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► **To cite this version:**

A. Martin, C. Margoum, Jérôme Randon, Marina Coquery. Silicone rubber selection for passive sampling of pesticides in water.. *Talanta*, 2016, 160, pp.306-313. 10.1016/j.talanta.2016.07.019 . hal-01546514

HAL Id: hal-01546514

<https://hal.science/hal-01546514>

Submitted on 16 May 2020

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Silicone rubber selection for passive sampling of pesticides in water

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Abstract

Silicone rubber can extract organic compounds with a broad range of polarities ($\log K_{ow} > 2-3$) from aqueous samples. Such compounds include substances of major concern in the protection of aquatic ecosystems and human health, e.g. pesticides. Silicone rubbers (SRs) with various characteristics have been successfully used in sorptive methods for water sample extraction in the laboratory (SPME, SBSE), and for passive sampling in aquatic environments. However, only few studies have evaluated variability in organic compound sorption due to the origin of SRs, particularly for pesticides. The aim of this study was to select an SR for the extraction of pesticides from water samples by passive sampling. To this end we measured the impact of seven SR formulations on sorption capacity, defined by the partition coefficient (K_{sw}). Kinetic experiments and sorption isotherms were performed to determine extraction recovery as a selection criterion for SRs, and pesticide partition coefficients. Very large differences in affinity for pesticides were found between two kinds of SRs: “Polymerized SR kits” and “Manufactured SRs”. One SR was chosen among the “Manufactured SRs”, and the K_{sw} values of 21 pesticides were determined, filling a gap in the literature ($1.50 < \log K_{ow} < 5.51$). In light of sorption properties, literature data and additional economic and technical factors, we suggest using SR from Goodfellow in future work to reduce the variability of K_{sw} literature values.

Keywords: Pesticide, Silicone rubber, Partition coefficient, Passive sampling, Liquid chromatography

Introduction

Intensive agricultural consumption of pesticides requires the accurate monitoring of these contaminants in the aquatic environment to protect aquatic ecosystems and human health. Pesticides are present in trace amounts, and comprise organic compounds with a wide range of properties, raising a challenge for sampling and analytical methods to evaluate water resource quality. A number of sorptive techniques based on silicone rubber (SR) materials have been developed over the past 30 years to extract organic compounds such as pesticides. Silicone rubbers were developed as sorptive extraction phases in the 1980s, the dominant polymer being polydimethylsiloxane (PDMS). The most popular sorptive methods using SR, combining robustness and reproducibility, are solid-phase microextraction (SPME) [1], stir bar sorptive extraction (SBSE) [2] and silicone rods/tubes [3]. SRs are mechanically resistant, insoluble in the common solvents used for analyte back-extraction, and allow thermal desorption at high temperatures (250–300 °C) [3]. Silicone rubbers will extract organic compounds with a broad range of polarities (PAHs, PCBs, pesticides, etc., with $\log K_{ow} > 2-3$) from aqueous solutions, despite their hydrophobic nature [4]. The characteristics of SRs have also been successfully exploited for in situ passive sampling in surface waters with the membrane-enclosed silicone collector (MESCO) [5], passive SBSE [6] and silicone rods/sheets/tubes [3], [7] and [8].

All extraction methods using SR are based on partitioning the analytes between the water sample and the silicone phase, which is governed by the partition coefficient (K_{sw}), defined as the ratio of the concentration of the analyte in the silicone to its concentration in water in equilibrium conditions. The partition coefficient is one of the key parameters in sorptive methods using SRs, as illustrated by the theoretical calculation of extraction recovery for SBSE in batch experiments (Eq. (1), from [9]) and calculation of in situ water concentration ($C_{w(in situ)}$, $\mu\text{g L}^{-1}$) for passive sampling of hydrophobic contaminants in field applications over a period of exposure (Eq. (2), from [5]).

$$\text{Extraction recovery} = \frac{K_{sw}}{K_{sw} + \frac{V_w}{V_s}}, \text{ (Eq. 1)}$$

$$C_{w(in situ)} = \frac{C_s(t)}{K_{sw} (1 - \exp(-R_s t / K_{sw} V_s))}. \text{ (Eq. 2)}$$

Other parameters are also required, such as volume of water in batch experiments (V_w , L), volume of silicone (V_s , L), sampling rate (R_s , $L d^{-1}$), and exposure time of a passive sampler (t , d).

The popularity of SRs as sorptive materials has prompted numerous studies using materials of varied origin and from different suppliers, raising concerns about the variability of sorption properties [3], [10] and [11]. Some components are present in SR formulations in varying proportions, resulting in physical-chemical properties specific to each material (e.g., density, hardness, elongation) [12]. Silicone rubber manufacturing requires additional components such as a base and a crosslinking agent (silicone oils) that react by various chemical mechanisms via a catalyst (platinum cure or peroxide activated cure), and often also a filler (amorphous or modified silica, calcium carbonate, metasilicate, etc.) for mechanical strength [12]. The base and the crosslinking polymer can be pure PDMS or modified polysiloxane with some phenyl, vinyl or fluoro groups (MVQ, PMVQ or FMVQ) of various molecular weights and low functional content. The complex manufacturing process, unfortunately not disclosed by silicone suppliers, also generates non-polymerized residuals such as small polymer chains (oligomers) and other impurities [13].

However, only few studies have investigated the impact of this diversity on the sorption of organic compounds [10], [11] and [14]. Rusina et al. [11] showed that differences in $\log K_{sw}$ values for several SRs reached 0.4 log units for four PAHs ($\log K_{ow}$ from 3.37 to 6.86), and noted that the presence of fluorinated groups resulted in slightly lower K_{sw} values. Ter Laak et al. [14] studied the uptake of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) ($\log K_{ow}$ 4.70–8.30) in PDMS fiber (SPME) and PDMS sheets, and found better performance for PDMS sheet, 0.21 ± 0.08 log units higher for the silicone-water partition coefficient. Yates et al. [15] and Smedes et al. [10] used a co-solvent method with methanol to determine the K_{sw} of PAHs and PCBs on SRs obtained from different suppliers, and showed different correlations between $\log K_{ow}$ and $\log K_{sw}$ for these two kinds of compounds. These results suggest that polymer-water partitioning is not driven exclusively by hydrophobic interactions, but also by compound-specific interactions with the polymer phase (electron-acceptor/donor characteristics of both) [10] and the free volume theory describing diffusion in polymers (size of the compound) [16]. Smedes et al. [10] also found that differences in $\log K_{sw}$ from different suppliers ranged from 0.16 to 0.58 and might differ by a constant SR-specific factor for PAHs and PCBs. These studies focused on the uptake of several specific classes of hydrophobic compounds with high affinity for SR, but

sorption of less hydrophobic compounds with $\log K_{ow} < 3-4$, such as pesticides, have been less thoroughly investigated, owing to lower affinity for SR material. Heterogeneity in chemical structures and properties of pesticides could also lead to greater differences than in previous studies on hydrophobic compounds in relation with SR material.

In this context, we investigated the sorption of pesticides over a broad polarity range by several SRs to select the best one for passive sampling in aquatic environments. Other economic factors and ease of applicability by laboratories were considered in the selection. The impact of SR formulation was tested using SRs from various suppliers, covering a broad diversity of silicone materials with different curing reactions, formulations and fields of application. We also highlighted the differences in material structure of the selected SRs by analyzing their functional groups, oligomer content and thermal resistivity. We performed batch kinetic experiments to determine experimental extraction recovery as an evaluation criterion for pesticide uptake capacity. We then measured pesticide partition coefficients K_{sw} , poorly documented in the literature, for the selected SR with a sorption isotherm in five experiments. Finally, these data were related to their $\log K_{ow}$ values with relevant literature studies for various classes of organic compounds to enable a wider use of SR as a sorptive material.

