud et al., 2017). CLD also accumulates in food chains and sporadically contaminates tap water, resulting in very high impregnation of the FWI population as reported by Dereumeaux et al. (2020) in the Kannari study; >90 % of the 746 tested subjects from Martinique and Guadeloupe showing detectable level of CLD in blood. Chronic exposure to CLD, known as an endocrine disruptor (Multigner et al., 2018), increases the risk of health problems such as prostate cancer and delayed motor and cognitive development in infants (Multigner et al., 2010; Dallaire et al., 2012; Brureau et al., 2020; Desrochers-Couture et al., 2022). Recently, several studies highlighted the possible (bio)degradation/(bio)transformation of CLD, both in laboratory and FWI environment, resulting in a series of transformation products (TPs) of varying polarity: hydrochlordecones (family A, hydroCLDs, $C_{10}Cl_{10-n}O_2H_{2+n}$, $1 \leq n \leq 5$), polychloroindenes (family B, $C_9Cl_{6-n}H_{2+n}$, $1 \leq n \leq 3$), polychloroindenecarboxylic acids (family C, $C_{10}Cl_{5-n}H_{3+n}O$, $1 \leq n \leq 5$), methyl polychloroindenecarboxylates (family D, $C_{11}Cl_{5-}nH_{5+n}O_2$, $1 \leq n \leq 2$), ethyl polychloroindenecarboxylates (family E, $C_{12}Cl_{5-n}H_{7+n}O_2$, $1 \leq n \leq 2$), chlordecthiol and chlordecol (CLDOH) and their derivatives (families F and G, respectively) (Schrauzer and Katz, 1978; Belghit et al., 2015; Chevallier et al., 2019; Della-Negra et al., 2020; Lomheim et al., 2020, 2021; Hellal et al., 2021).

Although TPs from families A, B, C, and E have been detected in surface waters as part of a recent prospective work (Chevallier et al., 2019), most CLD TPs are not routinely monitored due to the lack of commercially available standards. As a consequence, studies investigating CLD pollution of the FWI environmental waters are accumulating with limited or no information on TPs of CLD potentially present (Charlier et al., 2015; Crabit et al., 2016; Della Rossa et al., 2017; Mottes et al., 2017, 2020; Devault et al., 2018; Cattan et al., 2019; Rochette et al., 2020; Dromard et al., 2022; Voltz et al., 2023).

The aim of the present work was to develop a robust, efficient and environmentally friendly method for surface waters and groundwaters to analyze CLD, its main TPs such as hydrochlordecones, chlordecol, and polychloroindenes, other OCPs known to be used in the FWI (aldrin, dieldrin, hexachlorobenzene (HCB), lindane and other HCHs (hexachlorocyclohexanes)) as well as some other organochlorines (OCs) not routinely monitored (hexachlorobutadiene (HCBD), trichloroethylene (TCE) and perchloroethylene (PCE). Liquid-liquid extraction (LLE) has been used almost systematically in methods previously developed for CLD quantification in water matrix (Bristeau and Ghestem, 2012; Cimetiere et al., 2014; Devault et al., 2018; Chevallier et al., 2019; Mottes et al., 2020). However, LLE suffers from a number of drawbacks such as the large quantities of sample needed (generally, from 500 mL to 1 L), toxic solvents typically used such as dichloromethane or hexane (Devault et al., 2018; Chevallier et al., 2019; Mottes et al., 2020) and the operator intervention time required. Despite the pioneering work of Soler et al. (2014) who successfully replaced LLE with a solid-phase micro extraction (SPME) protocol to detect CLD, no SPME method has been published to date for the simultaneous detection of CLD, its TPs, and other FWI organochlorine contaminants. SMPE consists of solvent-free extraction *via* the use of a fused silica fiber coated with a polymeric stationary phase (Belardi and Pawliszyn, 1989). Some disadvantages exist such as fiber fragility, poor selectivity, presence of carryover, difficulties in extracting polar analytes, and detection of only dissolved analytes (Liu et al., 2004; Spietelun et al., 2010). However, this alternative method to LLE also offers several advantages such as solvent absence, simplicity, sample concentration, extraction automation, and good reproducibility, making it effective for the quantification of different compounds at trace levels in water samples (Spietelun et al., 2010). Therefore, we decided to switch to SPME instead of LLE for our new analytical developments. To increase the sensitivity of the GC–MS method, we used the SIM (selected ion monitoring) mode and selected a number of OCs, such as CLD and its main TPs as well as other FWI legacy pollutants and their derivatives. Finally, the SMPE-GC-SIM/MS method was applied to a series of 30 environmental water samples from FWI

highly polluted sites and compared to our previous LLE method (Chevallier et al., 2019) as well as two other well-established methods routinely used by La Drôme Laboratoire, formerly known as Laboratoire Départemental d'Analyses de la Drôme (LDA26, Valence, France) and the Bureau de Recherches Géologiques et Minières (BRGM, Orléans, France). Indeed, the LDA26 and BRGM laboratories have long been involved in monitoring CLD pollution in FWI (Bristeau and Ghestem, 2012; Arnaud et al., 2017; Della Rossa et al., 2017; Cattan et al., 2019; Mottes et al., 2020; Rochette et al., 2020; Dromard et al., 2022; Voltz et al., 2023) and are among the few laboratories capable of simultaneously quantifying CLD and some of its TPs: chlordecol (CLDOH), 8-monohydrochlordecone (IUPAC nomenclature; 5b-monohydrochlordecone for CAS nomenclature; A2) for both laboratories and 10-monohydrochlordecone (IUPAC nomenclature; 5-monohydrochlordecone for CAS nomenclature; A1) for BRGM only. Results demonstrated the promising interest of the developed SPME-GC-SIM/MS method for monitoring CLD, its TPs and several OCPs at environmental concentrations.

2. Material and methods

2.1. Chemicals

Chlordecone (CLD, hydrated form $C_{10}Cl_{10}O_2H_2$, purity >99 %) and chlordecol (CLDOH, $C_{10}Cl_{10}OH_2$, purity 98 %) were supplied by Sigma Aldrich and Azur Isotopes, respectively. 10-monohydrochlordecone (A1, $C_{10}Cl_9O_2H_3$), 8-monohydrochlordecone (A2, $C_{10}Cl_9O_2H_3$), 2,4,5,6,7-pentachloroindene (B1, $C_9Cl_5H_3$), 4,5,6,7-tetrachloroindene (B2, $C_9Cl_4H_4$), 2,4,5,7/2,4,6,7-tetrachloroindene (B3/B4, $C_9Cl_4H_4$), and chlordecthiol (F1, $C_{10}Cl_{10}H_2S$) were synthesized according to literature procedures (Wilson and Zehr, 1979; Chevallier et al., 2019; Della-Negra et al., 2020). The purity of the synthesized A2 was confirmed by comparison with a commercial solution of A2 (chlordecone-5b-hydro, 10 mg/L in cyclohexane, Dr. Ehrenstorfer, batch 40917CY, Fig. S39). The syntheses of other compounds derived from CLD are detailed in Supplementary Methods. Purity of all synthesized compounds was determined by NMR using an internal standard (IS) (Supplementary Methods). Pentachlorobenzene (PCBz, purity >96 %), trichloroethylene (TCE, purity >99.5 %), and perchloroethylene (PCE, purity >99.9 %) were obtained from Sigma Aldrich. Hexachlorobenzene (HCB, purity >99.8 %) and mirex (purity >99 %) were supplied by Fluka. α-hexachlorocyclohexane (α-HCH, purity >98 %), aldrin (purity >98 %), and 1,3-hexachlorobutadiene (HCBD, purity >99 %) were obtained from Supelco. Chlorobenzene (MCB, purity >99 %) and 1,3-dichlorobenzene (1,3-DCB, purity >98 %) were purchased from Merck. Other organochlorines, 1,2-dichlorobenzene (1,2-DCB, purity >98 %), 1,4-dichlorobenzene (1,4-DCB, purity >99 %), 1,2,3-trichlorobenzene (1,2,3-TCB, purity >99 %), 1,2,4-trichlorobenzene (1,2,4-TCB, purity >99 %), 1,3,5-trichlorobenzene (1,3,5-TCB, purity >99 %), β-hexachlorocyclohexane (β-HCH, purity >98 %), γ-hexachlorocyclohexane or lindane (γ-HCH, purity >97 %), δ-hexachlorocyclohexane (δ-HCH, purity >98 %), dieldrin (purity >95 %), 1,2,3,5-tetrachlorobenzene (1,2,3,5-TeCB, purity >98 %), 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB, purity >98 %), 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB, purity >98 %) were purchased from Sigma Aldrich.

The labelled internal standards, $^{13}C_{10}$-chlordecone ($^{13}C_{10}$-CLD, 100 µg/L in nonane, purity >98 %, enrichment $^{13}C/^{12}C$ > 99 %), $^{13}C_4$-hexachlorobutadiene ($^{13}C_4$-HCBD, 100 µg/L in isooctane, purity >98 %, enrichment $^{13}C/^{12}C$ > 99 %), $^{13}C_6$-hexachlorobenzene ($^{13}C_6$-HCB, 100 µg/L in nonane, purity >98 %, enrichment $^{13}C/^{12}C$ > 99 %) were supplied by Cambridge Isotope Laboratories. PCB 138 was supplied from Sigma Aldrich (purity >98 %). 5-Monodeuterochlordecol (CLDOH-d, $C_{10}Cl_{10}OHD$), 5-methylchlordecol (CLDOH-Me, $C_{11}Cl_{10}OH_4$), and 10-monohydro-5-methylCLDOH (−1Cl-CLDOH-Me, $C_{11}Cl_9OH_5$) were synthesized according to protocols described in Supplementary Methods. Working solutions stored at 4 °C in the dark were prepared in acetone, except for F1, prepared in ethanol, both solvents supplied by VWR (purity >99.9 %).

SPME fibers with 65 µm polydimethylsiloxane-divinylbenzene (PDMS-DVB), 7 µm PDMS, 30 µm PDMS, 85 µm Acrylate, and 95 µm Carbon coating were purchased from Restek. Ultrapure water was obtained with a Milli-Q system. Inter-sample blanks were composed of Milli-Q water and methanol (50/50, v/v), obtained from VWR (LC-MS grade, purity >99.9 %). Isopropanol, used to rinse fiber, was obtained from Merck (LC-MS grade).

2.2. Environmental water samples collection

The Observatory of Agricultural Pollution in the West Indies (OPALE) is composed of two catchments known to be highly polluted by CLD: the Pérou-Pères catchment in Guadeloupe and the Galion catchment in Martinique. In Martinique, three surface waters from the Galion River and its main tributaries were sampled in December 2021. 200-mL glass bottles were filled to maximum capacity after three rinses. In Guadeloupe, five surface waters from Saint-Denis, Pères and Pérou Rivers, as well as twenty-three groundwaters (from springs and wells) in Capesterre-Belle-Eau (Basse-Terre) were sampled over 2 campaigns (Spring/Summer and Autumn 2022) (Fig. S22; Table S1). The wells were sampled after pumping at least three purge volumes and the stabilization of the specific electrical conductivity of groundwater. One-liter amber glass bottles were rinsed twice before being filled to reach 1 cm from the top. These guidelines notably adhere to the recommendations of the following standards: French standard NF EN ISO 5667-3 and guidelines FD T 90-523-3 (2009) and FD X31-615 (2000). For the laboratory comparison, each sample was taken in triplicate at the same time. Samples were kept on ice in coolers for immediate transport (after 2 days maximum) to the three laboratories (BRGM, LDA26, and Genoscope which developed the SPME-GC-SIM/MS method). All samples were then kept at 4 °C in the dark before analysis. The geographical location and details of sampling points are available in SI (Fig. S22 and Table S1).

