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Investigating the Role of Sampler Compartments Employed by POCIS Devices in Pesticides Sampling

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Abstract Polar Organic Chemical Integrative Sampler (POCIS) is a passive sampler employed to monitor organic compounds in water (e.g. pesticides, drugs, etc.); in our case consists of a receiving phase, Oasis HLB, enclosed between two polyethersulfone (PES) membranes. In most cases, the analytes were extracted only from the receiving phase but recent works show that some compounds were also adsorbed on the PES membranes. Many aspects on the membrane behaviour are still unknown and this work aims to fill some knowledge gaps exploring the capability of PES membranes to adsorb pesticides. From experiments conducted in a controlled environment, it was seen that more than half of the investigated compounds were adsorbed more effectively by the PES membrane than the Oasis HLB phase. The affinity of these pesticides towards the two sampler compartments, can be explained only partially by the polarity of the compounds. However, a significant adsorption of the most hydrophobic compounds by the PES membrane was noticed, especially for values of LogKow higher than 4. From these experiments, it was possible to calibrate POCIS by comparing the pesticide concentration in water with the amount adsorbed by the two sampler compartments over time, with the estimation of two values of sampling rate for each pesticide ($R_{S,HLB}$ and $R_{S,PES}$). It was seen that the combination of the two adsorbent substrates allowed to intercept almost all the studied compounds satisfactorily and this behaviour was also confirmed by a field sampling campaign.

Keywords Pesticide · Polar Organic Chemical Integrative Sampler (POCIS) · Polyethersulfone (PES) membrane · Laboratory calibration · In-situ calibration · Sampling rate

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1 Introduction

Polar Organic Chemical Integrative Sampler (POCIS) has received increasing attention from environmental

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scientists over the last two decades, by its potential ability to provide Time Weighted Average (TWA) concentrations of pollutants in water at low cost and with a relatively small effort (Endo & Matsuura, 2018). The structure of this passive sampler is quite simple and robust, being characterised by a sorbent phase sandwiched between two sheets of polymeric membrane closed by two stainless steel rings. In this way, the porosity of the membrane allows the adsorbent phase to be contained and to come into contact with the external liquid. Although various combinations of sorbents and membranes have been tested, the most commonly used is: Oasis HLB phase, as sorbent, and polyethersulfone (PES), as membrane. Once POCIS is deployed in water, the organic compounds dissolved in water diffuse through the membrane and accumulate in the sorbent (Alvarez et al., 2004). Subsequently, the TWA concentration of pollutants in water can be calculated based on the accumulated amount in the sorbent, the deployment time, and the knowledge of the sampling rates ($R_{S,HLB}$) by assuming first-order kinetics (Wang et al., 2020). Previous studies have delved into the adsorption process on the adsorbent phase by considering a large number of variables that can affect the process, such as water flow velocity (Charlestra et al., 2012; Djomte et al., 2018), water temperature (Booij et al., 2020; Djomte et al., 2018; Yabuki et al., 2016), pH (Li et al., 2011), salinity (Togola & Budzinski, 2007), biofouling (Rosen et al., 2018), dissolved organic materials (Charlestra et al., 2012; Li et al., 2011) and suspended matter (Djomte et al., 2020). In addition, the material used for the membrane and its porosity also affects the pollutant uptake by the receiving phase (MacKeown et al., 2022). Recent studies showed that the PES membrane uptakes some organic compounds and intercepts them before they reach the Oasis HLB phase (Casari et al., 2023; Morin et al., 2018; Renaud et al., 2022; Silvani et al., 2017). Physical and chemical processes governing such uptake are partially known, such as hydrophobicity (Casari et al., 2023; Estoppey et al., 2019; Silvani et al., 2017), the presence of aromatic rings in the chemical structure (Silvani et al., 2017), the presence of electron withdrawing groups (such as nitro groups of nitroaromatics) (Estoppey et al., 2019) and ionisation (Morin et al., 2018; Silvani et al., 2017; Vermeirssen et al., 2012), among others. Although the number of works referring to membrane sampling rates ($R_{S,PES}$) is limited, the results currently available in literature suggest to extract the analytes also from the PES membranes in order to increase the sensitivity and the number of molecules that can be monitored by POCIS (Casari et al., 2023; Endo & Matsuura, 2018; MacKeown et al., 2022, 2024; Suchana & Passeport, 2022), but it would be necessary to know the value of $R_{S,PES}$ for a large number of pesticides to give a quantitative interpretation of the results.

In this work we conducted laboratory experiments to quantify the susceptibility of over 200 pesticides to accumulate on the PES membrane instead of on the Oasis HLB phase with the overall objective of evaluating which of these substances can be monitored using PES membrane as a sorbent. In these cases, we also estimated the sampling rate $R_{S,PES}$. In addition to the classical POCIS configuration, consisting of phase and membrane, we also evaluated the possibility of using the PES membrane as the sole substrate for the sampler, in a POCIS realised without the sorbent phase. In parallel, we compared the two sampling rates obtained in the laboratory and in the field. This last focus was performed using both sampler compartments to monitor a stream with a significant pesticide load. The studied compounds used as an experimental model were pesticides commonly used in viticulture and fruit farming, and some of their metabolites.