Materials and methods

2.1. Experimental section

2.1.1. Chemicals

The 23 pesticides selected, including two metabolites, covering a broad polarity range ($-0.06 < \log K_{ow} < 5.51$), are listed in [Table 1](#). Pesticides and one internal standard (diuron-d6) were purchased from Dr Ehrenstorfer (Augsburg, Germany) and Sigma Aldrich (Saint-Quentin Fallavier, France). Acetone and dichloromethane for pesticide residue analysis, UHPLC grade acetonitrile and methanol were purchased from Biosolve (Dieuze, France). LC-MS grade formic acid (purity 98%) was supplied by Fischer Scientific (Illkirch, France). Ultrapure water was obtained using a Millipore water purification system equipped with an LC-Pak cartridge to remove remaining organic contaminants present in trace amounts (Billerica, MA, USA). Nitrogen gas (purity 99.995%) used for thermal decontamination was purchased from Air Liquide (Juhem, France).

Table 1. List of selected pesticides and LOQ obtained by UHPLC-MS/MS analysis.

Pesticide	Abbreviation	Log K_{ow} ^a	LOQ ($\mu\text{g L}^{-1}$) ^b
Acetochlor	ATC	4.14	0.40
Atrazine	ATZ	2.70	0.10
Azoxystrobin	AZS	2.50	0.020
Carbendazim	CBZ	1.50	0.020
Chlorfenvinphos	CFV	3.80	0.16
Chlorpiryphos-ethyl	CPE	4.70	0.40
Chlorpiryphos-methyl	CPM	4.00	0.40
Chlortoluron	CTU	2.50	0.40
3,4-Dichloroaniline	DCA	2.69	0.40
3-(3,4-Dichlorophenyl)-1-methylurea	DCPMU	2.31*	0.16
Diflufenican	DFE	4.2	0.40
Diuron	DIU	2.87	0.40
Dimethomorph	DMM	2.68	0.16
Flazasulfuron	FLZ	-0.06	0.20
Fenitrothion	FNT	3.32	4.0
Isoproturon	IPU	2.50	0.16
Linuron	LINU	3.00	0.16
Metolachlor	MTC	3.40	0.040
Norflurazon	NFZ	2.45	0.40
Procymidon	PCM	3.30	1.6
Simazine	SMZ	2.30	0.020
Spiroxamine	SPX	5.51*	0.16
Tebuconazole	TBZ	3.70	0.16

^aUniversity of Hertfordshire, Pesticide Properties DataBase:<http://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm>^bLimit of quantification determined for direct analysis by UHPLC-MS/MS in Evian® water* Predicted by ChemAxon: <http://www.chemicalize.org/structure>

2.1.2. Selection of silicone rubber materials and conditioning steps

The most widely used SR, commercialized by Gerstel under the name Twister® (TW) for analytical SBSE and recently used as a passive sampler (MESCO/Passive SBSE), was taken as a reference SR in this study. Six other SRs were selected to cover the diversity of silicone rubber formulations (Table 2). They were purchased from different manufacturers, either as silicone oils (“Polymerized SR kits”: one-component or two-component kits ready for polymerization) or as SR already polymerized by the manufacturer (“Manufactured SRs”). For “Polymerized SR kits”, we followed the suppliers’ instructions to produce polymerized sheets of SR approximately 3 mm thick in plastic Petri dishes, with heat for SY, ultraviolet light for UV and water for SB to initiate cross-linking. Five of the selected SRs had already been studied as extractive materials: TW [9] and SL [3] for water extraction in the laboratory;

AL, ST and SL for passive sampling of hydrophobic compounds (organochlorine pesticides, PAHs, PCBs [2] and [5]), and SY for passive sampling of pesticides [17].

To facilitate the comparison of SRs, raw materials from different suppliers were shaped into closely similar volumes. Silicone sheets were cut with a clean cutter blade into rectangular cuboids measuring approximately 20×3×3 mm, and silicone thread into rods 20×3 mm. Twister® was purchased in 20×1 mm thick PDMS film ($V=126 \mu\text{L}$), and the magnetic stirring bar was removed before use. Rectangular cuboid SR samples were selected by weight ($170 \text{ mg} \pm 2.5\%$), and their exact volume was then calculated from their density (Table 2). Before use, SRs were cleaned by chemical and thermal conditioning to eliminate most residues, such as oligomers that can interfere with the instrumental analysis (particularly for thermodesorption (TD)-GC/MS analysis). First, SRs were chemically conditioned in a solvent mixture (dichloromethane: methanol, 50:50, v/v) under sonication for 15 min. Pieces of SRs were then wiped with lint-free tissue and dried at 70 °C for 1 h. Lastly, SRs were thermally treated in a Gerstel tube conditioner TC (Mülheim a/d Ruhr, Germany) under a nitrogen stream of 75 mL min^{-1} with a temperature ramp of 10 °C min^{-1} to 300 °C for 6 h.

Table 2. Main properties of the selected silicone rubbers (SRs)

Material (other name)	Abbreviation	Supplier (Country)	Application field	Supplier formulation	Shape (thickness or size)	Density (rod volume)	Curing reaction ^a (filler)
Sylgard®184	SY	Dow Corning (USA)	Electronics	Polymerized SR kits (two components)	Sheet (3 mm)	1.03 ^a (165 µL)	Hydrosilylation (Vinyl modified silica)
X-34-4184	UV	Shin Etsu (Japan)	Industrial	Polymerized SR kits (two components)	Sheet (3 mm)	1.03 ^a (165 µL)	Hydrosilylation (Not specified)
SILBIONE®MED ADH 4300 RTV	SB	Bluestar Silicones (USA)	Medical	Polymerized SR kits (one component)	Sheet (3 mm)	1.08 ^a (157 µL)	Condensation (Silica amorphous and/or treated)
Twister®	TW	Gerstel (Germany)	Analytical	Manufactured SRs	Stir bar (20 × 1 mm)	1.37 ^b (126 µL)	Not specified (Not specified)
Altessil® (Versilic® S60V34B)	AL	Altec (UK)	Laboratory	Manufactured SRs	Sheet (3 mm)	1.20 ^a (142 µL)	Peroxide-cured (Mineral fillers)
Silastic/Silopren	SL	Goodfellow (UK)	Industrial	Manufactured SRs	Thread/rod (3 mm)	1.20 ^b (133 µL)	Not specified (Some chalk)
SIL-TEC® (SILASTIC® BioMEDical Grade LSR)	ST	Technical Products (USA)	Medical	Manufactured SRs	Sheet (3 mm)	1.20 ^a (142 µL)	Hydrosilylation (Silica)

^a Information was collected from producers and/or internet sources

^b Experimental values by ratio of weight measured and theoretical volume ($n = 3, s = 0.05$)

2.1.3. Kinetic study

A kinetic study of the selected SRs was performed to compare extraction recoveries, and determine the equilibrium time of the 23 pesticides. One piece of each SR was inserted into a 60 mL amber glass vial containing 50 mL of Evian® water spiked with the pesticides studied (pH=7.2). Acetone content, for water spiking, was calculated so as not to exceed 0.1 vol% in the aqueous phase. The initial spiked concentration of each pesticide was adjusted from $0.4 \mu\text{g L}^{-1}$ to $15 \mu\text{g L}^{-1}$, depending on the analytical limit of quantification ([Table 1](#)), and affinity with SR materials already reported with SBSE in water sample laboratory extraction [[18](#)]. Stirring (800 rpm) was done with a glass magnetic stir bar on a Variomag magnetic stirrer purchased from Thermo (Waltham, MA, USA). The experiment ran for 48 h in batches with one piece of SR for each sampling point at 15 min, 1 h, 3 h (triplicate), 8 h, 24 h (triplicate) and 48 h, with seven experimental blanks without pesticides and three control batches without SR.

The extraction recovery is expressed as the ratio of the mass of analyte in the SR phase (m_s) to the initial mass of analyte in the water phase ($m_{w,0}$) corrected with the control batch.

For hydrophobic pesticides ($\log K_{ow} \geq 3$), m_s was computed by the difference in concentration of pesticides measured in water (C_w) between the control batch and the final state of the experiment. For hydrophilic pesticides ($\log K_{ow} < 3$), a direct determination by solvent back-extraction of the SRs (see [Section 2.2.2](#)) was preferred. For hydrophilic pesticides, differences in concentrations in water between initial and final states were too low to determine extraction recovery, resulting in high uncertainties in final results.