SPME-GC-SIM/MS analysis for each environmental water sample was repeated with a different operator and at a different time (after several weeks) to calculate mean concentrations and estimate standard deviations. For logistical reasons, some samples could not be analyzed by the three laboratories (Table S20). Furthermore, the limited commercial availability of CLD TPs restricted the set of TPs targeted by LDA26 and BRGM. LDA26 applied its routine analytical method, named CMO_MT02, based on LLE followed by a dual GC-MS/MS and LC-MS/MS analysis in order to quantify CLD, CLDOH, A2 (Rochette et al., 2017) and a number of OCs (Table S9). BRGM used an LLE-GC-MS/MS protocol and targeted CLD, CLDOH, A1, and A2 (Table S9). In addition, Genoscope used an LLE protocol followed by GC-SIM/MS and LC-HRMS analyses derived from the previous method that enabled the authors to detect several unexpected TPs in the FWI environment (Chevallier et al., 2019). Overall, each water sample resulted in five concentration values for CLD according to Genoscope (SPME-GC-SIM/MS, LLE-GC-SIM/MS, LLE-LC-HRMS), BRGM (LLE-GC-MS/MS) and LDA26 (LLE-LC-MS/MS) (Table S10, Table S21).

2.3. Development of the SPME procedure

The SPME procedure was developed with CLD, CLDOH, A1, B1, and F1. Various parameters were optimized: type of fiber, extraction temperature, extraction time, desorption temperature, desorption time, and addition of NaCl. All optimizations were performed using 20 mL of Milli-Q water contaminated with the five compounds mentioned above at a concentration of 1 µg/L, except for fiber screening carried out at a level of 100 µg/L for each compound. For details, see Supplementary Text and Table S2.

2.4. SPME-GC-SIM/MS procedure

2.4.1. SPME protocol

A 20-mL vial (20-mL Headspace screw top vial, Chromacol) was filled with 20 mL of environmental water, 10 µL of an acetone solution of IS (final concentrations: 0.5 µg/L for $^{13}C_{10}$-CLD and 0.1 µg/L for $^{13}C_4$-HCBD, $^{13}C_6$-HCB, PCB 138 and −1Cl-CLDOH-Me) and 120 µL of acetone. The vial was incubated at 80 °C and SPME extraction was performed under stirring for 40 min in the presence of PDMS-DVB fiber. Then, fiber was thermally desorbed in the GC-MS injector at 270 °C during 15 min. Fiber re-conditioning was carried out by immersion in isopropanol for 3 min followed by heating (see below for additional details). Since each vial was only extracted once, each water sample was prepared in duplicate, one for selected ion monitoring (SIM) analysis and one for full scan (FS) analysis.

2.4.2. GC-SIM/MS parameters

Analyses were performed with a gas chromatograph (Trace 1300, Thermo Fisher) coupled to a single-quadrupole mass spectrometer (ISQ 1700, Thermo Fisher). The chromatographic system was equipped with a TriPlus RSH autosampler and SPME tool for automated sample preparation (Thermo Fisher). Separation was carried out with a DB-5MS column (30 m × 0.25 mm, 0.25 µm film thickness) (Agilent J&W). Fiber desorption was achieved using a split/splitless injector heated at 270 °C with a split ratio of 1:5. Helium was used as carrier gas at a flow rate of 2.5 mL/min. Oven temperature program was set as follows: 45 °C hold for 15 min; increased to 140 °C at a rate of 50 °C/min (hold 1 min); then to 160 °C with a rate of 6 °C/min and finally to 282 °C with a rate of 7.5 °C/min. For fiber reconditioning, a programmed temperature vaporization injector (PTV) with a split ratio of 1:42 was heated at 340 °C for 10 min. The mass spectrometer was operating in electron ionization mode (EI) at 70 eV and spectra were acquired in the positive ion mode. Ion source and transfer line temperatures were set at 220 °C and 280 °C, respectively. SIM was applied by monitoring a quantifying ion and a qualifying ion for each targeted compound (Tables S3 and S4). FS analysis was also performed over an *m/z* range of 40 to 270 until 21 min, then between *m/z* 160 and 500 until the end of elution.

2.5. Performances of the SPME-GC-SIM/MS method

Natural volcanic mineral water (Volvic water) was used as a blank matrix. Linearity was evaluated with five calibration levels adapted to the expected environmental concentrations of each organochlorine (Tables 1 and S7 and Figs. S24 and S25). IS concentrations were kept constant: 0.5 µg/L for $^{13}C_{10}$-CLD and 0.1 µg/L for the others. Accuracies were evaluated at two concentration levels (n = 3) (low level at 2 µg/L for CLD and between 0.015 and 0.075 µg/L otherwise; high level at 12.5 µg/L for CLD and between 0.125 and 0.38 µg/L otherwise) and intraday relative standard deviations (RSD) of accuracy replicates were achieved (Tables 1 and S7). Matrix effects and recoveries were normalized by the isotopic dilution for CLD with $^{13}C_{10}$-CLD, HCB with $^{13}C_6$-HCB and HCBD with $^{13}C_4$-HCBD. Limits of detection (LOD) were evaluated using a signal-to-noise ratio of three and confirmed with the detection of each compound at the LOD concentration. Limits of quantification (LOQ) were set at three times the estimated LOD. For the environmental analysis campaign, a series of three successive samples were bracketed by five calibration levels analyzed in duplicate (two independent vials for each level).

2.6. LLE methods applied

2.6.1. LDA26 protocol

As part of the OPALE Observatory, environmental waters from Guadeloupe and Martinique are regularly analyzed by LDA26 using the previously described CMO-MT02 method (Charlier et al., 2015; Rochette et al., 2017) using LLE. LDA26 is accredited by COFRAC (French Accreditation Committee) and works under the ISO 17025 standard. Their multi-residue method includes the detection of: CLD, CLDOH, and A2 in LC-MS/MS; aldrin, dieldrin, HCHs (α, β, δ and γ), HCB, PCBz, 1,2,3,4-TeCB, 1,2,4,5,-TeCB, 1,3,4,5-TeCB, and mirex in GC-MS/MS. LOQs were estimated at 1 ng/L for 1,2,3,4-TeCB, 2 ng/L for α-, δ- and γ-HCH, 5 ng/L for 1,2,4,5-TeCB, PCBz, β-HCH and mirex and 10 ng/L for CLD, CLDOH, A2, 1,3,4,5-TeCB, dieldrin and aldrin (Table S9). Uncertainty was fixed at 30 % for all compounds.

2.6.2. BRGM protocol

BRGM adapted their previous LLE protocol from (Ollivier et al., 2020). Briefly, 500 mL of sample were acidified to pH 2–3 and IS were added ($^{13}C_{10}$-CLD and CLDOH-d). Samples were extracted twice with 50 mL of DCM. The extract was reduced by nitrogen stream and finalized with 0.5 mL of cyclohexane. Quantification of CLD, CLDOH, A1, and A2 was performed by GC-MS/MS (MRM scan modes). Analysis was performed with an Agilent system (Les Ulis, France) composed of a GC 8890 gas chromatography apparatus equipped with a split-splitless inlet, a Combi Pal (CTC) autosampler and a 7010B MS triple quadrupole mass spectrometer. The compounds were separated on an Rxi-1MS (30 m × 0.25 mm ID, 0.25 µm) column from Restek (Lisses, France). The key parameters of the method (linearity, repeatability, inter-day precision, specificity, extraction efficiency, and limit of quantification) were validated for CLD, CLDOH, and A2 in accordance with the NF T 90-210 standard method (AFNOR, 2018) based on carrying out tests under conditions of intermediate fidelity using natural samples. LOQs were estimated at 30 ng/L for CLD, CLDOH, A1, and A2 (Table S9). The uncertainties were determined at 20 % for CLD and 30 % for A2 and CLDOH. BRGM is accredited by COFRAC (French Accreditation Committee) and works under ISO 17025 standard.

Table 1
Performance criteria of the SPME-GC-SIM/MS method for CLD and its main TPs. RSD: relative standard deviation. n = 3.

	Concentration levels (ng/L)	Accuracies (%)	RSD (%)	Retention time (min)	Linearity range (ng/L)	Coefficient of determination (R^2)	LOD (ng/L)	LOQ (ng/L)
CLD*	2,000	103	2	31.48	0–25,000	0.999	5.0	15.0
	12,500	94	6					
CLDOH	75.0	75	23	34.33	0–1250	0.996	3.3	10.0
	380.0	101	24					
A1	25.0	119	24	30.41	0–270	0.997	3.3	10.0
	125.0	97	15					
A2	25.0	91	19	30.12	0–270	0.995	3.3	10.0
	125.0	94	18					
B1	25.0	109	22	27.16	0–270	0.989	3.0	9.0
	125.0	126	10					
−1Cl-CLDOH	25.0	77	5	33.13	0–270	0.996	3.3	10.0
	125.0	97	13					

* For the lower environmental concentrations of CLD, a dedicated calibration curve ranging from 0 to 2500 ng/L was used (R^2 = 0.997; Fig. S24a).

2.6.3. Genoscope protocol

LLE procedure was adapted from Chevallier et al. (2019). The final extract was divided into several portions in order to perform GC-MS analyses (SIM and FS modes) as well as LC-HRMS analysis. Further information is provided in the Supplementary Material (Supporting Methods).

3. Results and discussion

3.1. Choice of targeted organochlorines

In the FWI (Martinique and Guadeloupe), numerous OCPs have been used, in particular insecticides to control banana weevils: as early as the 1950s, technical-grade HCH began to be applied regularly; dieldrin and aldrin were then used, albeit to a lesser extent, finally replaced by lindane (γ-HCH) in the 1960s (Cabidoche et al., 2006; Landau-Ossondo et al., 2009). Strong resistance to all of these OCPs eventually forced farmers to switch to CLD and massively apply this insecticide from 1972 until its definitive ban in 1993. A structural analog of CLD, mirex, was also used in Guadeloupe to fight leaf-cutting ants in the 1980s (Cabidoche et al., 2006) and was one of the contaminants in the commercial formulations of CLD applied in the FWI (Soler et al., 2014). Since regular monitoring of the FWI water resources began in 1998, CLD, dieldrin, and β-HCH were often found at concentrations excessing environmental norms (0.1 µg/L or lower depending on OCPs) (Bonan and Prime, 2001; Rochette et al., 2017; Wintz and Pak, 2021; Taïlamé et al., 2023); the frequency and high levels of CLD making it by far the main contaminant of FWI hydric systems. In addition to CLD, we included the four major regioisomers of HCH (α, β, γ (also known as lindane) and δ), mirex, as well as dieldrin and aldrin (Fig. 1).