2 Materials and Methods

2.1 Chemicals and Materials

Pesticide reference standards (226) (purity ranging between 90–99%) were obtained from Merck KGaA (Darmstadt, Germany) and Dr. Ehrensdorfer GmbH (Augsburg, Germany); Stock solution of 5000 µg L^{-1} were prepared in Acetonitrile (ACN). Internal standard triphenyl phosphate (TPP) was purchased from Merck KGaA (Darmstadt, Germany). For chemical analysis methanol (MeOH), ACN and magnesium sulfate ($MgSO_4$) were obtained from Sigma-Aldrich (Milan, Italy). The ultrapure water was produced in the laboratory using an Arium pro UV (Sartorius Stedim, Gottingen Germany) water purification system. POCIS were home-made assembled using: (i) 200 mg of Oasis HLB (30 µm particle size, 810 m^2 g^{-1}, divinylbenzene N-vinyl-pyrrolidone) obtained from Waters (Guyancourt, France); (ii) polyethersulfone

(PES) membranes (normal pore size 0.1 µm, disk diameter 90 mm) purchased from GVS (Sanford, USA). The automatic sampler, model ASP 9461D, used for the water grab sampling, was purchased from Endress + Hauser Wetzer (Germany). Manual solid phase extractions with Oasis HLB cartridges (6 cc, 200 mg; Waters, Guyancourt, France) were carried out using a 10-port vacuum manifold (Supelco Visiprep SPE; Bellefonte, USA), while sample sonication was performed using a Branson 2200 Ultrasonic Cleaner (Connecticut, USA).

2.2 Membrane Role Study at Laboratory Scale

Laboratory experiments were carried out to investigate the allocation of pesticides between Oasis HLB phase and PES membrane in sampling by POCIS and to test the adsorbent capability of PES membrane used as single sampler, later called PES-single sampler. Adopting equipment that works continuously at constant pesticide concentration involves many difficulties such as operational complexity, the amount of pesticides needed, and the volumes of water to be treated; for these reasons, a discontinuous renewal approach was chosen using beakers as reservoirs. For each exposure time (4, 7 and 14 days) three glass beakers were filled with 4L of tap water each, fortified with 226 pesticides at about 0.1 µg L^{-1} (see Tables S1 and S7 for concentration in details). A disk of POCIS and a PES-single sampler were added together to each of these beakers. In order to minimise the reduction of analyte concentration and therefore to keep the concentration of the pesticide as constant as possible, the water solution was renewed every day. The beakers were covered with aluminium foil to avoid contact with light. The solution was stirred at a mean temperature of 21 °C (SD = 2.8 °C). At the beginning of the test a water sample was collected from each beaker to check the initial concentration of the pollutants and, at the end of each renewal, samples of water were collected in triplicate to monitor the fluctuation of pesticide concentration and to check compliance with the mass balance (see Fig. S1). After the deployment, POCIS were stored in a fridge, in aluminium envelopes, while the water samples were extracted and analysed on the same day on which they were collected.

To evaluate whether each compound was mainly uptake by the PES membrane or by the Oasis HLB phase, the fraction of the accumulated mass of analyte to that in the total POCIS, in both sampler compartments, was calculated, as follows:

$$f_{PES} = \frac{m_{PES}}{m_{PES}+m_{HLB}} \quad f_{HLB} = \frac{m_{HLB}}{m_{PES}+m_{HLB}} \tag{1}$$

where m_{PES} is the amount of pesticide adsorbed by the PES membrane and m_{HLB} is the amount adsorbed by the Oasis HLB phase in POCIS.

2.2.1 *Fraction (f_{PES}) of the Accumulated Mass of Analyte in the PES Membrane to that in the Total POCIS Data Analysis*

The fraction (f_{PES}) of the mass of analyte accumulated in the PES membrane compared to that of the total POCIS, calculated according to Eq. 1, varies between 0 and 100 percent. Due to this non-continuous distribution of the data, it was decided to normalise the data with the following function before applying the t-test, in order to assess the presence of relevant discrepancies between the f_{PES} values obtained from the laboratory tests and those obtained from the field sampling campaigns.

$$f_{pes}{}' = \arcsin(\sqrt{f_{pes}}) \tag{2}$$

2.3 Study Area and Sampling Strategy

2.3.1 *Sampling Site*

A sampling campaign was carried out on the artificial channel called Caldaro's canal, located in Trentino Region, North-East Italy (Fig. 1). This channel is the main canal draining an extensive network of irrigation ditches at the floor of the Adige valley. The catchment area upstream the sampling site (coordinates 46° 11′ 34.7"N and 11° 07′ 18.9''E; WGS84) is 160 km^2, and it is mainly used for cultivating permanent crops such as apple trees and vines.

2.3.2 *Sampling Strategy*

At the identified sampling station, two systems were applied synchronously for 14 days, from 12 to 25 May 2023. An automated sampling equipment was set to collect 50 mL of water every 30 min during the 14 days of