2.1.4. Partition coefficients

Following on from the kinetic study, we investigated sorption capacity of the preferred SR, SL, and TW as reference material ([Table 2](#)). With this aim, partition coefficients (K_{sw}) were calculated in an isothermal experiment with five levels of concentration (C1, C5, C10, C25 and C50) expressed relative to C1. Initial spiked concentrations were adjusted for each pesticide to allow a quantitative analysis of concentration in equilibrium conditions: C1 concentration level corresponded to spiking at $0.5 \mu\text{g L}^{-1}$, for pesticides with $\log K_{ow} < 3$ and at $10 \mu\text{g L}^{-1}$ for those with a higher $\log K_{ow}$. Like in the kinetic study, batch experiments were performed in triplicate, at an ambient temperature of 20.5 °C with an equilibrium time of 48 h. Partition coefficients were calculated as the slope of the unweighted linear regression of analyte concentration in SR ($C_{s, eq}$ in $\mu\text{g L}^{-1}$) plotted against concentration of pesticides in

water in batches ($C_{w,eq}$ in $\mu\text{g L}^{-1}$) at equilibrium. Linear regressions were also performed with errors in x and y axes by the Williamson-York bivariate method (in a Microsoft Excel spreadsheet adapted from Cantrell [19]). Linear regressions were forced through the origin, for non-detection of pesticides in SR blanks. The errors in x and y were specified as a confidence interval ($\alpha=0.05$, $n=3$) taking into account uncertainties of SR and water volumes for each experimental point. Slope uncertainty ($u(K_{sw})$) was also expressed as a confidence interval.

2.2. Analytical methods

2.2.1. Physical-chemical properties of silicone rubbers

To explain similarity or differences in the pesticide sorption properties of the SRs studied, we investigated the silicone chemical structure of raw SRs by infrared spectroscopy. Attenuated Total Reflectance spectroscopy (ATR-FTIR) is a rapid and easy technique for the identification of organic groups in cured organosilicon materials [13]. A spectrum Two with UATR accessory (Single Reflection Diamond) from Perkin Elmer (Roissy-en-France, France) was used with a resolution of 4 cm^{-1} and 16 acquisitions per spectrum in the range $4000\text{--}520\text{ cm}^{-1}$. Thermal gravimetric analysis (TGA) was carried out to obtain the residual content of SRs (expressed in %) at high temperature and to determine the SR degradation temperature on raw and conditioned materials. First, TGAs were performed on a TA Instruments Q50 (New Castle, USA) under nitrogen and air stream up to $800\text{ }^{\circ}\text{C}$ (90 mL min^{-1} and $50\text{ }^{\circ}\text{C min}^{-1}$), maintaining the target temperature for 30 min. Second, TGAs were performed under a helium stream of 45 mL min^{-1} with a temperature ramp of $10\text{ }^{\circ}\text{C min}^{-1}$ up to $500\text{ }^{\circ}\text{C}$ (raw and conditioned SRs). The release of residual oligomers by chemical and thermal conditioning steps of SRs was also estimated by measuring weight loss between raw material mass and conditioned SR. Scan chromatograms were also acquired by TD-GC/MS analysis in full scan mode (TD: $300\text{ }^{\circ}\text{C}$, 15 min, helium at 75 mL min^{-1}), as detailed in Assoumani et al. [20], to identify some oligomers and validate the usefulness of the conditioning steps.

2.2.2. Pesticide solvent back-extraction and sample preparation

Pesticides were desorbed from SRs by chemical extraction according to the protocol developed by Margoum et al. [18] for SBSE application. To compare SRs, optimization of the solvent back-extraction step was not required. Briefly, silicone rods were removed with clean tweezers from water, cleaned with ultrapure water and dried with a lint-free tissue. After

storage for at least 24 h at $-18\text{ }^{\circ}\text{C}$, SRs were desorbed with 200 μL of methanol/acetonitrile (50:50, v/v) in a 250 μL flat-bottom glass insert under sonication in an ultrasonic bath (FB11014, Fisher Scientific, UK) for 15 min; 150 μL of ultrapure water and 10 μL of internal standard solution (diuron-d6 at a concentration of 200 mg L^{-1}) in acetone were then added to 40 μL of the desorbate to make up the extracted sample for analysis. Four steps of solvent back-extraction on the same silicone rod confirmed that the proportion of hydrophilic pesticides ($\log K_{ow} < 3$) extracted with the first step exceeded 80% (SI-1) and was not statistically different from 100% (Student *t*-test, $n=3$, $CL=95\%$). For experiments, analysis of water samples was performed by direct injection. A volume of 10 μL of diuron-d6 at a concentration of 1000 mg L^{-1} was added to 990 μL of an aliquot of water to obtain a concentration of diuron-d6 of $10\text{ }\mu\text{g L}^{-1}$ as for SR extract analysis.

2.2.3. Analysis by liquid chromatography

Ultra-high-performance liquid chromatography (UHPLC) was performed on a Shimadzu series Nexera X2 UHPLC system (Marne-la-Vallée, France). Analytes were separated on an Acquity UPLC® HSS T3 $1.8\text{ }\mu\text{m}$ $2.1\times 100\text{ mm}$ column. Chromatographic separation of analytes was carried out with acetonitrile and ultrapure water, both with formic acid (0.1%) in an analytical gradient (from 10% to 90% acetonitrile) lasting 15 min at 0.4 mL min^{-1} . The UHPLC system was coupled to a triple-quadrupole mass spectrometer (MS/MS) API 4000 from AB Sciex (Les Ulis, France). The electrospray ion source (Turbo-Ionspray from AB Sciex) was set to positive mode at $600\text{ }^{\circ}\text{C}$. Quantification was performed with deuterated diuron-d6, used as injection internal standard. Settings for MS/MS analysis (SI-2) were from Margoum et al. [18] with additional pesticides optimized and validated later.

3. Results and discussion

3.1. Silicone rubber characteristics

The main readily available macroscopic SR parameter is density, which generally ranges from 1.05 to 1.60 [13]. In the data shown in Table 2, the densities of “Polymerized SR kits” sheets (SB, SY and UV) were lower than those of “Manufactured SRs” by 0.2 units. A higher density of SR reflects an increase in cross-link density or silica filler content, or substitution of methyl groups by other functional groups [12]. To our knowledge, few SRs with densities lower than 1.15 have been tested for compound sorption in water [10] and [11], but the density was not always known.

TGA at 800 °C under nitrogen ranked the SRs from lowest to highest content: SB(17.3%)>AL(31.0%)>TW(32.5%)>SL(35.5%)>SY(51.0%)>UV(60.4%)>ST(76.3%).

More abundant residues could not be directly linked to higher filler content owing to the complex thermal degradation of crosslinked PDMS [21]. The equivalent final amount of residues and the similar nitrogen/air ratio (SY and UV \approx 0.90 and TW, AL and SL \approx 0.75) observed between SRs can be explained by their similar components and formulations.

The amount of oligomers eliminated by the conditioning steps was also studied to highlight differences in SR formulations. The mean weight loss recorded for the SRs studied after chemical and thermal conditioning was 3.2%. The SRs could be ranked from highest to lowest release of residues: SY(5.5%)>UV(3.9%)>SB(3.5%)>ST(3.5%)>SL(2.5%)>AL(1.9%)>TW(1.9%). The amounts of residues released by chemical and thermal conditioning were similar to those obtained by Rusina et al. [11], ranging from 2 to 4.2% with ethyl acetate and shaking (3 days) followed by Soxhlet extraction with the same solvent for a further 3 days. This loss could be attributed to the release of small residue molecules (oligomers) from raw polymers or residues from thermal degradation of cross-linked PDMS chains. PDMS undergoes thermal rearrangement at high temperature (250–350 °C) with cleavage of the siloxane chains to form products that are predominantly cyclic siloxanes of low molecular weight [21]. These results were completed by the analysis of chemical organic groups of the SR backbone by ATR-FTIR (SI-3), and TGA analysis of SY and SL after each conditioning step (SI-4). We concluded that “Polymerized SR kits” contained higher amounts of residues than “Manufactured SRs”, owing to a non-stoichiometric ratio in the curing process. These findings also demonstrate the efficiency of our selected conditioning steps for eliminating residuals in SRs. Additional investigation of the nature of residues in SRs by TD-GC/MS analysis is reported in SI-6. Mainly cyclic PDMS chains were found from cycloterasiloxane (octamethyl-), (M=296.6 Da) to cyclodecasiloxane (eicosamethyl-) (M=741.5 Da), and small linear PDMS chains (approximately 500 Da) with seven and eight dimethyl siloxane groups. These results agree with those of Lykissa et al. [22], who identified the main oligomers released in SRs as cyclic PDMS of 200–1500 Da, along with smaller amounts of linear PDMS of 500–1500 Da.