In the 2010s, two TPs of CLD, namely 8-monohydrochlordecone (5b-monohydrochlordecone; A2) and chlordecol (CLDOH), were added in the regular FWI monitoring as they were known as contaminants of commercial chlordecone formulations (Curlone© and Kepone©) (Soler et al., 2014). Analyses have then demonstrated their regular presence in water samples, especially when high levels of CLD were observed (Cattan et al., 2019; Wintz and Pak, 2021). Recent results revealing the presence of other TPs of CLD (dihydroCLD, trihydroCLD, B1, B2, B3/B4,

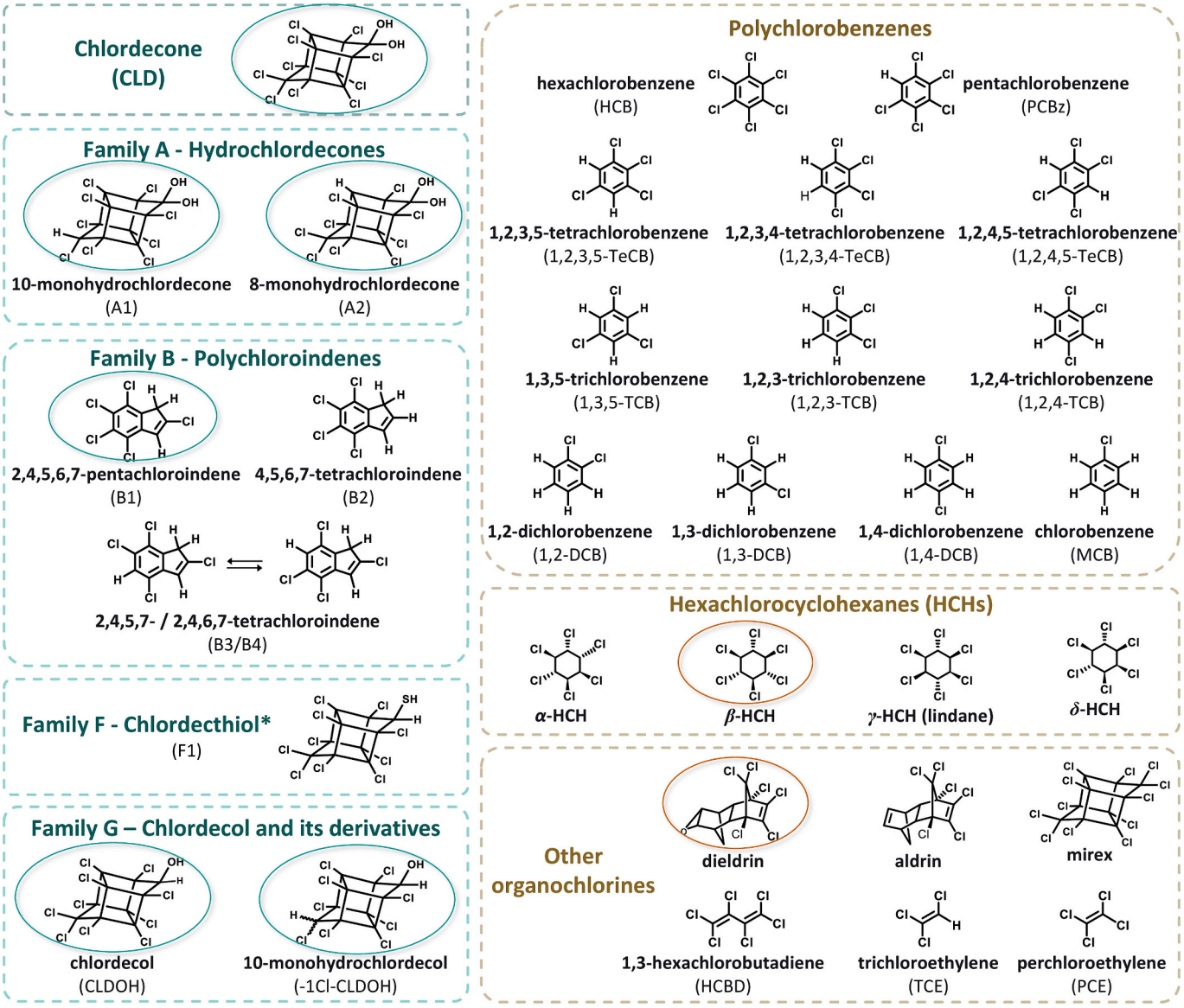

Fig. 1. Representation of the 31 OCs targeted for the SPME-GC-SIM/MS method developed. Chlordecone, 8-monohydrochlordecone and 10-monohydrochlordecone are represented in their more stable hydrated form, *i.e.* as gem-diols (Wilson and Zehr, 1979); *: Chlordecthiol, initially included in the set of OCs, was later excluded due to unsatisfactory results during SPME optimization; surrounded compounds were detected in at least one of the 30 studied FWI environmental water samples.

C1/C2, E1/E2) (Chevallier et al., 2019) in Martinique's river and mangrove waters called for expanding the list of monitored TPs in the FWI. Overall, given the fact that six out of the seven known families of CLD TPs could be detected by GC–MS, we chose this technique for our new analytical developments. As a result, TPs from family C, *i.e.* C1/C2 and C3/C4, only detectable by LC-MS, were excluded. The same applied to dihydroCLD, trihydroCLD, and E1/E2 previously found in environmental water (Chevallier et al., 2019) and excluded from the present study as they suffered from incomplete identification and/or not yet described synthetic access. Hence, a final set of eight TPs of CLD was retained: A1, A2, B1, B2, B3/B4, F1, CLDOH, and −1Cl-CLDOH (Fig. 1).

Given the occurrence of HCH in the FWI environmental waters, we wondered about the possible presence of TPs resulting from HCH degradation. To date, no TPs of HCH are listed in the OCs targeted by the laboratories in charge of environmental monitoring. We therefore decided to include several known and commercially available TPs, namely 1,2,4-TCB, indicative of aerobic degradation and also 1,3-DCB, 1,2-DCB, and MCB products from anaerobic degradation pathways (Zhang et al., 2020). We also targeted hexachlorobenzene, detected in the blood of FWI population (Kannari study) (Dereumeaux et al., 2020), and we completed the series of polychlorobenzenes, as several of them are known to be formed by reductive dechlorination of HCB in soil (Brahushi et al., 2004). The developed SPME-GC-SIM/MS method was expected to be particularly well suited for volatile OCs, so we took the

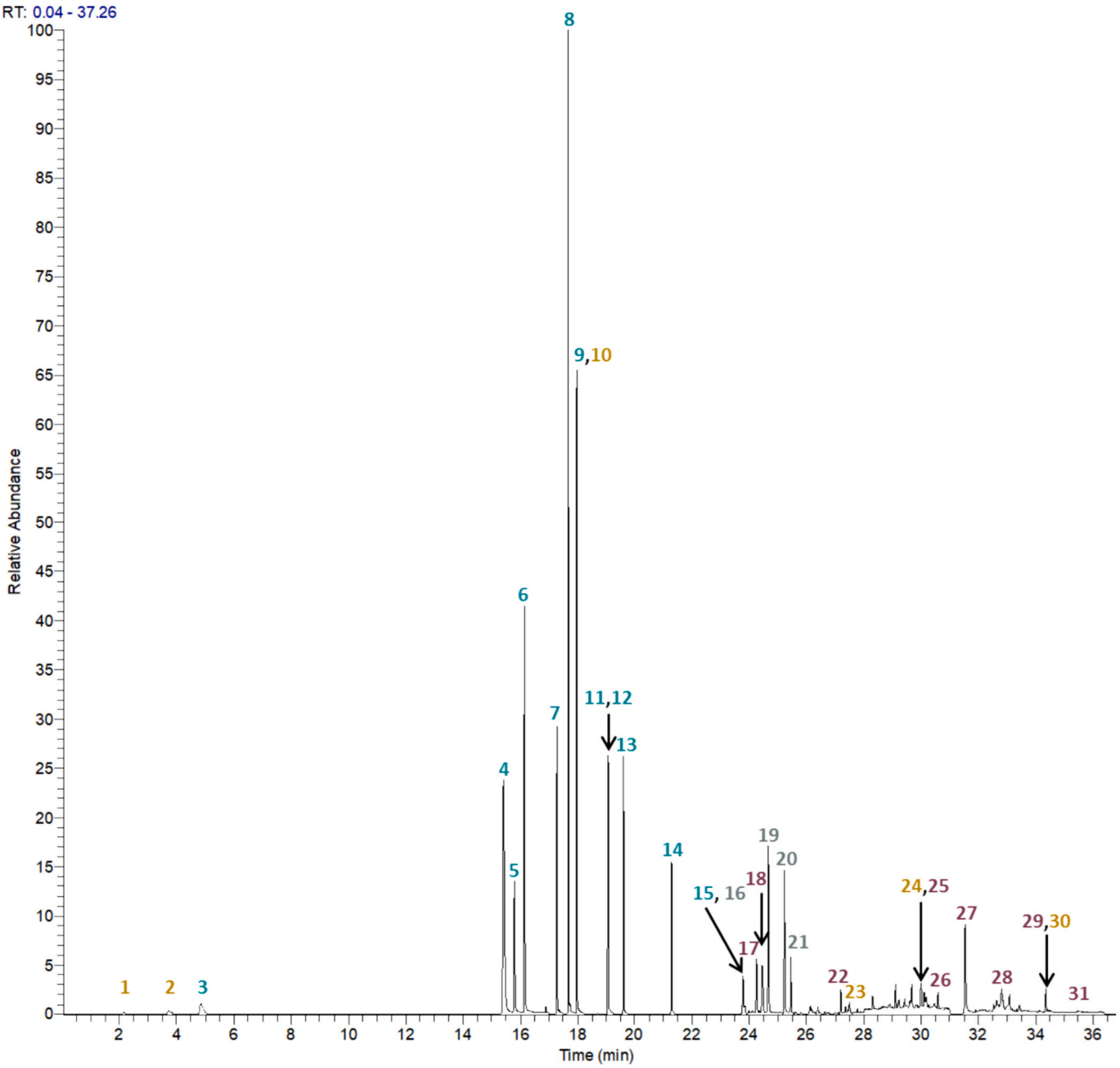

Fig. 2. Total ion chromatogram obtained by SPME-GC-SIM/MS (not optimized method) of the targeted organochlorines at 1 μg/L in water. For HCB and its TPs (blue): 3 = MCB; 4 = 1,3-DCB; 5 = 1,4-DCB; 6 = 1,2-DCB; 7 = 1,3,5-TCB; 8 = 1,2,4-TCB; 9 = 1,2,3-TCB; 11 = 1,2,3,5-TeCB; 12 = 1,2,4,5-TeCB; 13 = 1,2,3,4-TeCB; 14 = PCBz; 15 = HCB. For HCH (grey): 16 = α-HCH; 19 = β-HCH; 20 = γ-HCH (lindane) and 21 = δ-HCH. For CLD and its TPs (purple): 17 = B3/B4; 18 = B2; 22 = B1; 25 = A2; 26 = A1; 27 = CLD; 28 = −1Cl-CLDOH; 29 = CLDOH and F1 = 31. For others (yellow): 1 = TCE; 2 = PCE; 10 = HCBD; 23 = aldrin; 24 = dieldrin and 30 = mirex.

opportunity to include trichloroethylene (TCE), perchloroethylene (PCE), and hexachlorobutadiene (HCBD), which were not routinely monitored until then in the FWI. Altogether, the complete list illustrated in Fig. 1 comprised 31 compounds representing OCPs, several of their TPs, as well as other OCs. Finally, we decided to carry out additional acquisitions in FS mode to scrutinize other possible isotopic fragmentation patterns characteristic of non-targeted chlorinated compounds.