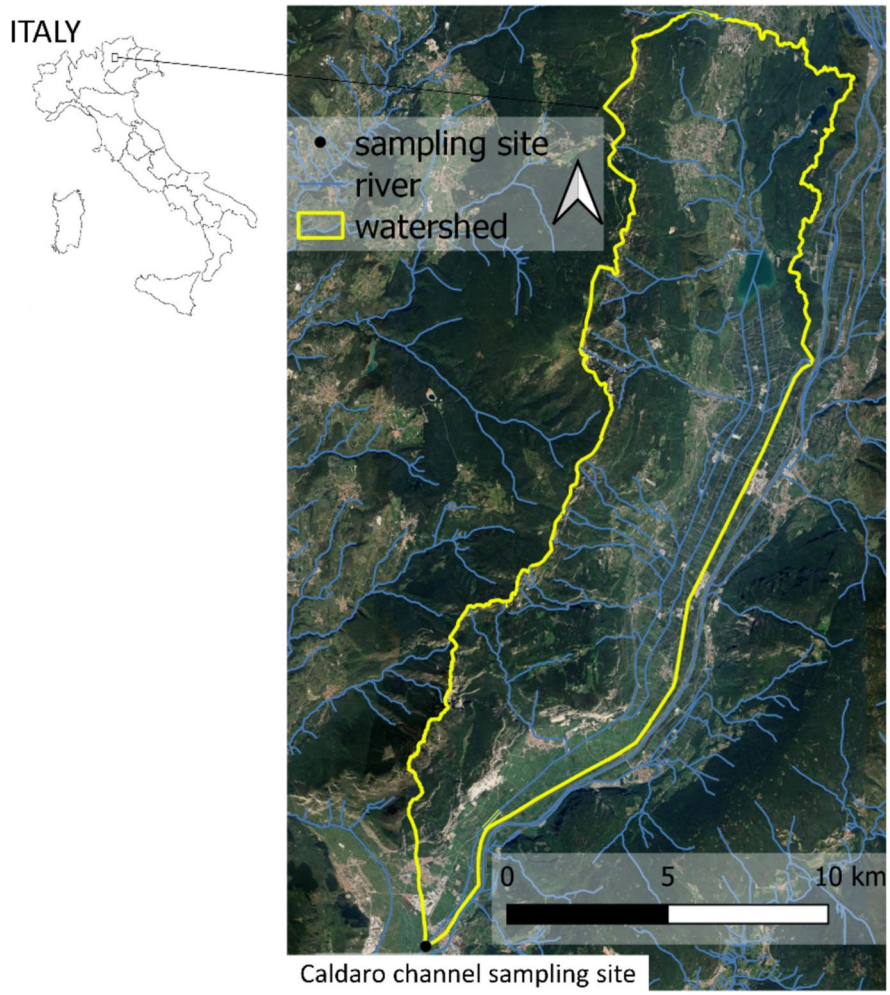

Fig. 1 Map of the Caldaro canal catchment and location of the sampling point

sampling, storing the volumes in one-litre dark glass bottles, each filled to 800 mL. Every 2 days, technical staff collected and replaced the bottles to bring them to the laboratory using insulated containers. To prevent the growth of algae or bacteria, methanol (1% v/v final) was added to the water samples. In parallel, four triplets of POCIS were exposed in the channel for periods of 3, 7, 10 and 14 days. Finally, POCIS and water samples were stored in the refrigerator (< 8 °C) and then analysed at the conclusion of the 14-days sampling campaign.

2.4 Samples Preparation and Analysis

2.4.1 Sample Extraction

After exposure, POCIS sorbent phases were extracted following the procedure described in our previous study (Casari et al., 2023). Briefly, the outer surface of the POCIS was washed with ultrapure water to remove any debris; then the POCIS was disassembled and the Oasis HLB phase and the PES membranes were placed in two different plastic test tubes (PET, 15 mL and 50 mL, respectively). The test tube containing the Oasis HLB phase was added 10 mL of ACN and 0.2 mg of $MgSO_4$, while the test tube containing the PES membranes was added 20 mL of ACN and 0.2 mg of $MgSO_4$. Extraction under sonication was performed for 20 min in an ultrasonic bath, the extracts were then filtered through 0.22 µm filter (PVDF) and concentrated to 1 mL under a gentle nitrogen stream.

Before extracting the water grab samples collected in the field by the autosampler, these were mixed to make average samples over 3, 7, 10 and 14 days,

equivalent to the exposure period of POCIS; which were prepared and analysed in triplicate. These average samples of water collected in the field and the water samples collected from laboratory experiments were extracted and analysed following the same approach reported by Casari et al. (2023). The procedure consisted of filtering the sample by 1.2 µm filter (cellulose acetate) and extracting it manually using a vacuum manifold (SPE, Oasis HLB cartridges). The cartridge, after being conditioned with MeOH and ultrapure water, was loaded with 100 mL of water sample and then dried. The adsorbed pesticides were eluted twice with 10 mL of MeOH and the entire collected volume was evaporated to dryness under a gentle nitrogen stream. The sample was reconstituted with 1 mL of ACN containing triphenyl phosphate (0.1 mg L^{-1}) as internal standard and then analysed by GC–MS/MS and LC–MS/MS systems.

2.4.2 Instrumental Analysis

A Waters Acquity UPLC (Waters Corporation, Milford, MA), coupled to a Xevo TQ MS mass spectrometer equipped with an electrospray ion source (Waters) was used in all the experiments. The chromatographic column was an Acquity UPLC BEH C18 column (1.7 µm, 2.1 mm X 100 mm) working at 40 °C, using as mobile phase 0.1% aqueous formic acid (solvent A) and 0.1% formic acid in methanol (solvent B) at a flow rate of 0.45 mL min^{-1}. The gradient conditions of the LC mobile phase were as follows, based on times (t): t = 0–0.25 min, hold 95% A, 5% B; t = 0.25–6 min, ramp linearly to 70% B; t = 6–7.5 min, hold 70% B; t = 7.5 – 9.5 ramp linearly to 100% B; t = 9.50–12 min, hold 100% B. The mass spectrometer was used both in positive and negative mode, and the source conditions were set as follows: capillary voltage 0.6 kV; source temperature 150 °C, cone gas flow (nitrogen, 20 L h^{-1}) desolvation gas flow (nitrogen, 1000 L h^{-1}), desolvation temperature 500 °C. Collision gas was Argon, at 0.20 ml min^{-1} and the triple quadrupole was operated in MRM mode and all the transitions had been set as reported in Table S2.