3.2. Kinetic study and determination of extraction recoveries

No pesticide degradation or adsorption was observed for the control batch during the 48 h of experimentation, except for PCM, with a mean decrease in concentration of 50%. The

half-time of hydrolysis in water of PCM is about 25 days (University of Hertfordshire, Pesticide Properties DataBase), so this decrease was probably due to adsorption on glass in the experimental system. The most hydrophilic pesticide studied, FLZ ($\log K_{ow} = -0.06$), was not sorbed in any of the SRs studied; no data are therefore presented for this compound. Repeatability of results between batches tested at 3 h and 24 h, expressed as RSD ($n=3$), was less than 15% for every SR.

For all the compounds, a first-order kinetic model of accumulation [9] was applied according to the SBSE theory, and a satisfactory correlation coefficient was obtained ($r > 0.87$). For hydrophobic pesticides, the mass of pesticides sorbed remained stable after 24 h, as shown for DFF (Fig. 1a). For hydrophilic compounds, such as SMZ (Fig. 1b), equilibrium was reached more slowly (after 24–48 h). Uptake of hydrophilic compounds in SRs was lower in mass, consistent with the lower affinity for the SR phase. Differences between SRs in the uptake kinetics of hydrophilic compounds could be due to variations in the volume or apparent surface area of each silicone rod. The surface area of silicone rods can affect uptake kinetics but not equilibrium state. Different polymer diffusion coefficients can also influence kinetic parameters. Considering SR as an absorbent material [14], a strict comparison and selection of the best SR was required to normalize extraction recoveries to the same volume for all SRs.

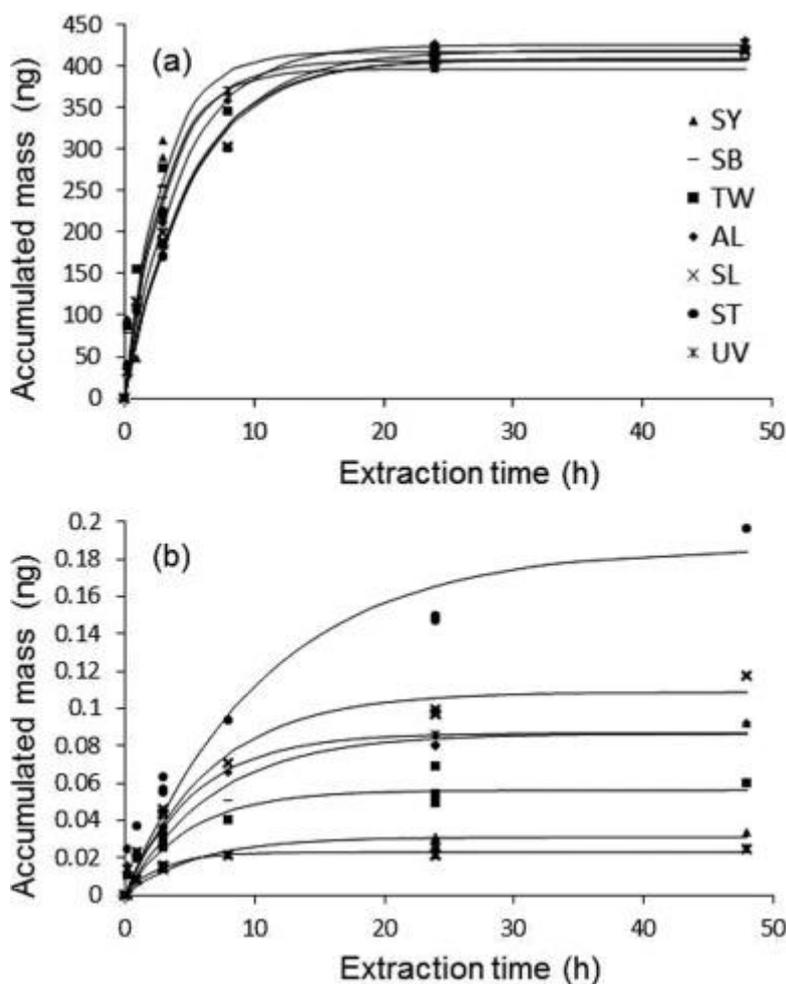


Fig. 1. Uptake kinetics of (a) diflufenican (DFE, $\log K_{ow}=4.2$) and (b) simazine (SMZ, $\log K_{ow}=2.3$) by studied SRs with first-order kinetic model. Triplicate at extraction time of 3 h and 24 h.

Accordingly, extraction recoveries (R), calculated at 24 h ($n=3$), were normalized to a volume of 150 μL (mean volume, V_{NS}) of SR based on Eq. (1), to give a new criterion R_{NV} (extraction recovery normalized by volume) using Eq. (3).

$$R_{NV} = \frac{R \frac{V_W}{V_S}}{R \frac{V_W}{V_S} + (1-R) \frac{V_W}{V_{NS}}} \quad (\text{Eq. 3})$$

The normalized R_{NV} took into account uncertainties in SR volume (2.5% for weight measurement and 5% for density). Overall, for all the SRs, pesticides with $\log K_{ow} \geq 3$ had higher affinities, with $R_{NV} > 20\%$ (Fig. 2), in line with chemical properties of SRs [3] and [9]. However, the high affinity of AZS ($\log K_{ow}=2.5$, $R_{NV}=17\%$) toward SRs could be explained by stronger interactions with SRs, related to specific molecular structure and properties.

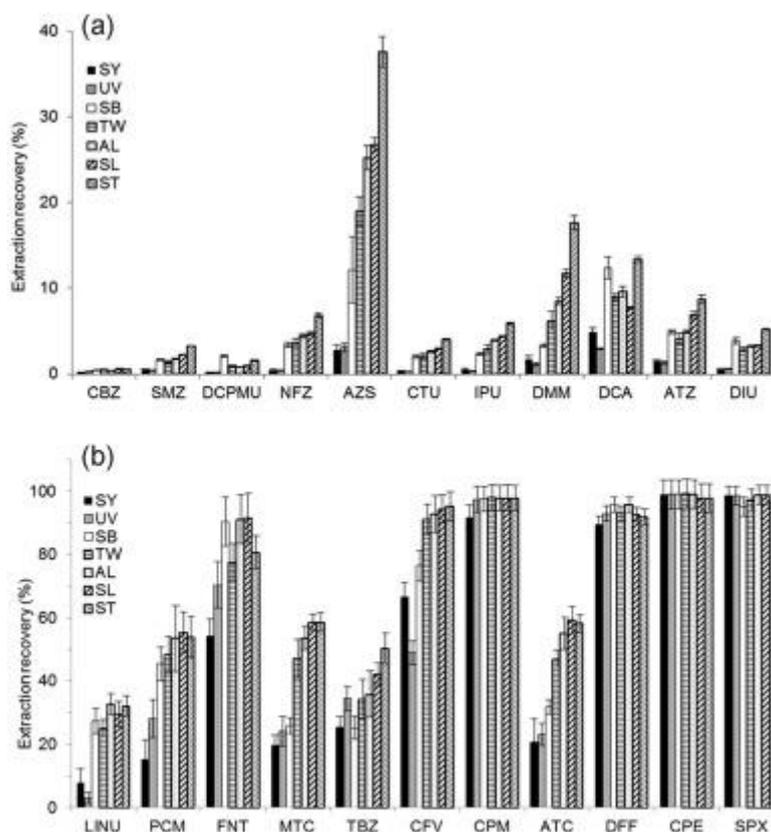


Fig. 2. Extraction recoveries of studied pesticides on selected SRs normalized to volume of 150 μL (R_{NV}) after 24 h. Pesticides were ranked in ascending order of $\log K_{ow}$ with $\log K_{ow} < 3$ (a) and $\log K_{ow} \geq 3$ (b). Error expressed as standard deviation ($n=3$).