3.2. Optimization of GC-SIM/MS method

Optimization of the GC method allowed the perfect chromatographic separation of 23 over 31 OCs studied (Fig. 2). Retention times (Rt) for six compounds were found to be very close (HCBD/1,2,3-TCB, 17.97 min *vs.* 17.98 min; *α*-HCH/HCB, 23.84 min *vs.* 23.85 min; dieldrin/A2, 30.07 min *vs.* 30.09 min), so we ensured that their selected quantifying and qualifying ions did not interfere. Finally, two TeCB regioisomers (1,2,3,5- and 1,2,4,5-TeCB) with overlapping peaks (19.05 min *vs.* 19.07 min) and same fragmentation patterns turned out to be

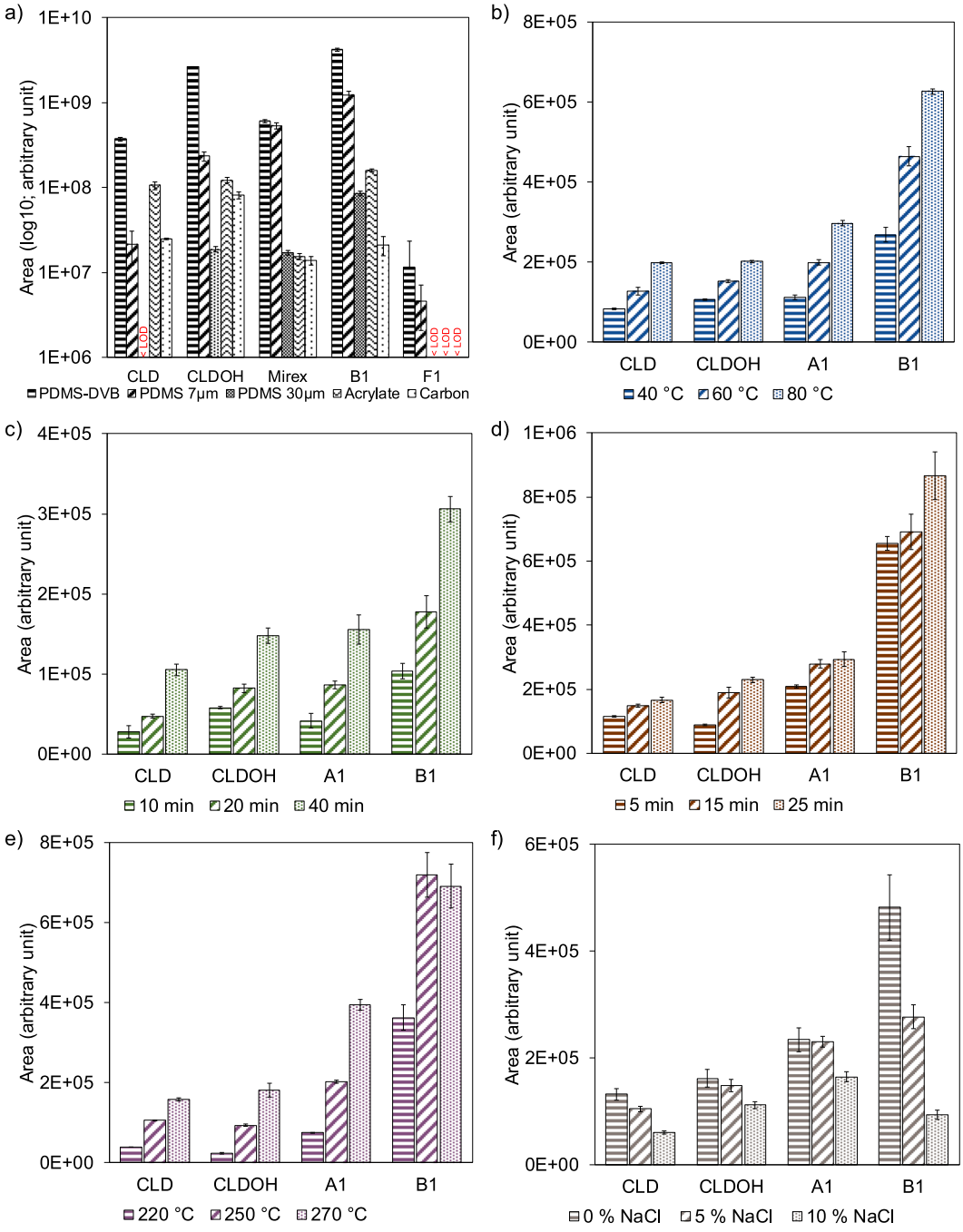

Fig. 3. Responses in SPME-GC-SIM/MS for CLD and its derivatives depending on: a) the SPME coating fiber (all concentrations set at 100 µg/L), b) the extraction temperature (all concentrations set at 1 µg/L), c) the extraction time (all concentrations set at 1 µg/L), d) the desorption time (all concentrations set at 1 µg/L), e) the desorption temperature (all concentrations set at 1 µg/L) and f) the addition of NaCl (all concentrations set at 1 µg/L). Error bars refer to standard errors (n = 3), <LOD: not detected.

indistinguishable with the GC-SIM/MS method developed.

3.3. Optimization of SPME procedure

3.3.1. Comparison between direct immersion and headspace modes

SPME can be operated in two distinct modes: direct immersion (DI) and headspace (HS). HS mode usually offers a higher selectivity by reducing matrix effects and increasing the lifetime of the fiber (Gionfriddo et al., 2015). However, it is limited to volatile and certain semi-volatile compounds. In their pioneering work on CLD quantification by SPME-GC-MS, Soler et al. (2014) used DI-SPME without mentioning any attempt with HS-SPME. We therefore decided to carry out a comparison between DI- and HS-SPME modes for CLD and several other semi-volatile compounds (A1, A2, B1, CLDOH, and mirex) adapting the protocol published by Soler et al. (2014). Results clearly demonstrated a higher efficiency of HS-SPME for the most hydrophobic compounds, B1 and mirex, whereas CLD, A1, A2, and CLDOH were barely extracted by HS-SPME (Fig. S29). Although mirex appears less volatile based on its molecular weight and later retention time, the formation of hydrogen bonds between the hydroxyl moiety of CLD, A1, A2, and CLDOH and water makes these molecules less prone to volatilization from an aqueous sample. Consequently, we retained the original approach of Soler et al. (2014) using direct fiber immersion.

3.3.2. Choice of SPME fiber

CLD and its main TPs were used for optimizing SPME parameters. Five commercial fibers were tested: two fibers in polydimethylsiloxane with varying thickness (PDMS, thickness 7 μm and 30 μm), one fiber in PDMS-divinylbenzene (PDMS-DVB, 65 μm), one fiber in acrylate (85 μm) and one fiber in carbon (95 μm). Extractions were performed in triplicate for CLD, CLDOH, mirex, B1, and F1 simultaneously at 100 μg/L. The general trend observed showed a higher response obtained with PDMS-DVB fiber for all compounds (Fig. 3a). The coupling between these two phases allowed the analysis of polar and volatile compounds (Burgot, 2019). Indeed, PDMS-DVB fiber was used by Soler et al. (2014) for CLD analysis. More generally, PDMS-DVB fiber was often selected for the analysis of OCPs, such as HCB, lindane, dieldrin, aldrin and mirex (Gonçalves and Alpendurada, 2004; Derouiche et al., 2007; Concha-Graña et al., 2010). Hence, to achieve high sensitivity for CLD and its TPs while including a large range of OCPs, the PDMS-DVB fiber was chosen.

It is worth noting that F1 did not perform well in the fiber screening. The best result, which was obtained with PDMS-DVB fiber, yielded an intensity 130 times lower than that observed for CLD. Taking into account LOD previously obtained in SPME-GC–MS for CLD (35 ng/L) (Soler et al., 2014) and the environmental concentrations for F1, expected at best in the range of 10-1000 ng/L if similar to A2 (Wintz and Pak, 2021; Taïlamé et al., 2023), we decided to exclude F1 from further developments.

3.3.3. Optimization of SPME parameters with PDMS-DVB fiber

An overview of the optimization pipeline can be found in Table S2. Firstly, extraction temperature was investigated at 40 °C, 60 °C, and 80 °C for CLD, A1, B1, and CLDOH. Results clearly demonstrated that extraction efficiencies were improved by increasing temperature for all compounds (Fig. 3b), thus confirming the initial observation made by Soler et al. (2014) on CLD. Derouiche et al. (2007) observed the same trend for aldrin, dieldrin, and mirex, with the highest response at 80 °C too. However, for HCB and lindane, which are more volatile, they noted similar responses at both 60 °C and 80 °C (Derouiche et al., 2007). As a result, a temperature of 80 °C was set for further analytical developments.

Secondly, we optimized the extraction time of the SPME procedure using PDMS-DVB fiber incubated at 80 °C. In fact, the Thermo Fisher SPME-GC–MS system allows to carry out the extraction step on sample n + 1 in a masking time, *i.e.* while sample n is being analyzed by GC–MS. Since the developed chromatographic method required around 40 min, we chose to test extraction times up to 40 min. As previously observed (Soler et al., 2014), results showed that a longer extraction time led to a significant increase in extraction efficiency (Fig. 3c). At that stage, we therefore retained an extraction time of 40 min. In comparison, Soler et al. (2014), who apparently could not use such a masking time, preferred a reduced 10-min extraction time to avoid any increase in analytical duration.

Thirdly, the desorption time parameter was optimized, and three durations were tested: 5, 15, and 25 min. While for B1, the best efficiency was achieved after 25 min, no significant differences were found for A1, CLD, and CLDOH between 15 and 25 min (Fig. 3d). In order to limit the total duration of the method, the time of desorption was finally set at 15 min.

Fourthly, the temperature of the fiber desorption was studied at three levels. A general trend was observed with better desorption at the highest temperature of 270 °C, except for B1, for which 250 °C might be slightly more favorable (Fig. 3e). To maximize the desorption of other compounds, 270 °C was chosen.

Modifying the ionic strength by adding a small amount of NaCl was reported to improve extraction yields for OCPs such as HCB and aldrin (Wang et al., 2019). However, other studies described a decrease in extraction yields for HCHs, aldrin, dieldrin, endrin, endosulfan, and DDT (Brondi and Lanças, 2005; Merib et al., 2013). Indeed, the addition of salts increases the ionic strength, possibly decreasing the solubility of compounds and facilitating their adsorption on the fiber. On the contrary, the salting-out effect can also reduce the diffusion of the organic analytes in the solution and increase the viscous resistance, thus decreasing the overall sorption rate on the fiber (Wang et al., 2019). It may also lead to an earlier deterioration of the fiber (Natangelo et al., 1999). To complete the optimization of SPME parameters, we evaluated the effect of NaCl addition up to 10 % (w/v). In the case of B1 and CLD, increasing the amount of NaCl salts significantly decreased the extraction performance, while no difference was observed for CLDOH and A1 with 0 % and 5 % NaCl loadings, 10 % of NaCl being deleterious (Fig. 3f). We therefore decided to avoid any addition of NaCl salts.

3.3.4. Development of a cleaning method for the SPME fiber

CLD is a recalcitrant pesticide due to its physico-chemical properties and known to adsorb strongly onto various materials such as organic matter or plastic (Woignier et al., 2013; Sandre et al., 2019). Soler et al. (2014) reported that a simple cleaning under a nitrogen stream for 30 min at 250 °C was sufficient to eliminate CLD adsorbed on the PDMS-DVB fiber. However, we observed a substantial carryover after each CLD analysis that could not be easily eliminated even after introducing several blanks in the analysis sequence (Fig. S36a). Testing several solvents (methanol, isopropanol, and hexane) for fiber washing and modifying the thermal desorption parameters did not bring much improvement, so we had to examine other ways to remove CLD from the SPME fiber.

To achieve a satisfactory fiber cleaning, we based our strategy on the application of numerous blanks between samples. We began by studying the nature of these inter-sample blanks. Indeed, the SPME efficiency for a specific compound relies on its equilibrium between the solution and the sorbent (Spietelun et al., 2010). Hence, adding a water-miscible solvent well suited to CLD could shift the equilibrium and thus enhance the release of CLD from fiber into the water-solvent mixture. For that, after the analysis of a 10-μg/L solution of CLD, three independent vials composed of either water:methanol (H_2O:MeOH; v/v; 50/50), water:isopropanol (H_2O:IPA; v/v; 50/50) or pure water were successively analyzed with the same method. Results showed a slightly greater improvement in CLD elimination for the series containing H_2O:MeOH blanks (Fig. S36b). This mixture was selected as the inter-sample blank and we proceeded with further optimization. Next, we decided to reduce the analysis time of inter-sample blanks and developed a fast method dedicated to fiber cleaning. As changing the incubator

temperature was very time-consuming, we left the incubator temperature at 80 °C and worked on the other SPME parameters to shorten the method while maintaining efficient performances in CLD removal. Several durations were tested for the incubation, desorption, washing, and conditioning steps; modulation of the number of blanks was also made to never exceed a total time of 75 min for each series of inter-sample blanks (Table S8). It turned out that the number of blanks and the desorption time played the most critical roles. Taking into account the total run time, the overall abatement rate, and the absolute intensity of the remaining CLD signal, we selected the following fast method: 0.5-min incubation in H_2O:MeOH at 80 °C, then 5-min desorption at 300 °C and finally, 0.5-min washing step in IPA followed by 0.5-min thermal conditioning at 340 °C in PTV injector in split mode (1:42) (Method S10); and applied it on eight successive blanks for an overall analytical time of 73.6 min (Table S8).