An Agilent 8890 GC coupled to an TQ 7010B mass spectrometer (Agilent Technologies Inc, USA) equipped with an electron impact ion source (EI, 70 eV) was employed. GC analysis was conducted on a Restek Rxi-5Sil MS capillary column (20 m × 0.18 mmID × 0.18 µm df) (Restek, USA) using the following experimental conditions: Helium (1 mL min^{-1}), injection temperature 260 °C, injection volume 1 µL (split ratio, 1:10), MS transfer line temperature 280 °C, temperature program: 60 °C (1 min); then 60–170 °C at 60 °C min^{-1}; 170–320 °C at 20 °C min^{-1}; 320 °C (1 min). The acquisition, as well as for the LC–MS/MS system, was carried out in MRM mode (Table S3).

2.4.3 Validation Method

Validation data such as recoveries (Rec%), repeatability (RSD%), limits of quantification (LOQ) and matrix effect were evaluated according to SANTE, 11312/2021 guidelines, and all details are reported in the Supplementary Materials (Tables S4-S6). For the "surface water" matrix, recovery and repeatability were performed on the "blank water samples" (water without pesticide contamination) adding pesticides at three concentration levels (0.005, 0.050 and 0.500 µg L^{-1}); each level was analysed in triplicate. A matrix-matched calibration was always employed to compensate for the matrix effect. The magnitude of the matrix effect for each compound is shown in Table S4 and was calculated according to the indications reported in the SANTE guidelines.

As regards the two adsorbent substrates (PES membrane and Oasis HLB phase), the recoveries and repeatability were evaluated on three levels of added quantities (0.001, 0.050, 0.500 µg) and, such as for the water sample each level was analysed in triplicate; using new and dry substrates of both PES membrane and Oasis HLB phase. Every addition was performed depositing drop by drop an accurate volume of an acetonitrile solution, containing a known concentration of pesticides, on all external surface of substrate and then everything was stored in a controlled environment until the solvent was completely evaporated. For each POCIS substrate, two curves were constructed to assess the matrix effect: an acetonitrile solvent calibration curve from the extraction of white POCIS substrate and a matrix-matched calibration curve constructed using acetonitrile extract from real samples (POCIS samplers left in a small 'clean' river for 15 days), subtracting the possible contribution of pesticides already present. The magnitude of the matrix effect (see tables S5 and S6), calculated

by comparing the signals of the two curves, has assumed absolute values averaging less than 9% for both POCIS substrates. For this reason, it was possible to use the calibration curves performed with the solvent derived from the extract of a white POCIS substrates. The sensitivity of two analytical method was estimated by establishing the LOQs according to SANTE method, and limits of detection (LODs) were estimated as one third of the quantification limit (Magnusson & Örnemark, 2014).

2.5 Rs Calculation

The traditional approach to study the uptake regime on the Oasis HLB phase based on a linear relationship between the CF_{HLB} and time (t), is performed as follows (Ahrens et al., 2015; Yabuki et al., 2016):

$$R_{S,HLB} = \frac{CF_{HLB}}{t} = \frac{m_{HLB}}{TWA_C} \cdot \frac{1}{t} \quad (3)$$

where $R_{S,HLB}$ is the sampling rate referred to the Oasis HLB phase, expressed dimensionally as a volume per unit time, and TWA_C is the Time Weighted Average concentration of the pollutant in water. It was chosen to use this linear regression law by accepting the assumption that, at the beginning of the test, the amount of pesticide adsorbed by the passive sampler is null, and by using a linear trend to interpolate the data, because the number of the available observations is not enough to be robustly interpolated with a more complex model. The implementation of this approach doesn't exclude that some compounds could exhibit a saturation process or a nonlinear uptake trend, highlighted with a low correlation coefficient (R^2). The compounds that exhibited this criticality were not further investigated, because the actual available data are not enough to correctly describe their uptake trend.

Based on these observations, this approach can be used also to study the uptake regime on the PES membrane, estimating the $R_{S,PES}$ as follows:

$$R_{S,PES} = \frac{CF_{PES}}{t} = \frac{m_{PES}}{TWA_C} \cdot \frac{1}{t} \quad (4)$$

In view of using both POCIS compartments for monitoring watercourses, the analytes can be extracted from the two matrices simultaneously and the sampling rate R_S has been computed from a relation (Eq. 5) that is analogous to Eqs. (3,4), in which M_S is the total amount of pesticide adsorbed by both the phase (m_{HLB}) and the membranes (m_{PES}) and R_S is the global sampling rate:

$$R_S = R_{S,HLB} + R_{S,PES} = \frac{CF}{t} = \frac{m_{HLB} + m_{PES}}{TWA_C} \cdot \frac{1}{t} = \frac{M_S}{TWA_C} \cdot \frac{1}{t} \quad (5)$$

Following this approach, the $R_{S,HLB}$, $R_{S,PES}$ and R_S of each compound was therefore estimated from a linear interpolation (least squares linear regression method) of the CF_{HLB}, CF_{PES} and CF over time, respectively.

3 Results and Discussion

3.1 Investigation of Partition between PES Membrane and Oasis HLB Phase

From the comparison between the amount adsorbed by the two sampler compartments, the analytes partitioning between the PES membrane and the Oasis HLB phase (Eq. 1) was first evaluated. For more than half of the studied compounds, the PES membrane was able to adsorb a higher amount than the Oasis HLB phase. This phenomenon occurs especially for the more hydrophobic compounds, i.e. with higher values of LogKow, in agreement with previous results reported by other authors (Silvani et al., 2017; Vermeirssen et al., 2012). As reported in Fig. 2, the adsorbent capability of PES membrane is typically weak for the pesticides with LogKow < 2, such as acetamiprid (insecticide, LogKow = 0.8), carbendazim (fungicide, LogKow = 1.51) and flonicamid (insecticide, LogKow = 0.3), which are adsorbed almost exclusively by the Oasis HLB phase. Conversely, substances having LogKow ≥ 4 were adsorbed mainly by the PES membrane, such as etofenprox (insecticide, LogKow = 6.9), fluazinam (fungicide, LogKow = 4.87) and piperonyl butoxide (insecticide, LogKow = 4.75). Such low levels of adsorption exhibited by the Oasis HLB phase may be caused by a higher affinity of these compounds with the PES membrane, which retains them before they reach the phase. This retention can delay adsorption by the phase, causing a "lag effect" (Belles et al., 2014; Bernard et al., 2018;