3.3. Comparison of sorption capacities and selection of the best SR

The extraction recovery normalized by volume, R_{NV} , was used as a discriminating criterion for comparison of SR sorption capacities for pesticides. One-way ANOVA (ANalysis Of VAriance) with a *post hoc* Tukey HSD (Honest Significant Differences) (XLStat software, 2015.4.1) was used to find SRs that were significantly different from each other, for each pesticide. Four pesticides (CPE, CPM, DFF and SPX) showed no significantly different extraction recoveries for the SRs studied. During the experiment, pesticide concentrations in water after 24 h lay below the limit of quantification (LOQ) (Table 1) in three cases (CPM, CPE and SPX). Consequently, differences in extraction recoveries, all near 100%, could not be deduced from the experimental data. Significant differences between the different types of SRs were found for the other 19 pesticides, as illustrated by CFV, with R_{NV} ranging from 49% to 95% depending on the SR (Fig. 2). To our knowledge, this is the first time that such differences in sorption have been demonstrated between different formulations of SR for a broad range of pesticides. The earlier study of Rusina et al. [11], which compared sorption of PAHs and PCBs by several SRs, found differences in $\log K_{sw}$ below 0.4 log units

(corresponding to an R_{NV} variation of 10% according to Eq. (1) and approximation for CFV of $\log K_{sw} \approx \log K_{ow} = 3.8$).

A principal component analysis (PCA) ($\alpha=0.05$) was performed to discriminate SRs ($n=7$) by extraction recoveries of relevant pesticides ($n=19$) (Fig. 3). The F1 and F2 axes explained respectively 82.9% and 9.2% of the data variability. The 19 variables were mainly positively linked to the F1 axis, which represents the mean value of extraction recoveries for each SR. Some pesticides were correlated positively (DCPMU) or negatively (TBZ) to the F2 axis, reflecting a special affinity of the silicone rubber SB for these compounds. Graphical representation of observations discriminated SRs mainly with regard to the F1 axis. The seven SRs investigated fell into three groups. SY and UV had very similar coordinates on the F1 and F2 axes, and showed the lowest pesticide sorption properties. For SB, we observed a medium affinity for pesticides, with the narrowest range of extraction recoveries. The last group presented the highest sorption properties for pesticides, with increasing effect on F1 axis: ST > SL > AL > TW, and similar F2 coordinates. These groups of SRs were the same as those obtained with the ratio of final residues (TGA under nitrogen and air, see results in SI-5), which identified similar components and formulation of SRs, with the exception of ST, which had a higher sorption capacity for pesticides than SL, AL and TW, and a higher final amount of residues than the other SRs. These results demonstrate that “Polymerized SR kits” (SY, UV and SB) were significantly less efficient for pesticide extraction than “Manufactured SRs” (AL, SL, ST, TW). This difference can be attributed to differences in formulation of the SRs, observed with ATR-FTIR spectroscopy (SI-3), showing a more complex internal network of PDMS chains in “Polymerized SR kits”. Macroscopically, the differences seem to result from lower SR densities (Table 2). Specific behavior of SB, compared with SY and UV, could be attributed to different cross-linking reactions (condensation vs. hydrosilylation). These conclusions are supported by the observations of Ter Laak et al. [14], who suggested that differences in SR formulations, such as cross-linking and polymer length, might modify the solubility of the chemicals in the SR, and thus modify K_{sw} . An accurate understanding of SR sorption differences for pesticides would require further data on the formulation of the different SRs tested, unfortunately not disclosed by manufacturers. This point was not taken further in this study.

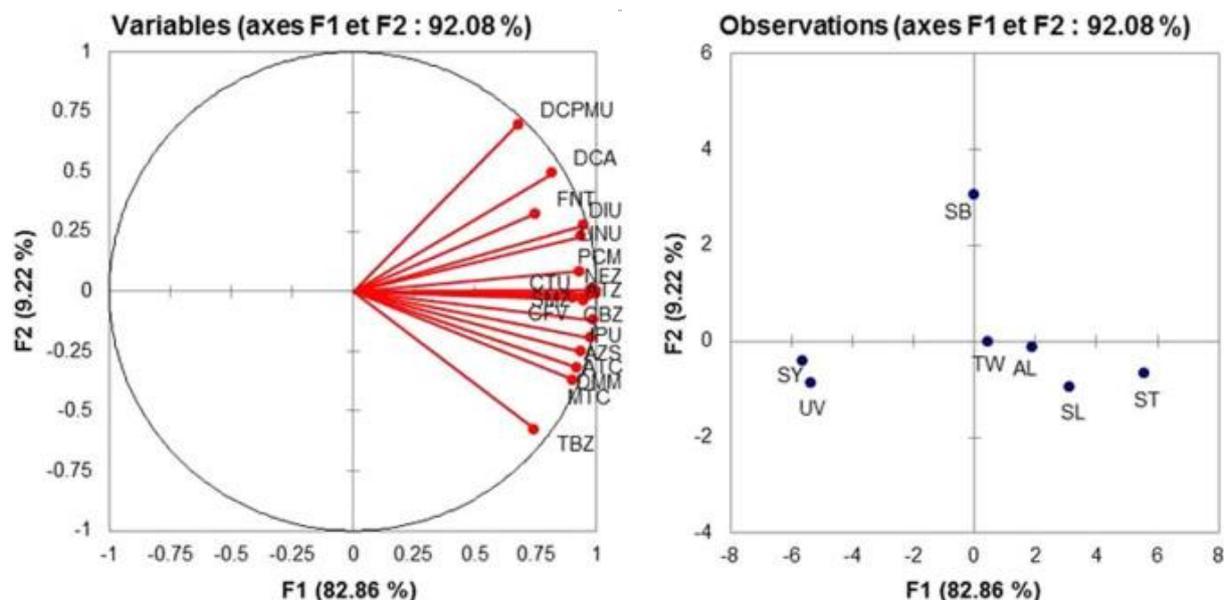


Fig. 3. Comparison of SRs sorption properties for pesticides with PCA analysis (variables=19, individuals=7).

Using the results of the comparison of SR sorption capacities for pesticides, we then chose an SR from the group of “Manufactured SRs” with the best sorption properties for pesticides. Additional variables such as cost, commercial availability, available shapes (rods, sheets, etc.) and results of previous studies, were also taken into account. The production of AL was recently discontinued by the manufacturer. We selected the SR called SL (Table 2). This SR was also the one previously chosen to replace commercial Twister® in a MESCO passive sampler [23]. Further investigation is needed for other hydrophobic compounds to replace AL (no longer available) by SL.

3.4. Partition coefficients

To use SL as an extractive material for laboratory applications or as a passive sampler, the K_{sw} of pesticides with SL and TW (as reference) were assessed by an isothermal experiment at five concentration levels. In this experiment, the mass balance of control batches (i.e. without SR) was verified for the five spiked levels with all the pesticides, except for PCM (owing to its adsorption, see 3.2) and for DFF for the two highest spiked levels, because the initial water concentrations (see 2.1.4) exceeded solubility in water for this compound ($50 \mu\text{g L}^{-1}$ at 20°C).

Linear sorption isotherms were obtained for 13 pesticides (ATZ, CBZ, CPE, DCA, DCPMU, DFF, DIU, IPU, NFZ, SMZ and SPX) with a satisfactory correlation ($r^2 > 0.95$) (all sorption isotherms are available in SI-7) as predicted by absorption theory [14]. However, sorption isotherms of 10 other pesticides (ATC, AZS, CFV, CPM, CTU, DMM, FNT, LINU,

MTC, and TBZ) deviated from linear to curvilinear sorption isotherms at high concentration levels (C25 and C50). Equilibrium state at 48 h for C50 level was confirmed by further kinetic experiments over one week. Thus the Freundlich empirical model was applied for these compounds $C_s = K_F C_w^{1/n}$ (Eq. (3)), with K_F and n dimensionless Freundlich parameters.