The last optimization step consisted of determining the number of inter-sample blanks required for a satisfactory fiber cleaning with the newly developed fast cleaning method. For that, a mixture of CLD and its TPs CLDOH, A1, and B1, representative of the main families of CLD TPs, was prepared and analyzed. Concentrations were set to mimic a highly contaminated environmental sample, *i.e.* 1 μg/L for B1 and CLDOH, 0.5 μg/L for A1, and 10 μg/L for CLD. While no difference in efficiency was observed between 8 and 14 blanks for removing CLDOH, A1 and B1 carryover, CLD, initially injected at a higher concentration, was better removed after fourteen blanks (266-fold *vs.* 174-fold) (Fig. S30). However, this improved removal was associated with a significant 43 % increase in run time. We found it less time-consuming to proceed as follows: 1. analyze in a row all environmental samples and group them into two categories, namely low and high CLD content; 2. perform the accurate analyses of each group using an adapted calibration curve and eight inter-sample blanks. As a precaution, we maintained fourteen blanks between the highest level of the calibration range and the following sample. A typical sequence is detailed in the Supplementary material (Fig. S26).

3.3.5. Choice of the internal standards

When commercially available, ^{13}C-labelled IS generally represents a significant cost. In addition, using numerous IS in environmental samples could mask compounds and limit the performance of the analytical method by increasing the number of ions or transitions to be monitored simultaneously. For these reasons, we tested and validated a unique IS, namely $^{13}C_6$-HCB, for HCHs, HCB, PCBz, TeCBs, and TCBs (Figs. S25e–p). For HCBD, we worked in isotopic dilution with $^{13}C_4$-HCBD (Fig. S25s). While the other volatile compounds, *i.e.* DCBs, MCBs, PCE, TCE, were also corrected by $^{13}C_4$-HCBD (Figs. S25a–d and S25r–s) and we chose PCB 138 as IS for aldrin and dieldrin (Figs. S25t–u).

Synthesis of CLD TPs labelled with ^{13}C isotope was not possible due to the high cost of the starting material ^{13}C-CLD. In the present study, $^{13}C_{10}$-CLD was only used for the quantification of CLD, monohydroCLDs (A1 and A2), and mirex (Figs. S24a–d; Fig. S25v). In our previous work on the biodegradation of CLD under methanogenic conditions, we showed that HCB and PCBz gave a similar analytical response to that of B1 for the complex digestate matrix. At that time, we chose PCBz as IS for practical reasons (Martin et al., 2023). None of these compounds could be used as IS in the present study since they belong to the list of targeted OCs. We thus opted for $^{13}C_6$-HCB as IS for B1 and obtained a satisfactory calibration curve in SPME-GC-SIM/MS (Fig. S24e).

Recently, Saint-Hilaire et al. (2018a) developed an LC-MS/MS method for quantifying CLDOH in urine using $^{13}C_8$-CLDOH as IS. Due to the high cost and irregular commercial availability of $^{13}C_8$-CLDOH, we imagined three alternative IS for CLDOH: monodeuteroCLDOH (CLDOH-d), previously synthesized by Fariss et al. (1982) and used by BRGM for their routine analysis, 5-methylCLDOH (CLDOH-Me) and 10-monohydro-5-methylCLDOH (−1Cl-CLDOH-Me). Indeed, CLD, best represented as a gem-diol, is in equilibrium with a minor ketone form (Fig. S31). CLD, with its carbonyl moiety, therefore, remains reactive towards chemical reduction and nucleophilic addition, as illustrated by the synthesis of several alcoholic analogs of CLD in the 1960s, *e.g.* CLDOH and the insecticide Kelevan (Gilbert et al., 1966). Hence, CLDOH-d was readily obtained in excellent yield after the reduction of CLD by $NaBD_4$ (Fig. S31). In contrast, the addition of Grignard reagent CH_3MgBr onto CLD and A1 afforded CLDOH-Me and −1Cl-CLDOH-Me, respectively, in low yield (Fig. S31).

Electron ionization of CLDOH generated the major fragment $[C_5Cl_4OH_2]^{+\bullet}$, which allowed the monitoring of ion *m/z* 218 ($[^{12}C_5^{35}Cl_4OH_2]^{+\bullet}$ as qualifying ion and ion *m/z* 220 ($[^{12}C_5^{35}Cl_3^{37}ClOH_2]^{+\bullet}$) as quantifying ion (Table S3, Figs. S21a and S21c, for simulated and experimental patterns, respectively). At first glance, CLDOH-d would appear to be the best IS candidate. Notably, CLDOH-d led to an apparent similar fragmentation pattern as CLDOH, the main fragment $[C_5Cl_4OHD]^{+\bullet}$ providing analogous ions at *m/z* 219 and 221, respectively (Fig. S21b and d, for simulated and experimental patterns, respectively). To go a step further with CLDOH-d, we needed to estimate the level of contamination of CLDOH in the batch of synthesized CLDOH-d. According to HRMS and NMR analyses, the presence of CLDOH was in the range of 4 % to 6 % (Fig. S3c; Fig. S4), which would have to be taken into account for the development of the SPME-GC-SIM/MS method. Furthermore, due to the low resolution of the GC–MS system, several ions from CLDOH fragmentation experimentally contributed to the signals observed at *m/z* 219 and 221 (Fig. S21c), initially selected for the monitoring of CLDOH-d. Closer examination of the experimental isotopic pattern of $[C_5Cl_4OH_2]^{+\bullet}$ also revealed the presence of $[C_5Cl_4OH]^+$ with ions at *m/z* 217, *m/z* 219 and *m/z* 221 (Fig. S21c). From the simulation, we concluded that CLDOH gave rise to fragments $[C_5Cl_4OH_2]^{+\bullet}$ and $[C_5Cl_4OH]^+$ in a ratio of 88:12 (Fig. S21e). The full contribution of CLDOH to ions at *m/z* 219 and 221 thus came from ions $[^{12}C_5^{35}Cl_3^{37}ClOH]^+$, $[^{12}C_5^{35}Cl_2^{37}Cl_2OH]^+$, $[^{12}C_4^{13}C^{35}Cl_4OH_2]^{+\bullet}$ and $[^{12}C_4^{13}C^{35}Cl_3^{37}ClOH_2]^{+\bullet}$. Overall, this demonstrated that the ions selected for the qualification and the quantification, on the one hand, *m/z* 218 and *m/z* 220 for CLDOH and, on the other hand, *m/z* 219 and *m/z* 221 for CLDOH-d, suffer significant interferences (>10 % of the most intense signal) from ions of CLDOH-d and CLDOH, respectively. To definitely discard CLDOH-d as a possible IS of CLDOH, we studied the CLDOH *vs.* CLDOH-d response in SPME-GC-SIM/MS and confirmed the non-linear relationship (Fig. S23a).

After ruling out CLDOH-d, we focused on CLDOH-Me as a possible IS. From the main fragment $[C_6Cl_4OH_5]^{+\bullet}$ of CLDOH-Me, we selected the most intense ion *m/z* 234 and confirmed the excellent linearity of the SPME-GC-SIM/MS response between CLDOH-Me and CLDOH (Fig. S23b). However, the presence of the methyl group on CLDOH-Me induced a slightly longer retention time when compared with CLDOH (34.43 min *vs.* 34.33 min, respectively; Table S3), eventually resulting in a partial overlap with the signal of mirex (34.48 min; Table S4). Since CLDOH-Me and mirex shared the same fragment $[C_5Cl_6]^{+\bullet}$ originating from the retro-Diels-Alder cleavage of the perchlorobishomocubane cage, CLDOH-Me could definitely not be used as IS. The last candidate −1Cl-CLDOH-Me, gave rise in electron ionization to the main fragment $[C_6Cl_4OH_5]^{+\bullet}$ with maximum intensity at *m/z* 234 (Fig. S16b). Although −1Cl-CLDOH-Me was synthesized as an approximately 1:1 diastereoisomeric mixture according to LC-HRMS analysis (Fig. S16c), it led to a unique sharp signal easily integrable in GC-MS (Fig. S16a). Its retention time turned out to be very close to that of −1Cl-CLDOH, but its respective monitored ions were perfectly distinguishable (Table S3). SPME-GC-SIM/MS responses of CLDOH and −1Cl-CLDOH-Me satisfactorily correlated (Fig. S23c) finally allowing −1Cl-CLDOH-Me to be chosen as IS of CLDOH and −1Cl-CLDOH.

3.4. Evaluation of the performance of the SPME-GC-SIM/MS method

3.4.1. CLD and its TPs

The performance of the SPME method was evaluated through the linearity, accuracy, relative standard deviation (RSD), LOD, and LOQ.

Calibration curves were constructed with five levels of concentrations and the use of previously selected IS (Table S3). Excellent linearity in the SPME-GC-SIM/MS responses was obtained with correlation coefficients between 0.989 and 0.999 (Table 1). Accuracies ranged from 75 to 119 %, while RSD were found below 25 %, demonstrating the good performances of the SPME method for CLD and its TPs.

LOD and LOQ were estimated in the range of 3 to 5 ng/L and 9 to 15 ng/L, respectively (Table 1). Hence, we obtained a better sensitivity when compared to the analogous SPME-GC-SIM/MS method of Soler et al. (2014), who reported a LOQ of 80 ng/L for CLD. The difference in performance probably stems from the longer incubation time we chose compared to them (40 min *vs.* 10 min). Indeed, the use of an MS/MS method with a more advanced analytical system coupled with SPME enabled Soler and al. (2014) to reach an LOQ of 2.0 ng/L for CLD. LLE-based methods by BRGM (GC–MS/MS) and LDA26 (LC-MS/MS) led to LOQ close to the newly developed method (30 ng/L and 10 ng/L, respectively) but required a larger sample volume, the use of organic solvent(s) for extraction and advanced facilities.

3.4.2. Other OCPs

From the linear regression method, good linear responses (R^2 = 0.986–0.9998), accuracies (54–133 %), and RSD (4–56 %) were obtained for all studied OCs, except MCB, which showed lower R^2 (0.973) and higher RSD (61 %) (Fig. S25; Table S7). LDA26 also targeted several of these compounds with LOQ ranging from 1 to 10 ng/L, depending on the OCs (Table S9). Our estimated LOQ (Table S7) were slightly lower for all these OCs, the principle of SPME, *i.e.* selective adsorption onto the fiber enabling analytes to accumulate while limiting the extraction of interferences from the matrix. In the case of LLE, the concentration step prior to analysis increased both compounds concentrations and matrix interferences. Overall, these performances confirmed that the SPME-GC-SIM/MS could be used with confidence for the analysis of the listed OCs in environmental waters.