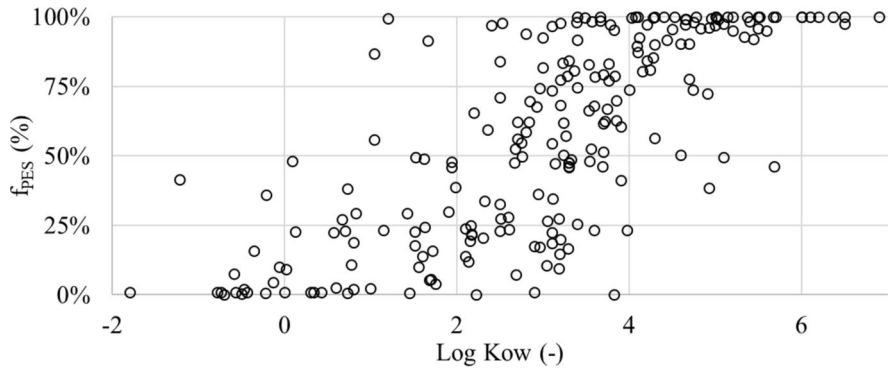

Fig. 2 Fraction (f_{PES}) of the mean accumulated mass of analyte in the PES membrane to that in the total POCIS, for the examined compounds ordered according to their polarity (LogKow). Numerical values are reported in the Supplementary Materials (Table S9)

Endo & Matsuura, 2018; Noro et al., 2020; Silvani et al., 2017; Vermeirssen et al., 2012), or preventing it completely. The "lag effect" is widely studied in literature, and it can be reduced by either using a membrane with a less adsorbent capability to pesticides, or by increasing the pore size dimension of the membrane (Belles et al., 2014; Endo & Matsuura, 2018; MacKeown et al., 2022, 2024; Noro et al., 2020), thereby reducing the effect of the membrane.

For compounds with a LogKow between 2 and 4, a less pronounced preference for one of the two sampler compartments was observed (Fig. 2). Some of these compounds are more effectively accumulated by the phase, others are more effectively accumulated by the membrane, and others are adsorbed by both compartments in comparable amounts. Three examples are: fluazifop (herbicide, LogKow = 3.2; more effectively adsorbed by the phase), mandipropamid (fungicide, LogKow = 3.2; more effectively adsorbed by the membrane) and promecarb (insecticide, LogKow = 3.1; adsorbed by both materials in comparable amounts). Thus, polarity alone does not completely predict the affinity of these compounds towards one of the two materials. The general trend reported here is in agreement with the result reported by Renaud et al. (2022). This poor correlation between f_{PES} and the LogKow, especially observed for intermediate values of LogKow (Fig. 2) can be justified by the fact that, besides the polarity, other physicochemical properties of the analytes affect the accumulation in the PES membrane, such as: ionisation of the pollutant (Morin et al., 2018), occurrence of π-π interactions between aromatic rings of the PES and the aromatic rings of the pesticides (Silvani et al., 2017), and others (Suchana & Passeport, 2022). Unfortunately, the currently available knowledge does not offer a robust prediction of the phenomenon (MacKeown et al., 2024).

Overall, the results of our experiments show that, after 14 exposure days, 102 of the 226 studied compounds were more effectively adsorbed by the Oasis HLB phase ($f_{PES} < 50\%$) while, 122 were more effectively adsorbed on the PES membrane ($f_{PES} \geq 50\%$). These results indicate that the extraction of both sampler compartments allows detection of a wide number of compounds and that the use of PES membrane as sorbent therefore allows to consistently broaden the range of molecules that can be monitored using POCIS. Only a limited number of compounds (2: cloquintocet and ethirimol) that were present in the water solution were not adsorbed by any of the two compartments in amounts higher than LOD.

3.2 Sampling Rate Estimation

This section reports the estimation of the sampling rate values ($R_{S,PES}$, $R_{S,HLB}$ and R_S) for the molecules for which the variation of concentration factors factors (CF_{PES}, CF_{HLB} and CF) over time exhibited a linear uptake trend. First of all, the correlation coefficient (R^2) obtained adopting the linear regression reported in Section 2.5 has been calculated. Figure S2 reports the value of R^2 obtained for the compounds adsorbed by the two sampler compartments (195 compounds by the PES and 171 by the HLB) and showed that, for the majority of the compounds, R^2 assumed values close to unity. For 90% of the compounds, the R^2 value of the linear regression is equal to or higher than 0.945 for the uptake on the PES membrane, than 0.902 for the uptake on the HLB phase and than 0.948 for the uptake on the POCIS. These values have been set as the lowest R^2 limits to assume that the linear regression gives

an acceptable representation of the data. Therefore, compounds with a lower R^2 than these limits (for each category) were not further investigated, because more data at several time instants would be needed to study their uptake trends. Follows that a total of 20 out of 195 for PES membrane, 17 out of 171 for HLB phase and 21 out of 212 for POCIS were excluded from the study. Among these compounds there are pesticides that followed a non-linear trend for both the PES membrane and HLB phase; the others either have exhibited a delay on the uptake, or a fluctuating signal, or they are compounds which were adsorbed almost exclusively by the other substrate. The data show that the PES adsorption capacity decreased over time, and the compounds affected by these behaviours are especially the polar and moderately polar compounds, for which the increase of adsorbed amount after 14 days is less than proportional. The change in the uptake rate could be due to a different mechanism of sorption (Morin et al., 2018; Suchana & Passeport, 2022). However, our studies do not allow us to understand the prevailing mechanism or predict the behaviour of these molecules; further studies are needed.