These curvilinear sorption isotherms conflict with linear absorption isotherms generally accepted for SR with hydrophobic compounds [3]. This can be explained by double sorption mechanisms: absorption in the PDMS bulk, and adsorption onto other SR constituents such as amorphous or treated silica used as filler. In such adsorbent material, competition for pesticide adsorption can occur, and the material can be saturated, these two processes leading to a curvilinear sorption isotherm [24].

Sorption isotherms at low concentrations tested in our batch experiments, C1, C5 and C10 ($0.5 \mu\text{g L}^{-1}$ to $100 \mu\text{g L}^{-1}$), are the most relevant part of SR sorption isotherms, as these concentrations lie in the range of those generally found in environmental waters and assessed by passive sampling. Partition coefficients (K_{sw}) with SL silicone rubbers could thus be deduced satisfactorily for all the pesticides studied by a linear regression over the whole concentration range with the Williamson-York bivariate method, which gives more weight to low concentration levels due to reduced experimental errors (SI-7).

We compared K_{sw} values determined for SL to those of TW determined in the same experimental conditions. A linear correlation was found, described by $\log K_{sw}(\text{SL}) = 0.93 \log K_{sw}(\text{TW}) + 0.44$ ($r^2 = 0.96$). Thus, SL showed better extraction properties than TW, with an increase of 0.44 $\log K_{sw}$ unit for the pesticides. This difference between SRs was in line with the conclusions of Smedes et al. [10], who suggested a constant difference factor (from 0.16 to 0.58 \log unit) for SR from five different suppliers with PAHs and PCB. These results also confirm previous conclusions drawn from sorption capacity comparisons (SL > TW) as demonstrated by PCA analysis (Fig. 3).

3.5. Correlation between $\log K_{sw}$ and $\log K_{ow}$

As shown by other authors [25], the estimation of K_{sw} as a function of the polarity of organic compounds, expressed as K_{ow} , is expected to follow a linear correlation. We therefore compiled K_{sw} and K_{ow} from various compound families and SRs (only “Manufactured SRs”) obtained by laboratory studies in the literature (anilines: this study (DCA) and [25]; chlorobenzenes: [25]; PAHs: [10], [15], [25] and [26]; PCBs: [10], [14], [15], [25] and [26]; pharmaceuticals: [27] and [28]; phenols: [25]; pesticides: this study and [25], [28] and [29])

(Fig. 4). Data with $\log K_{ow} > 3.5$ (chlorobenzenes, PAHs, PCBs and pesticides) are well represented in numerous studies, whereas data for more hydrophilic compounds (anilines, pesticides, pharmaceuticals and phenols) come from few studies. Previously studied pesticides were mainly organochlorine pesticides ($n=30$) with $\log K_{ow} > 3$ from Hestley [29] with “Virgin PDMS” ($d \approx 1$, Diversified Silicone Products Inc.); and a few polar pesticides from Kwon et al. [25] ($n = 5$), with medical grade SR ($d=1.17$, Specialty Silicone Products), and from Magner et al. [28] ($n=5$) with SR tubing (unknown density, Noax Lab). Recent work on passive sampling of 124 pesticides using SR in river water [30] was not taken into account in this study because uptake kinetic of pesticides were insufficiently described (four points in an experiment over 25 days) and highly variable over time (no confirmation of the equilibrium state for several compounds). Thus data from our study on pesticides covering a broad range of $\log K_{ow}$ (1.50–5.51), fill an important gap in the literature, enabling wider use of SR as a sorptive material (Fig. 4).

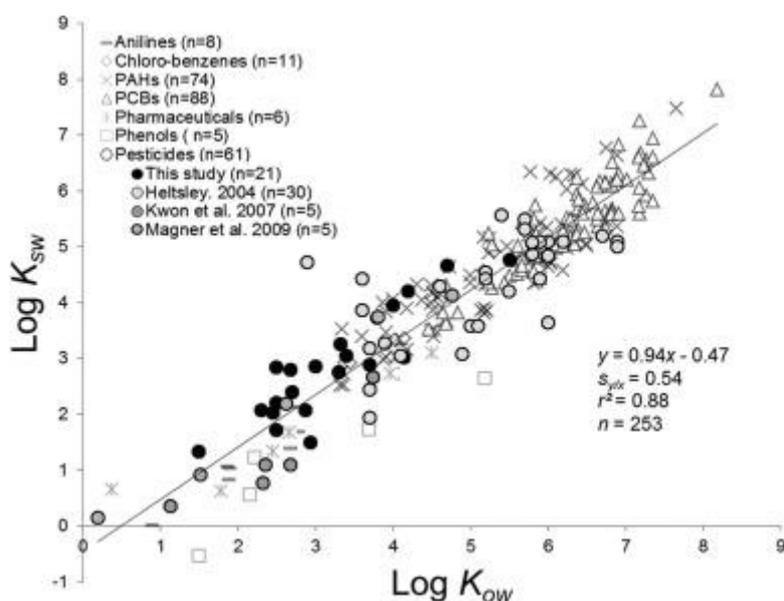


Fig. 4. Correlation between $\log K_{sw}$ and $\log K_{ow}$ from this study and literature data sorted by class of compounds: anilines (bars), chlorobenzenes (diamonds), PAHs (crosses), PCBs, (triangles), pharmaceuticals (stars), phenols (squares), and pesticides (circles colored by study).

A single linear relationship of data for all compounds ($\log K_{sw} = 0.94 \log K_{ow} - 0.47$; $n=253$; $r^2=0.88$; $s_{y/x}=0.54$) (Fig. 4), resulted in a high standard error of estimate of K_{sw} ($s_{y/x}$). This relationship extends the conclusions of Smedes et al. [10] for differences of sorption between SRs to compounds other than PAHs and PCBs. However, we restrict these conclusions to “Manufactured SRs” (i.e. polymerized by manufacturers), given the very large differences observed with “Polymerized SR kits”. A better standard error of the estimate of K_{sw} could be obtained with this linear model by restricting the diversity in the formulation of

the SRs used, and by plotting data for compounds with closely similar molecular structures. Other predictive models for K_{sw} have also been developed on PDMS fiber (SPME) data, such as multiparameter linear solvation energy relationships (LSER) [31]. However, they have not been validated on SR, and require physiochemical parameters that are not readily available.

4. Conclusion

The selection procedure used in this study discriminated seven SRs from various suppliers for the extraction of pesticides in water. We found very large differences in affinity for pesticides between “Polymerized SR kits” and “Manufactured SRs”, never demonstrated before. These differences were linked to the broad diversity of the SR formulations studied. Accordingly, partition coefficients (K_{sw}) of 21 pesticides were determined with SL to fill a gap in the literature for hydrophilic to moderately hydrophobic compounds ($1.5 < \log K_{ow} < 5.5$). $\log K_{sw}$ from this study and data from the literature plotted against $\log K_{ow}$, showed satisfactory linear correlation for the prediction of K_{sw} for non-studied compounds, with an error in the estimate of 0.54 log units. Finally, given sorption properties, literature data and other economic and technical factors, we suggest using SRs from Goodfellow (SL) in future work to reduce variability of K_{sw} values in the literature. We hope that the use of SR, as an extracting material for a wide range of organic compounds, and especially as a passive sampler, will thereby be simplified.