3.5. Application to environmental waters

3.5.1. Occurrence of chlordecone in environmental waters and comparison of the methods used for its detection

CLD was detected in all water samples from the two highly polluted FWI catchments. According to the results of the SPME-GC-SIM/MS method, CLD concentrations generally ranged in river water, spring water, and well water from 0.2 to 4 µg/L, 4 to 8 µg/L and 6 to 29 µg/L, respectively, as previously observed in historical surveys (Charlier et al., 2015; Wintz and Pak, 2021) (Table S10). The data from the SPME-GC-SIM/MS method were compared with the concentrations obtained by the other methods (Fig. S27). Good agreements were found with LLE protocols of Genoscope (LLE-GC-SIM/MS and LLE-LC-HRMS) (Table S10) and BRGM (LLE-GC-MS/MS) (Fig. 4a). In particular, the error estimated by the SPME-GC-SIM/MS (standard deviation, n = 2) and the 20 % uncertainty of the BRGM method well explained the minor differences observed (correlation factor: $R = 0.98$, p-value $< 2 \times 10^{-16}$, Fig. S32). On the contrary, a very strong divergence (3- to 10-fold ratios)

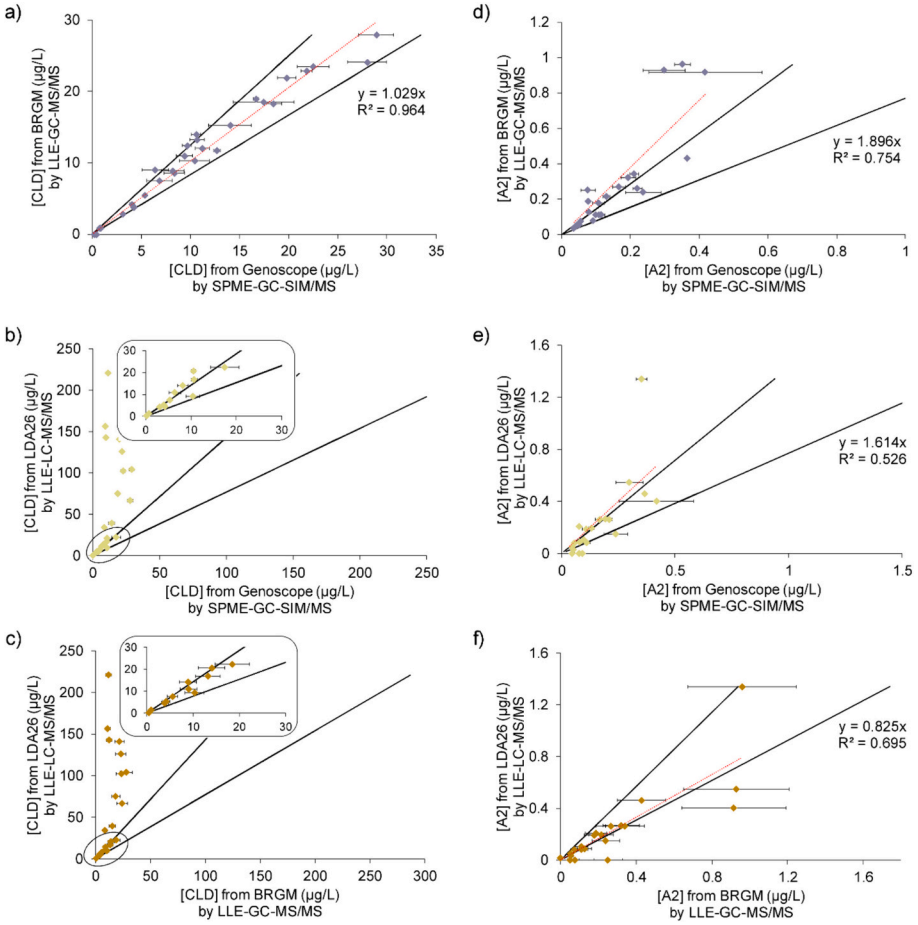

Fig. 4. Comparison of concentrations in environmental waters obtained for: a) CLD for BRGM (LLE-GC-MS/MS) *vs.* Genoscope (SPME-GC-SIM/MS) b) CLD for LDA26 (LLE-LC-MS/MS) *vs.* Genoscope (SPME-GC-SIM/MS), c) CLD for LDA26 (LLE-LC-MS/MS) *vs.* BRGM (LLE-GC-MS/MS), d) A2 for BRGM (LLE-GC-MS/MS) *vs.* Genoscope (SPME-GC-SIM/MS), e) A2 for LDA26 (LLE-LC-MS/MS) *vs.* Genoscope (SPME-GC-SIM/MS) and f) A2 for LDA26 (LLE-LC-MS/MS) *vs.* BRGM (LLE-GC-MS/MS). Black lines correspond to an uncertainty of 20 % for CLD (a) and 30 % for A2 (d) for BRGM and 30 % for LDA26 (b, c, e, and f). Error bars correspond to the standard deviation for Genoscope (n = 2; a, b, d, and e) and the uncertainty of 30 % estimated for BRGM (c).

was observed at high concentrations with the routine LLE-LC-MS/MS protocol applied by LDA26 (Fig. 4b and c). With the concentrations obtained with SPME-GC-SIM/MS (Genoscope), the correlation factor (R) was estimated at 0.52 (p-value = 0.0096) (Fig. S33). A similar correlation factor ($R = 0.51$; p-value = 0.014) was determined between BRGM and LDA26 data (Fig. S34). The Durbin-Watson test showed autocorrelations among the residuals demonstrating that these correlations are not valid on the entire studied domain (Fig. S33 and S34). We empirically determined a threshold of 8 μg/L that allowed a satisfactory agreement between LDA26 values and the other data sets (Fig. S35).

Values above the established confidence interval [0, 8 μg/L] correspond to highly contaminated groundwaters. As part of the OPALE program, CLD pollution of these groundwaters has been monitored since 2015 (Taïlamé et al., 2023). The results showed stable levels of very high contamination ranging from 1 to 50 μg/L depending on the well or spring water studied. The CLD concentrations obtained by Genoscope and BRGM are in good agreement with all historical measurements of these groundwaters, so we concluded that values of LDA26, especially the nine concentrations above 50 μg/L, were not relevant and should be discarded from further environmental studies. In addition, unlike the two other laboratories, LDA26 exhibited substantial variations in CLD concentrations over hours, days, and months for the same wells (Boulangerie, Gendarmerie_1, and Lacavé_2; Table S10).

One might suggest specific matrix effects arising in groundwaters, but we excluded this hypothesis because the particulate fraction is absent from groundwaters, unlike surface water, which is subject to soil erosion deposits. Indeed, none of the three extraction protocols did include a filtration step, which might have been a source of bias. Given that BRGM and LDA26 both applied the LLE technique and obtained divergent results, we ruled out the hypothesis of a systematic bias when switching from LLE to SPME protocols. Genoscope and BRGM focused on CLD and its TP and used $^{13}C_{10}$-CLD as an internal standard. In contrast, LDA26 applied a more general pesticide method (CMO_MT02) with several extraction markers as hexabromobenzene (HBB), triphenyl phosphate (TPP), and desisopropyl atrazine-d_5 (DIA-d5) and added after extraction the internal standards 2,4-dichlorophenoxyacetic acid-d_3 (2,4-D-d3) and atrazine-d5 to correct LC-MS/MS analyses (Rochette et al., 2017). HBB, TPP, DIA-d5, 2,4-D-d3 and atrazine-d5 structurally differ from CLD, which bears a rare perchlorinated bishomocubane cage coupled to a seldom stable hydrated carbonyl moiety. Due to its physicochemical properties, namely its hydrophobicity and preferential adsorption onto any organic matter, CLD is a particularly difficult molecule to handle and analyze. As the discrepancies between laboratories occurred after a threshold concentration, we suspected an inadequacy between tracers concentrations and CLD concentrations. It is worth mentioning that the high levels (>several μg/L) observed for CLD in groundwaters are well above the concentrations observed for other pesticides in environmental waters and can correspond to several thousand times the LOQ set for CLD by LDA26. Furthermore, one could not exclude that the combination of extraction and injection tracers structurally not related to CLD might not perfectly correct CLD signals over such a magnitude of concentrations. Hence, we suggest adding a dedicated internal standard for CLD quantification, ideally an isotopically-labelled molecule such as $^{13}C_{10}$-CLD or $^{13}C_8$-CLD, at a level appropriate to the environmental concentrations expected (*e.g.* 1 μg/L).

3.5.2. *Occurrence of chlordecol in environmental waters and comparison of the methods used for its detection*

CLDOH was detected and quantified in 29 out of the 30 waters analyzed with the SPME-GC-SIM/MS method. Concentrations in surface waters and spring waters never exceeded 0.5 μg/L, while well waters showed CLDOH concentrations ranging from 0.4 μg/L up to 2.7 μg/L (Table 2). Comparison with BRGM and LDA26 results revealed wide disparities. LDA26, having the lowest LOQ (0.01 μg/L), detected CLDOH only five times, whereas BRGM, with an LOQ of 0.03 μg/L, reported the presence of CLDOH 25 times out of the 28 water samples tested

Table 2
Comparison of CLDOH concentrations (expressed in μg/L) obtained by the three laboratories for the 31 environmental waters. nd: not detected, na: not analyzed.

			Genoscope SPME-GC-SIM/MS	BRGM LLE-GC-MS/MS	LDA26 LLE-LC-MS/MS
Martinique	River water	Grand Galion	0.04	na	nd
		Base de Loisirs	nd	na	nd
		La Digue	1.09	na	0.05
Guadeloupe	River water	Pérou_exutoire	0.10	nd	0.06
		Pères_80m	0.33	0.14	0.14
		Pérou_exutoire	0.08	0.04	na
		Saint-Denis	0.51	0.12	na
		Pères_80m	0.19	0.14	na
	Spring water	Marigot	0.23	0.07	nd
		Captée	0.14	0.08	nd
		Marigot	0.23	0.15	nd
		Pérou	0.39	0.42	nd
		Captée	0.29	0.33	na
		Sarlaconne	na	nd	nd
	Well water	Gendarmerie 1_1h	2.74	0.13	nd
		Gendarmerie 1_24h	1.38	0.14	nd
		Gendarmerie 1_48h	1.64	0.15	nd
		Boulangerie_1h_bis	1.98	0.82	na
		Boulangerie_1h	1.11	0.27	nd
		Boulangerie_24h	1.11	0.31	nd
		Fromager	0.89	1.06	na
		Lacavé 2_24h	0.89	0.19	nd
		Lacavé 2_48h	0.62	0.11	nd
		Lacavé 2_1h	1.17	0.17	nd
		Saint-Denis 2	0.40	0.08	0.02
		Gendarmerie 1	1.11	1.24	nd
		Gendarmerie 2	1.79	1.15	0.03
		Boulangerie	0.85	0.82	nd
		Fromager	0.89	0.74	nd
		Lacavé 2	0.57	0.51	nd
		Saint-Denis 2	1.50	0.65	nd

(Table 2). Furthermore, the five concentrations obtained by LDA26 did not match neither BRGM nor Genoscope results. For eight samples only, the 30 % uncertainty of the BRGM protocol could explain the difference observed with the SPME-GC-SIM/MS method. In all other cases, BRGM concentrations were systematically lower than those obtained by the SPME-GC-SIM/MS method. However, these two methods agree on the high occurrence of CLDOH contrary to the routine method of LDA26, according to which CLDOH was not a recurrent contaminant in these series of environmental waters. The failure to detect and quantify CLDOH, if confirmed, could not simply be explained by the lack of appropriate internal standards, as was previously suggested in the case of CLD. Indeed, detection of CLDOH by LC-ESI-MS in the negative ion mode using multiple reaction monitoring was challenging as CLDOH barely fragments under ESI conditions. Indeed, Saint-Hilaire et al. (2018a) used the transition m/z 498 → 35 and the pseudo transition m/z 498 → 498 for their analytical developments in urine. Finally, the authors obtained a 13-fold higher LOQ for CLDOH than for CLD in urine (1.3 *vs.* 0.1 μg/L) (Saint-Hilaire et al., 2018a).

Significant differences in CLDOH concentrations between Genoscope and BRGM were observed for approximately 70 % of the water samples analyzed by the two laboratories. We excluded discrepancies at the extraction stage, SPME *vs.* LLE, as both methods yielded concordant concentrations of CLD, known to be particularly difficult to extract and handle. Indeed, the BRGM protocol differed in the use of tandem mass spectrometry and the choice of CLDOH-d as IS. The multiple reaction monitoring employed by BRGM is intrinsically more sensitive than the selected ion monitoring applied by Genoscope. Nevertheless, the use of CLDOH-d as IS of CLDOH led to limitations as the fragmentation patterns, and consequently, the MS/MS transitions selected to monitor CLDOH and CLDOH-d overlap to some extent (Fig. S21). To avoid this, BRGM systematically checked that the resulting CLDOH concentrations had no significant impact on the intensity of the CLDOH-d signal; if necessary, the sample was diluted and re-analyzed. In contrast, during the development of the SPME-GC-SIM/MS method, we preferred to

switch to −1Cl-CLDOH-Me as IS (see Section 3.3.5). One alternative IS, albeit not regularly marketed, $^{13}C_8$-CLDOH, was successfully used by Saint-Hilaire et al. (2018a, b). In fact, its addition improved recoveries from 78 % to 102 %, to achieve a trueness of 10 % in liver matrix (Saint-Hilaire et al., 2018b).