Based on the above reported observations and following the procedure reported in Section 2.5, it was possible to calculate the values of $R_{S,PES}$, $R_{S,HLB}$ and R_S respectively for 175, 154 and 191 compounds (some examples have been reported in Fig. 3). The values of $R_{S,PES}$ assumed a median value (5th, 95th percentage) of 0.214 (0.009, 1.172) L day^{-1}, while the $R_{S,HLB}$ assumed a median value (5th, 95th percentage) of 0.138 (0.038, 0.218) L day^{-1}. The entire range of variation of the $R_{S,PES}$ and of $R_{S,HLB}$ is shown in Fig. 4(a,b) and the individual numerical values are reported in the SI (Table S8). Although it is problematic to predict the values of sampling rates from the polarity of the compounds (LogKow) for all molecules, however it can be noticed that:

- The $R_{S,PES}$ was typically higher than $R_{S,HLB}$ for compounds with LogKow higher than 3 (see Fig. 4d);
- it was possible to estimate $R_{S,PES}$ for compounds with LogKow higher than 6, which would have been undetectable if they had been extracted only from the HLB phase;
- $R_{S,HLB}$ was less affected by polarity than $R_{S,PES}$;
- the coefficient of variation (CV%) of $R_{S,HLB}$, calculated on all detected compounds, is equal to 45% and, for an approximate estimate of the concentration of pesticides in water, the medium value of $R_{S,HLB}$ could be employed for all investigated compounds.

From the combination of the two POCIS compartments (PES membrane and the HLB phase), it was finally possible to estimate a single value of R_S per each compound, referred to the total amount of analytes detected in the POCIS. The median of the distribution of all these R_S values (5th, 95th percentiles) equals 0.313 (0.062, 1.194) L day^{-1}. Figure 4c shows that compounds with LogKow smaller than 2 have R_S values similar to $R_{S,HLB}$ and that the R_S value of the other compounds weakly increases with LogKow and that, in the same way, the membrane contribution ($R_{S,PES}$) becomes increasingly important.

3.3 PES as Single Passive Sampler (Without Oasis HLB Phase)

In this section, the values of sampling rates estimated from the amount of pesticide adsorbed by the PES membrane in PES-single sampler, $R_{S,PES,alone}$, were compared to the values of $R_{S,PES}$ to evaluate the possible interference due to the Oasis HLB phase and the possible use of the PES as a single sampler. First of all, for each compound, the value of $R_{S,PES,alone}$ was calculated by following the same procedure explained in Section 2.5 and 3.2 and then divided by the corresponding value of $R_{S,PES}$. It was found a gap between the two values of sampling rates (see Fig. 5a), which was typically due to a higher amount adsorbed by the PES-single sampler than the PES membrane of classic-POCIS, similarly to results previously reported by Suchana and Passeport (2022). Indeed, the ratio between the $R_{S,PES,alone}$ and $R_{S,PES}$ was higher than 1.5 for 49 of 167 and higher than one for almost all the compounds, with a gap that decreases with the LogKow. This difference in yield leads to the idea that the PES membrane alone can be used as a sampler also for the hydrophilic compounds; however, a comparison with the total (phase and membrane) POCIS extraction shows that the $R_{S,PES,alone}$ does not reach the value of R_S for the most hydrophilic compounds (see Fig. 5b). It follows that if one wanted to use the membrane alone as a sampler for hydrophilic and moderately polar compounds, it would be desirable to increase its surface area in contact with the