Acknowledgments

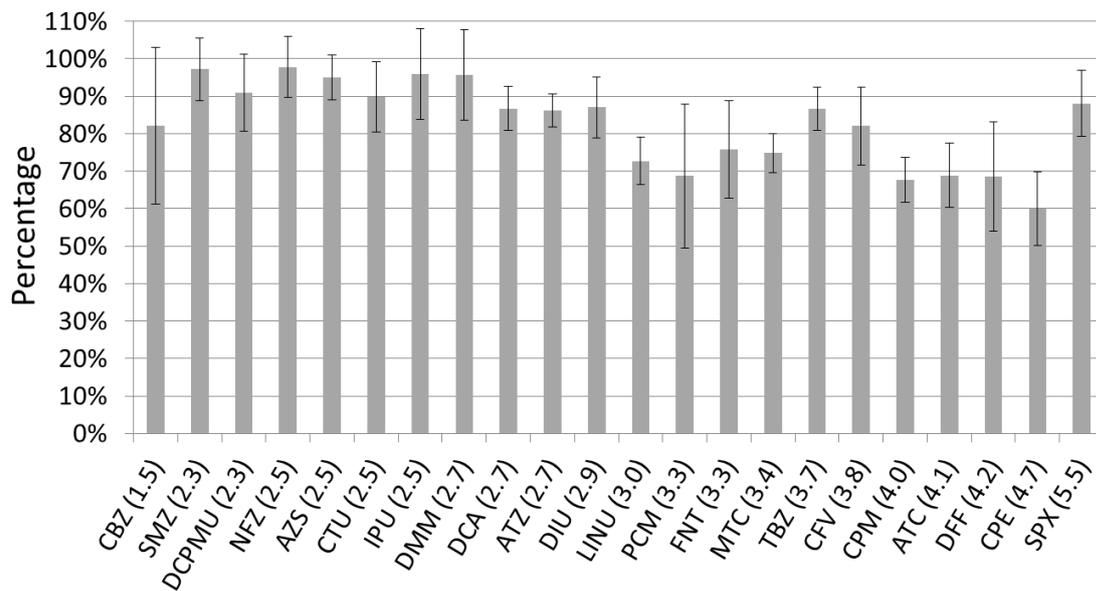
The authors thank G. Raffin and M. Hangouët (ISA, UMR 5280) for TGA analysis and interpretation, and C. Guillemain (Irstea) for analytical support. This work was funded by the French National Agency for Water and Aquatic Environments (ONEMA) and the French National Research Agency (ANR) through the PoToMAC project ([ANR 2011 CESA 022 02](#)). We thank ATT for English language editing.

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SI-1. Percentage of pesticide recovered with first solvent back-extraction step over four cumulated steps with SL in kinetic experiment (24 h) with standard deviation ($n = 3$).

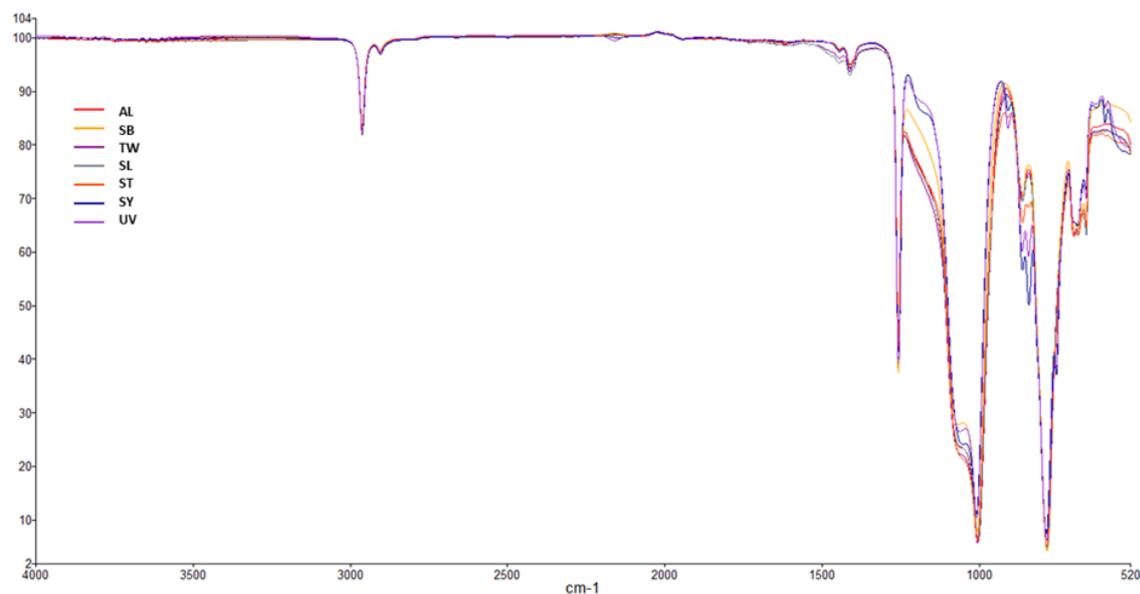


SI-2. Pesticide parameters for UHPLC-MS/MS analysis.

Pesticide	Abbreviation	Quantification transition (m/z)	Declustering potential (V)	Collision energy (V)	Collision exit potential (V)
Acetochlor	ATC	269.9>224.2;	31	15	16
		269.9>148.1	31	27	14
Atrazine	ATZ	215.9>174.1;	66	25	16
		215.9>104.1	66	41	8
Azoxystrobin	AZS	404>372;	61	33	26
		404>344	61	35	28
Carbendazim	CBZ	192>160;	56	25	16
		192>132	56	41	24
Chlorfenvinphos	CFV	359>155;	76	17	20
		359>99	76	43	8
Chlorpiryphos-ethyl	CPE	352>200;	45	30	38
		350>97	61	55	4
Chlorpiryphos-methyl	CPM	322>125;	71	29	22
		322>290	71	23	54
Chlortoluron	CTU	213>72;	51	25	12
		213>140	51	37	6
3,4-Dichloroaniline	DCA	162>127;	51	31	24
		162>74	51	73	14
3-(3,4-Dichlorophenyl)-1-methylurea	DCPM U	219>162;	66	21	26
		219>127	66	37	22
Diflufenican	DFE	395>266;	86	35	28
		395>246	86	47	40
Diuron	DIU	233>72;	46	51	6
		233>46	46	37	8
Diuron-d6	DIU-d6	239>78;	66	43	14
		233>52	66	37	10
Dimethomorph	DMM	388>301;	76	31	36
		388>165	76	43	28
Flazasulfuron	FLZ	408>182;	81	59	34
		408>227	81	57	14
Fenitrothion	FNT	278>125;	71	29	22
		278>109	71	25	16
Isoproturon	IPU	207>72;	51	37	8
		207>165	51	19	28
Linuron	LINU	249>160;	61	25	32
		249>182	61	19	12
Metolachlor	MTC	284.1>252.2;	46	21	20
		284.1>176.2	46	37	4
Norflurazon	NFZ	304>284;	101	35	26
		304>88	101	61	16
Procymidon	PCM	284>256	76	25	46
Simazine	SMZ	202.1>132.2;	56	29	10
		202.1>124.1	56	27	10
Spiroxamine	SPX	298>144;	51	31	8
		298>100	51	45	18
Tebuconazole	TBZ	308>70;	76	51	12
		308>125	76	57	12

SI-3. Attenuated Total Reflection Fourier Transform Infrared Spectroscopy

(ATR-FTIR) spectrum of silicone rubbers (SRs) studied and interpretation (color printing).