Inspecting the origin of the eight samples that showed good consistency between Genoscope and BRGM methods, we realized that all samples came from the second Guadeloupe campaign. Indeed, the trends of CLDOH concentration in the same location over the two sampling campaigns differed according to each laboratory. While Genoscope measurements indicated little fluctuations in CLDOH levels over time, BRGM results showed a significant increase in CLDOH concentrations in well waters between spring/summer 2022 and autumn 2022 (Table S13). Overall, Genoscope analyses are indicative of the higher CLDOH levels observed for each well.

The discrepancies in CLDOH concentrations between Genoscope and BRGM might be due to minor differences in the sampling and homogeneous partitioning at each laboratory, the storage duration, and/or the final sub-sampling required to fit the extraction volumes of each method (20 mL *vs.* 500 mL (concentration lower 0.25 μg/L) or 50 mL (concentration upper 0.25 μg/L) for Genoscope and BRGM, respectively). CLDOH, being more hydrophobic than CLD, may be prone to greater adsorption and precipitation phenomena, notably in cold storage and in the presence of suspended particles.

3.5.3. Occurrence of 8-monohydrochlordecone in environmental waters and comparison of the methods used for its detection

The SPME-GC-SIM/MS method enabled the detection and quantification of 8-monohydrochlordecone (A2) in all groundwaters except one sample of Fromager well (first campaign), with concentrations varying from 0.042 μg/L to 0.366 μg/L. Analysis of river waters revealed the presence of A2 in four out of eight samples, with concentrations ranging from 0.036 to 0.064 μg/L (Table S12). As expected from previous observations (Cattan et al., 2019), the four river waters showing the absence of A2 correspond to the samples least contaminated with CLD (concentrations below 1 μg/L).

Then, we compared A2 concentrations obtained by the SPME-GC-SIM/MS method and the LLE protocols (Fig. 4d–f). Error deviations and uncertainties did not explain the observed discrepancies. Moderately good linear relationships were found for the correlations Genoscope *vs.* BRGM and BRGM *vs.* LDA26. In fact, for several water samples, the LLE-LC-MS/MS and the SPME-GC-SIM/MS methods failed to detect A2, whereas the LLE-GC-MS/MS applied by BRGM (with the higher LOQ of 30 ng/L) did quantify it (Table S12). This also resulted in a weaker correlation between A2 concentrations measured by Genoscope and LDA26 (Fig. 4e). Complementary LLE-GC-SIM/MS and LLE-LC-HRMS analyses by Genoscope were consistent with the levels of A2 concentrations previously found and included in the range of [0, 1 μg/L] but did not particularly agree with any of the other methods (Table S12). However, it is worth noting a systematic slight over/underestimation of A2 concentrations between laboratories: on average, BRGM concentrations were 1.90 times and 1.21 times higher than Genoscope and LDA26 concentrations, respectively (Fig. 4d–f). It could be due to biases in the calibration curve used, including the quality of the A2 standard employed. Indeed, the commercialization of A2 (in solution in cyclohexane) has been interrupted for several years before being relaunched very recently. Thus, for the SPME-GC-SIM/MS developments as for previous works (Chevallier et al., 2019; Martin et al., 2023), the Genoscope laboratory decided to synthesize A2 in-house according to the literature (Wilson and Zehr, 1979). The high purity estimated by NMR of the synthesized A2 was confirmed by comparison with a commercial solution of A2 (Fig. S39). For the laboratory comparison, daily calibration curves, including A2 itself at five levels, bracketed the water samples to be analyzed for the SPME-GC-MS method (Fig. S26). The quality of the A2 stock solution used for the calibration curve was regularly checked according to an in-house GC-FID procedure (Supporting Method M9).

3.5.4. Occurrence of the other transformation products of chlordecone in environmental waters

10-Monohydrochlordecone (A1) was detected by the SPME-GC-SIM/MS method in 22 out of the 30 samples analyzed, mostly in groundwaters. The very low concentrations observed, close to LOQ, were systematically below those of CLDOH and A2, which were also present in the same samples. In fact, the greater sensitivity of the SPME method compared with the LLE-GC–MS/MS method (LOQ of 30 ng/L) clearly explained why BRGM detected and quantified A1 in six water samples only (Fig. S28, Table S11). Due to limitation in commercial standard A1, LDA26 did not include this TP in its list of targeted OCs (Table S9).

The SPME-GC-SIM/MS was also used to search four additional TPs, namely pentachloroindene B1, tetrachloroindenes B2 and B3/B4, and 10-monohydrochlordecol (−1Cl-CLDOH) which were not targeted by BRGM and LDA26. While B1 could scarcely be detected in two groundwater samples from the same well (Lacavé_2; Guadeloupe) (Table S15), −1Cl-CLDOH was quantified in one river water of Martinique and five groundwater samples of three wells (Gendarmerie_1, Gendarmerie_2 and Lacavé_2; Guadeloupe), albeit at very low level ranging from 0.012 μg/L to 0.056 μg/L (Table S14). In contrast, no trace of tetrachloroindenes B2 and B3/B4 were visible (Tables S16 and S17). In fact, laboratory biodegradation experiments of CLD always led to low amount of these tetrachloroindenes, while pentachloroindene B1 systematically appeared as the predominant congener of this family of TPs (Chevallier et al., 2019; Hellal et al., 2021; Martin et al., 2023). In view of the very rare occurrence of B1, the total absence of tetrachloroindenes in environmental waters seemed logical. It should be noted that, when detected, B1 was only visible in the first analytical replicate, the second analysis being scheduled several weeks later. In our past prospective analytical campaign, during which B1 was detected at higher level in two samples of the Galion River (Martinique), the LLE protocol was applied immediately upon receipt of the water samples (Chevallier et al., 2019). Therefore, we wondered about the stability of B1 and other polychloroindenes in environmental waters under storage.

For each water sample, an additional SPME-GC-MS analysis with full scan acquisition was performed. Examination of this data set did not reveal any other TP included in our in-house library containing over 50 TPs of CLD (Chaussonnerie et al., 2016; Chevallier et al., 2019; Della-Negra et al., 2020; Hellal et al., 2021).

3.5.5. Occurrence of other organochlorines in environmental waters

In addition to CLD and its two TPs, A2 and CLDOH, many other OCs are regularly screened by LDA26 as part of the monitoring carried out by the OPALE observatory. The multi-residue method targeted both active substances and some of their metabolites, such as aldrin, dieldrin, HCHs (α, β, δ and γ), HCB, PCBz, 1,2,3,4-TeCB, 1,2,4,5,-TeCB, 1,3,4,5-TeCB. To illustrate the interest in the developed SPME-GC-SIM/MS method, we chose these OCs, including lower chlorinated congeners of HCB and three volatile OCs (HCBD, TCE, and PCE) not yet searched for in the FWI, which are known legacy pollutants of environmental waters (Kong et al., 2020; Jin et al., 2022).

Among the list of 22 OCs targeted by the SPME-GC-SIM/MS method, only two were detected and quantified. The first one, β-HCH, was found in 6 river waters and 13 groundwaters at low concentrations ranging from LOQ to 0.246 μg/L (Table S19). β-HCH proved to be the most recalcitrant HCH among the four contained in the commercial formulation used in the FWI (Bhatt et al., 2009). The second OC detected, dieldrin, was visible exclusively in groundwaters at levels similar to β-HCH (Table S18). Comparing the results with those of LDA26 revealed several inconsistencies in the presence/absence of these two OCs. No particular trend, *e.g.* over/underestimation, could be concluded. We hypothesized that the very low concentrations estimated, close to the LOQ of both methods, may explain the observed discrepancies. The sporadic presence at low concentrations of these two legacy OC

contaminants in FWI environmental waters was consistent with previous observations (Rochette et al., 2017; Wintz and Pak, 2021).

3.5.6. Relevance and added value of the present environmental campaign

Historically, surface waters and groundwaters have been analyzed by LDA26 using its LLE-LC-MS/MS method for the regular monitoring at the OPALE observatory. Although stable levels of pollution were usually observed (Voltz et al., 2023), with some river waters even showing a slight decrease in CLD concentrations over time (Cattan et al., 2019), occasional high concentration peaks were sometimes reported. For river waters usually associated with low CLD concentrations in the range [0, 8 μg/L], these irregularities are likely more frequently due to the consequence of hydrological phenomena such as seasonal fluctuations and flood events (Mottes et al., 2020). However, for groundwaters, based on our results, and considering the longer regulation time of aquifer systems buffering physico-chemical changes, we suggest interpreting the outlier concentrations of LDA26 as overestimations, thus unlikely to hold significant environmental relevance.

Since the pioneering work of Devault et al. (2016), significant emphasis has been placed on A2/CLD concentration ratios to investigate CLD pollution and its presumed natural degradation (Cattan et al., 2019; Comte et al., 2022). However, CLDOH levels in FWI soils with concentrations at least ten times higher than those of A2 (Chevallier et al., 2019) have not garnered much attention. Indeed, CLDOH appears to be as toxic as CLD according to the few limited toxicological studies available (Desaiah and Koch, 1975; Soileau and Moreland, 1983, 1988);