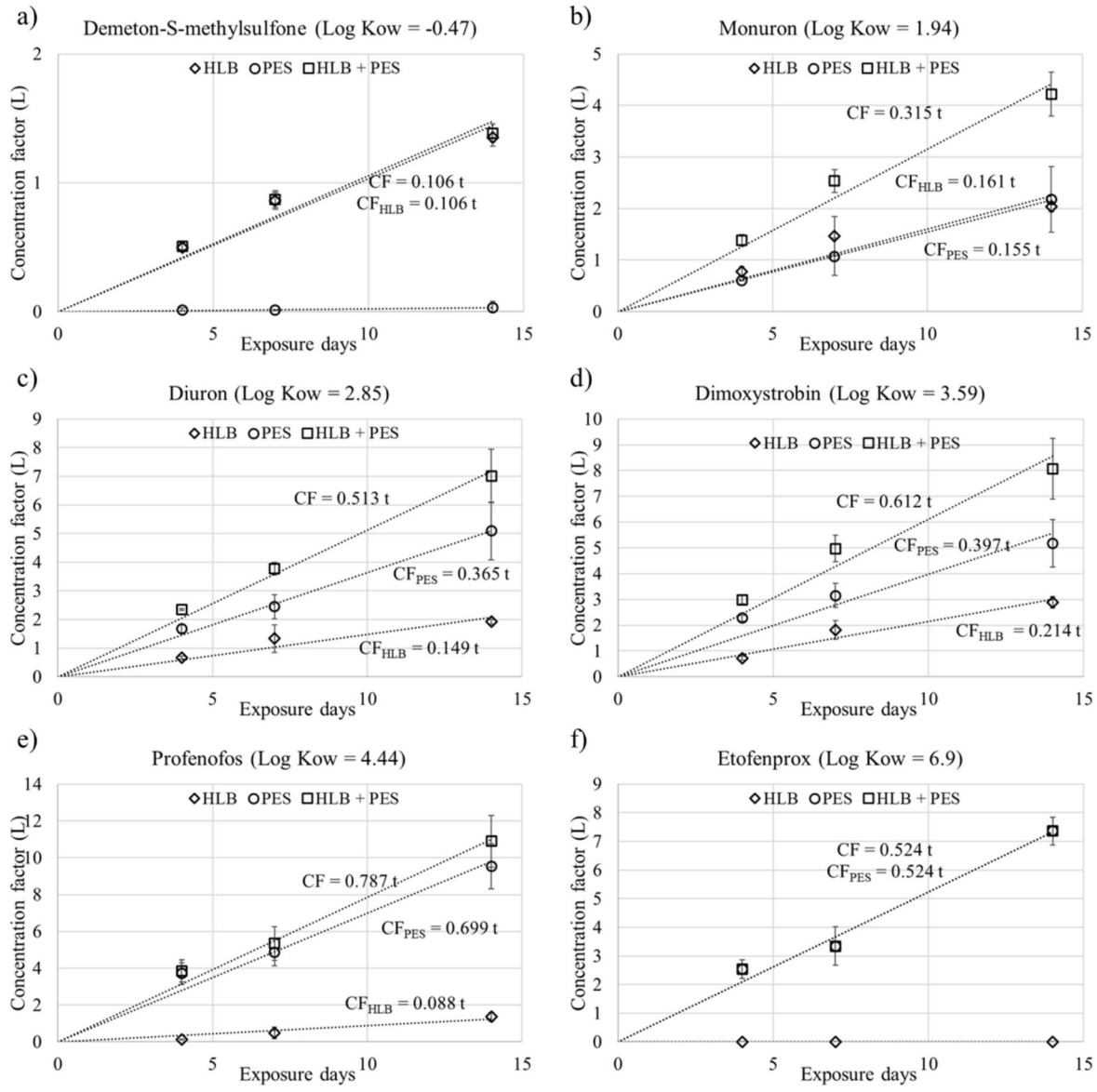

Fig. 3 Uptake trend in terms of concentration factors (CF_{HLB}, CF_{PES} and CF) over time: **a**) demeton-S-methylsulfone, **b**) monuron, **c**) diuron, **d**) dimoxystrobin, **e**) profenofos and **f**) etofenprox

fluid. But, for the configurations here studied, it can be said that the best solution is the combined use of PES membrane and Oasis HLB phase.

3.4 Results from Field Activities

Here differences between the results obtained in the laboratory and obtained in the field (see Table S10) are discussed, firstly in terms of allocation of the pesticides between the Oasis HLB phase and the PES membrane, then in terms of sampling rate. To this purpose, the accumulated mass fractions of every analyte in the two sampler compartments, to that in the total POCIS, was calculated using the data collected from the field (Eq. 1). These mass fractions were compared with the values obtained from laboratory experiments. Of the 226 investigated compounds, 20 were intercepted by the POCIS during the field sampling campaign. Results

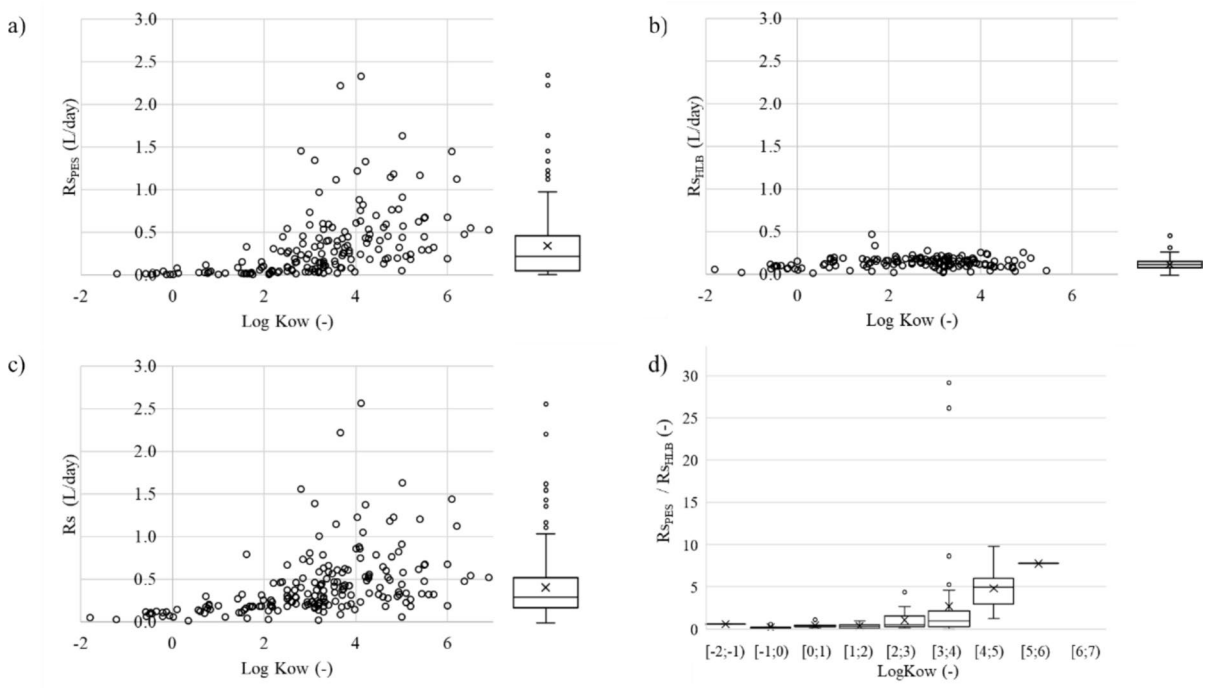

Fig. 4 Values of sampling rate arranged in polarity order, plotted for: **a**) PES membrane, **b**) Oasis HLB phase and **c**) POCIS. **d**) Ratio between $R_{S,PES}$ and $R_{S,HLB}$ for the molecules which have been adsorbed from both sampler compartments. In the sections a), b) and c) were reported the distribution of sampling rates in boxplots