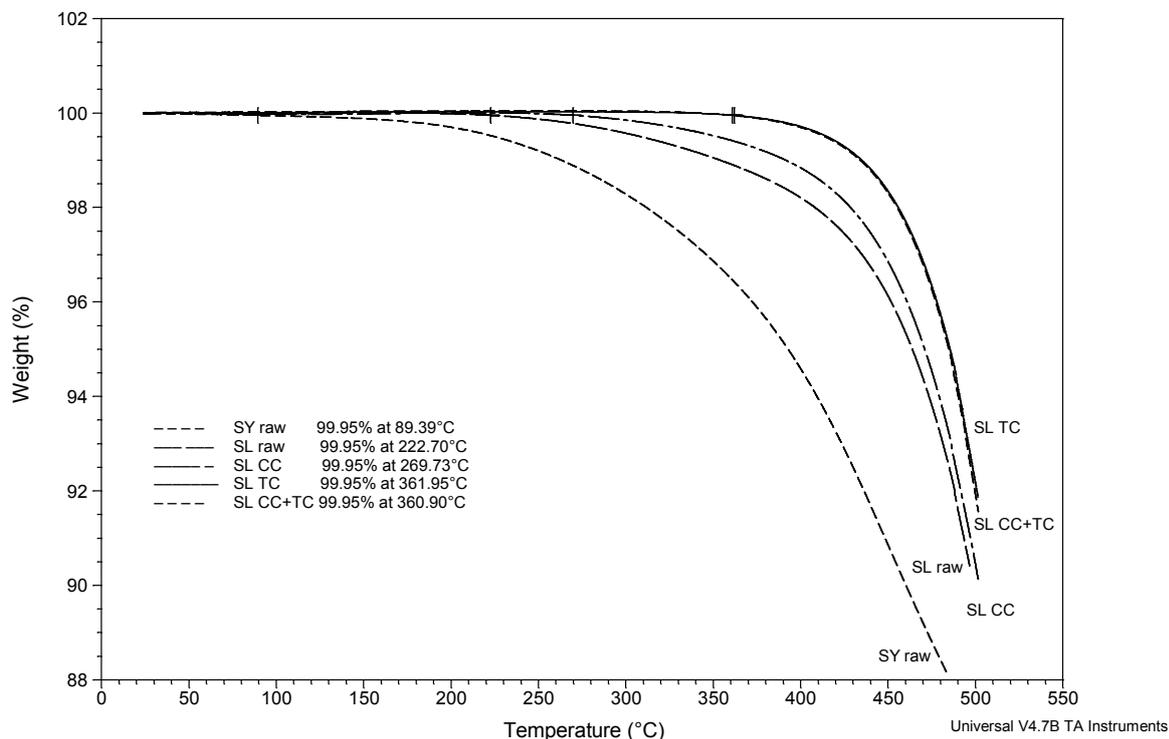


Chemical organic groups of the SR backbone were studied by interpreting ATR-FTIR spectra for each SR. The characteristic band for symmetrical CH_3 deformation occurs at 1260 cm^{-1} (with one or more in the range $865\text{--}750 \text{ cm}^{-1}$) and with CH stretching absorption around 2910 and 2970 cm^{-1} for all the SRs, confirming methyl groups are the main components identified in PDMS chains of SRs (Lipp and Lee Smith, 1991; Launer, 2013). Although infrared spectra are largely similar between SRs, there are some differences. For example, when the characteristic weak band of dimethyl units shifts from 860 cm^{-1} to 845 cm^{-1} , as observed for SY and UV, units on siloxane chains are random or alternating, and not block (Launer, 2013). We also observe a broader and more complex Si-O-Si absorption ($1130\text{--}1000 \text{ cm}^{-1}$), showing two overlapping bands, especially for SB, SY and UV, which highlights longer or more branched siloxane chains. Hence SY, SB and UV have more complex internal networks of PDMS chains than other SRs. In addition, for SY and UV SRs, a weak band in the range $2100\text{--}2300 \text{ cm}^{-1}$ and at 910 cm^{-1} confirm a residual content of reactive Si-H groups for raw materials, confirming a non-stoichiometric ratio for the curing process by hydrosilylation. No other functional groups such as phenyl or vinyl are clearly identified with this analytical technique.

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SI-4. Thermal gravimetric analysis (TGA) of silicone rubbers SY and SL for raw and conditioned materials (CC: chemical conditioning and TC: thermal conditioning)

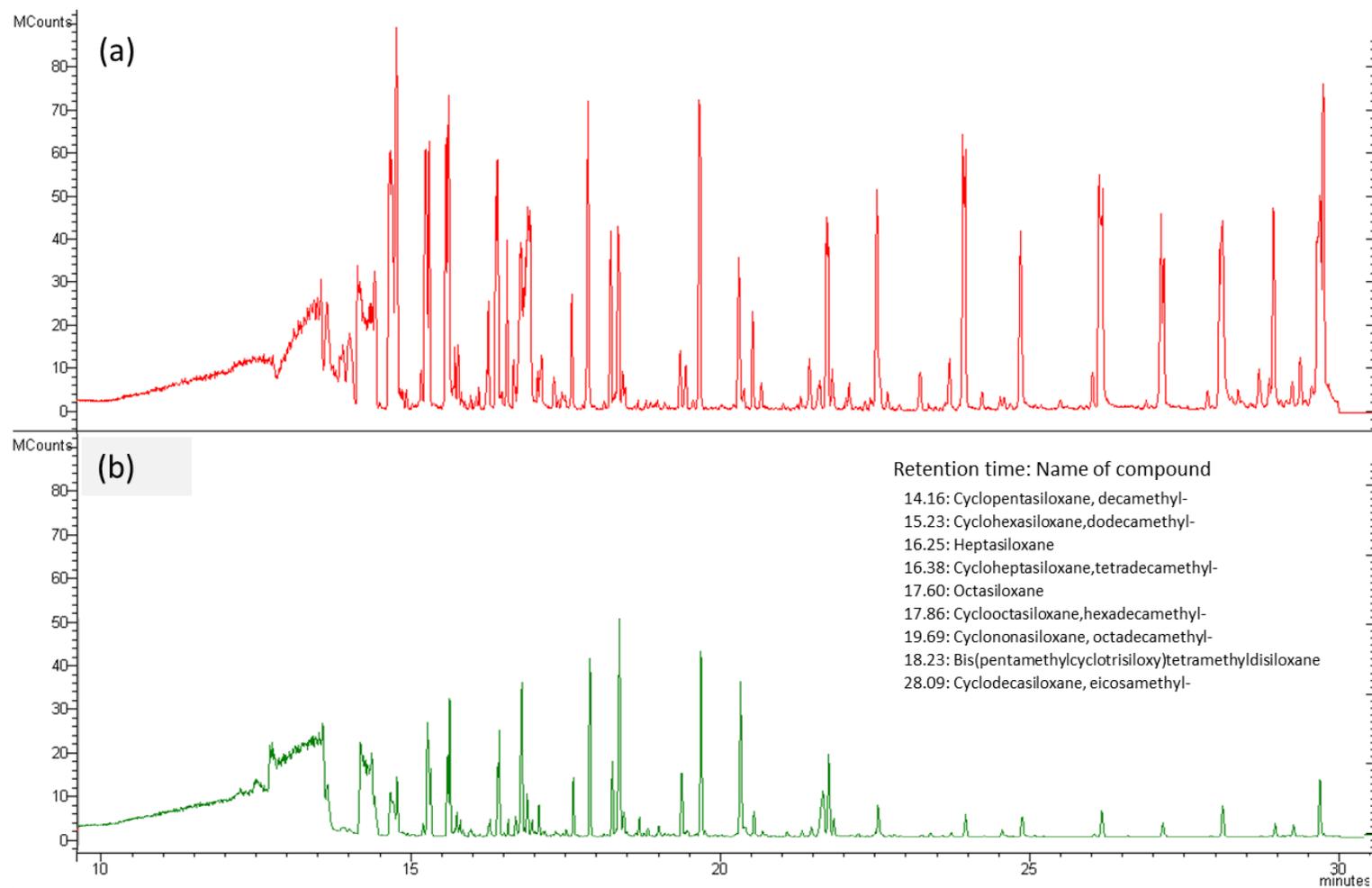


The degradation temperatures of the two raw SRs from “Polymerized kit” and “Manufactured” materials (SY and SL) were determined by TGA analysis. A first weight loss of 0.05% was recorded at 89 °C for SY and 223 °C for SL. The very large difference underlines differences in SR formulation, and suggests a higher content of oligomers in SY than in SL. Complementary TGA analysis on conditioned SL shows that the thermal conditioning step increases the temperature of the first weight loss (0.05%) from 223 °C to 360 °C. This finding suggests that oligomers are released before the thermal degradation of the material. It also highlights the reliability of conditioning steps for the elimination of residual oligomers in raw SR.

SI-5. Final percentage residue by thermal gravimetric analysis (TGA) of silicone rubbers under nitrogen and air at 800 °C (isothermal temperature for 30 min)

SR	Residue under nitrogen (%)	Residue under air (%)	Nitrogen/ air ratio
SY	51.0	57.6	0.89
UV	60.4	67.1	0.90
SB	17.3	34.6	0.50
TW	32.5	42.7	0.76
AL	31.0	40.9	0.76
SL	35.5	47.2	0.75
ST	76.3	71.0	1.07

SI-6. Scan chromatograms of two blanks of raw (a) and conditioned (b) silicone rubber (SL) by TD-GC-Fullscan analysis (TD: 300 °C, 15 min, 75 mL min⁻¹) and non-exhaustive identification of residuals with REPLIB NIST 05 Library (Probability >80%).



SI-7. Sorption isotherms of 21 pesticides for SL silicone rubber with linear (WY linear) and Freundlich (WY Freundlich) regression by the Williamson-York bivariate method and least square linear regression (LS linear). Confidence interval (95%, $n = 3$)