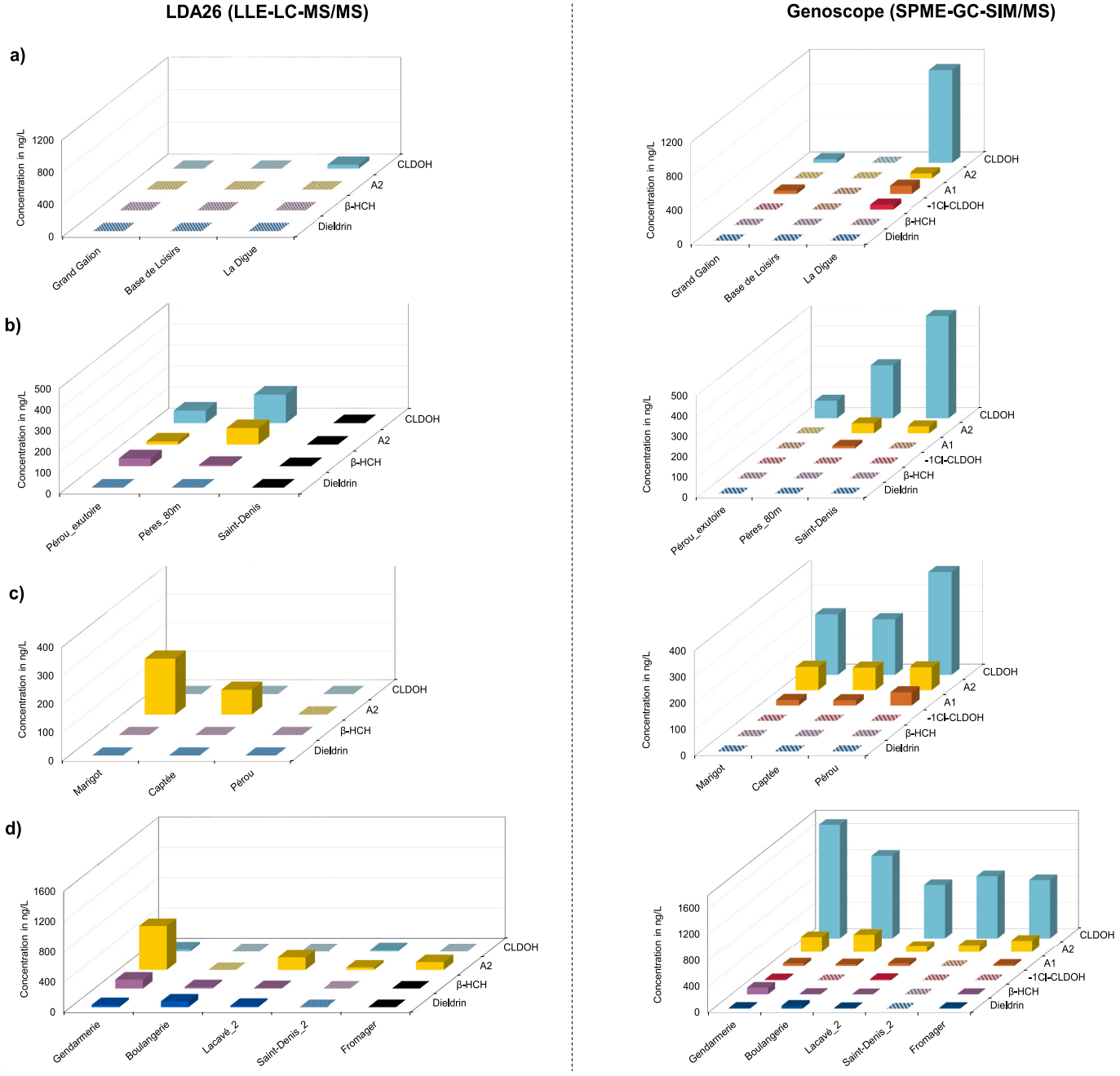

Fig. 5. Comparison of time-averaged contamination profiles (CLD excluded for clarity) of environmental waters in the FWI using either LDA26 (LLE-LC-MS/MS) (left) or Genoscope (SPME-GC-SIM/MS) (right) analytical methods: a) for river waters from Guadeloupe, b) for spring waters from Guadeloupe, c) and d) for well waters from Guadeloupe. Shaded boxes indicate the absence of compounds (<LOD). Black boxes indicate that the absence of analyses performed for a defined couple of sampling sites and OCs. Time-averaged concentrations were calculated from the two sampling campaigns carried out in 2022 (Tables S11–S19).

it is also produced and excreted as a metabolite by several types of livestock exposed to CLD in the FWI (Saint-Hilaire et al., 2018a, 2021). The CLDOH/CLD concentration ratios that can be calculated for soils are consistent with the few percentages of CLDOH present in the commercial formulations of CLD (Kepone© and Curlone©) (Soler et al., 2014). Surprisingly, years of environmental waters monitoring in the FWI using the LDA26 method have consistently shown higher levels of A2 relative to CLDOH (Cattan et al., 2019; Wintz and Pak, 2021; Taïlamé et al., 2023; Voltz et al., 2023). This observation could be attributed to various environmental phenomena, such as the contrasting mobilization of the molecule from soil to leaching waters. However, in the light of the present laboratory comparison, we propose an additional hypothesis, namely a potential analytical bias minimizing CLDOH concentrations in water samples. The suggested underestimation of CLDOH by LDA26 is also supported by: 1. the BRGM measurements, although not always in good agreement with Genoscope concentrations; 2. the detection by Genoscope of −1Cl-CLDOH for the first time in environmental waters. Indeed, −1Cl-CLDOH could be formed by the reduction of A1, as observed during the metabolization of CLD giving rise to CLDOH (Fariss et al., 1980), or by reductive dechlorination of CLDOH, similar to the conversion of CLD into A1 observed in microbiological degradations (Chaussonnerie et al., 2016; Chevallier et al., 2019).

When we examined the temporal average of OC pollution observed for each sampling site using the newly developed SPME-GC-SIM/MS, we obtained a contamination profile that substantially differed from the FWI routine monitoring based on LDA26 protocol. While CLD systematically emerged as the main pollutant, albeit in slightly lower levels (Fig. S27), the second largest contributor turned out to be CLDOH followed, in decreasing order, by A2, β-HCH, dieldrin and −1Cl-CLDOH according to the SPME-GC-SIM/MS analyses (Genoscope) (Fig. 5). Higher CLD levels were generally correlated to the more frequent and more intense presence of CLD TPs, regardless of the type of environmental waters.

The suspected over- and underestimations of CLD and CLDOH concentrations respectively by the LDA26 protocol prompted us to re-examined some temporal monitoring data of FWI waters accumulated over years: two groundwaters from Guadeloupe (Fromager and Saint-Denis_2 wells), as well as three surface waters (Pérou and Pères rivers in Guadeloupe and La Digue river in Martinique). Groundwaters were associated with high CLD levels above the threshold of 8 µg/L that showed divergences between LDA26 protocol and the others (Fig. 4). On the contrary, CLD concentrations in the river waters rarely exceeded 8 µg/L. We applied the Rosner test to identify potential outliers in the temporal monitorings of CLD, CLDOH and A2 (for details see Supporting Text). In the case of CLD, all five environmental waters showed statistical outliers (Fig. 6). Among them, several values could not be explained by hydrological fluctuations. Fewer statistical outliers were found in the temporal monitorings of A2 (Fig. S37). No match between CLD and A2 outliers could be found. Except for the La Digue river, CLDOH concentrations were generally very low, *i.e.* closed to the limit of

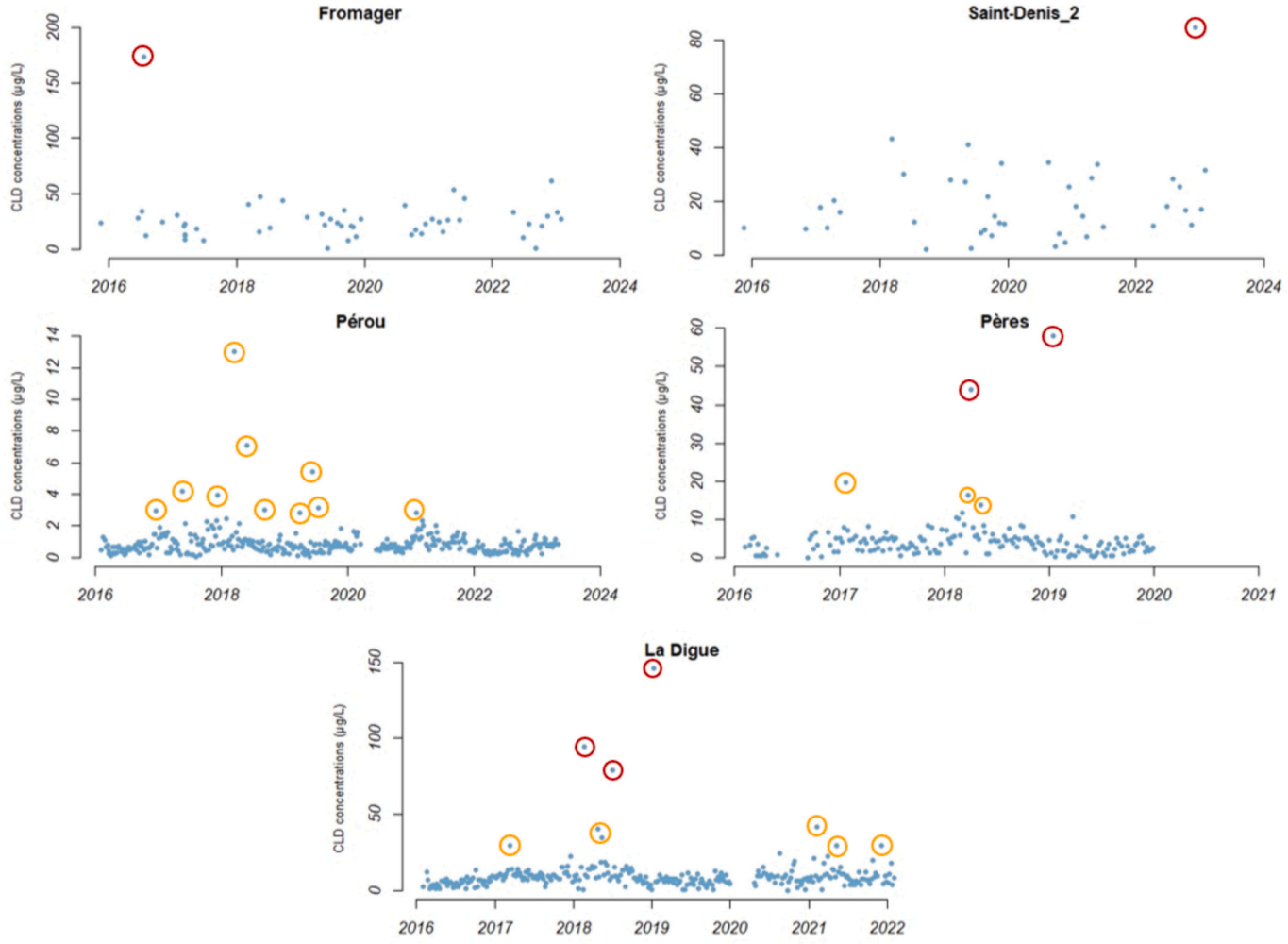

Fig. 6. Statistical outliers in the measured concentrations of CLD (in µg/L), marked with circles, in different environmental waters (three surface waters, namely the Pères and Pérou rivers in Guadeloupe and La Digue river in Martinique, as well as two groundwaters, Fromager and Saint-Denis_2) identified with Rosner test. Orange circles indicate values with potential hydrological significances. Red circles highlight values without any hydrological significances.

quantification of 0.010 μg/L (Fig. S38). While these data did not permit to highlight any pertinent statistical outliers, they confirmed the recurrent low CLDOH levels from LDA26 in contradiction with the much higher values obtained by Genoscope and BRGM (Table S13). Altogether, these temporal monitorings confirmed the potential overestimation of CLD concentrations and underestimation of CLDOH in the LDA26 protocol, initially observed in the laboratory comparison.

4. Conclusion

The regular monitoring of the FWI environmental waters carried out by the LDA26 laboratory for years has demonstrated the extent of pollution caused by CLD, by far the major organic pollutant of FWI waters. Two TPs of CLD, namely A2 and CLDOH, known contaminants of the commercial formulations of CLD, also belong to the short set of OCs found recurrently in surface waters and groundwaters of the FWI. In recent years, numerous other TPs have been reported to be formed during laboratory (bio)degradation of CLD and present in FWI soils. To facilitate and expand the monitoring of FWI environmental waters, we successfully developed a simple, robust, and green analytical protocol based on the SPME technique to analyze CLD, seven TPs, and several OCs. The performance of the SPME-GC-SIM/MS method enabled the detection of CLD, five TPs (CLDOH, A2, A1, −1Cl-CLDOH and B1) and two OC insecticides, β-HCH and dieldrin in the 30 environmental waters studied. These results should modify the view of CLD pollution mainly focused on CLD levels and A2/CLD concentration ratios. Comparison of our results with those obtained by two other laboratories allowed the validation of the SPME-GC-SIM/MS method for the quantification of CLD. Several discrepancies between methods with presumed overestimates of CLD and underestimates of CLDOH for one laboratory call for intensified efforts to reliably quantify CLD and the maximum of TPs. We also emphasize the need to use IS ^{13}C-labelled and/or IS structurally related to the targeted compounds spiked at relevant concentration levels in order to obtain accurate and robust results. In the case of long-term pollutions such as CLD in the FWI, whose duration was estimated to range from several decades to several centuries (Cabidoche et al., 2009; Comte et al., 2022; Saaidi et al., 2023), the quality and the reproducibility of the analyses over many years are of paramount importance.

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CRediT authorship contribution statement

Déborah E. Martin: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Delphine Muselet:** Formal analysis. **Hussein Kanso:** Formal analysis. **Perla Alnajjar:** Writing – review & editing, Data curation. **Juliette Mexler:** Formal analysis. **Yves Le Roux:** Writing – review & editing, Data curation. **Lai Ting Pak:** Writing – review & editing, Data curation. **Antoine Richard:** Writing – review & editing, Data curation. **Jean-Baptiste Charlier:** Writing – review & editing, Supervision, Funding acquisition, Data curation. **Pierre-Loïc Saaidi:** Writing – original draft, Writing – review & editing, Supervision, Investigation, Funding acquisition, 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.2024.174610.

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