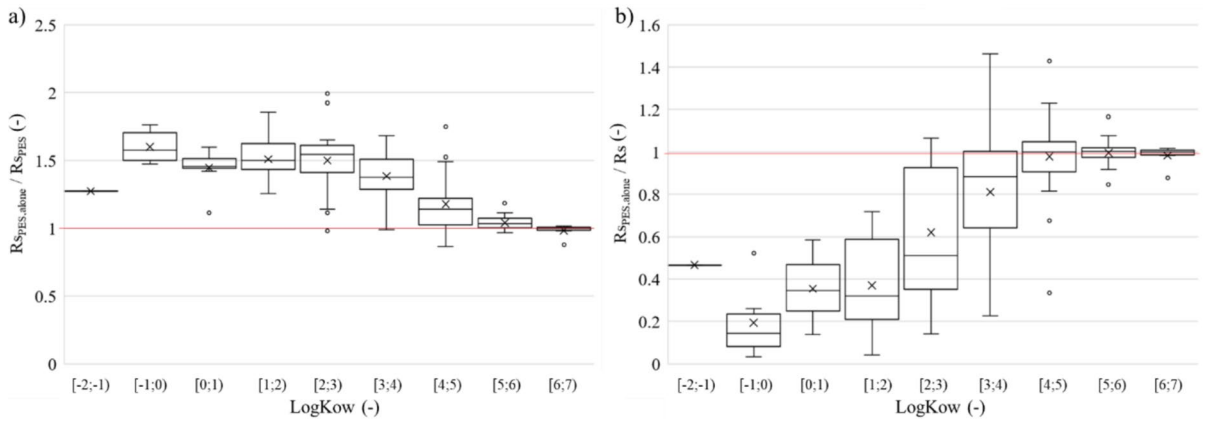

Fig. 5 Distributions of the ratio **a**) between the $R_{S,PES,alone}$ and the $R_{S,PES}$ and **b**) between the $R_{S,PES,alone}$ and the R_S. The distributions (boxplots) are arranged in polarity order (LogKow)

obtained from the laboratory tests for these 20 pesticides showed that 3 were almost exclusively adsorbed by the HLB phase ($f_{PES} < 10\%$), 13 were adsorbed preferably by the PES membrane ($f_{PES} \geq 50\%$) and 4 of them were almost exclusively adsorbed by the PES membrane ($f_{PES} \geq 90\%$). Results obtained from data collected from field sampling campaign showed a similar f_{PES} profiles of the lab tests even the repartition of pesticides varies depending on polarity of the compounds, as shown in Fig. 6. A t–test ($\alpha = 0.05$) was adopted to evaluate if there were significant differences between the results obtained from laboratory tests and

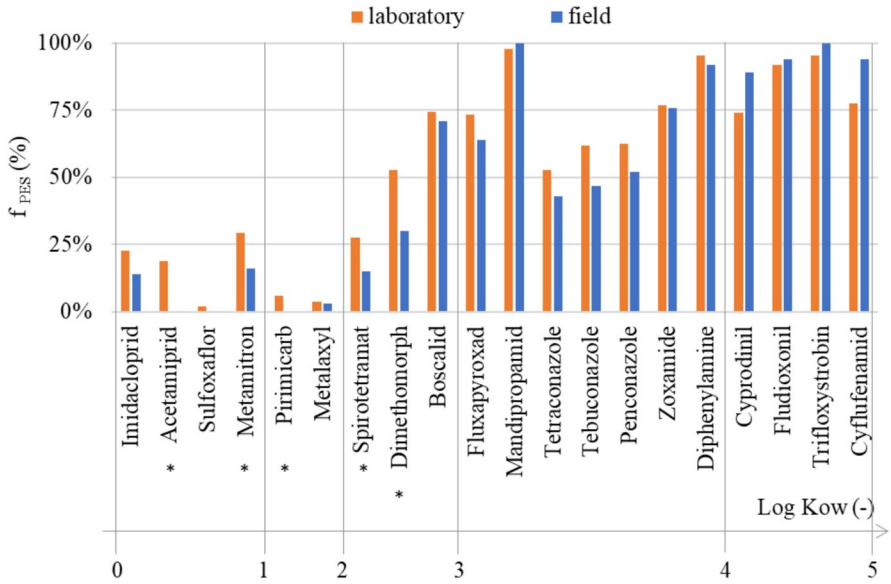

Fig. 6 Percentage of adsorbed amount by PES membrane in laboratory experiments and in the field. Compounds are arranged for increasing value of LogKow. *The asterisked molecules exhibited a significant difference between the results obtained in the laboratory and in the field (t-test, $\alpha = 0.05$), following the procedure explained in paragraph 2.2.1

from field sampling following the procedure explained in paragraph 2.2.1. A significant discrepancy was evidenced for 5 compounds, see asterisked molecules in Fig. 6. From this comparison it emerged that the repartition of pesticides with a LogKow > 3 between the two adsorbent substrates kept constant on varying the environmental conditions.

Values of sampling rate, $R_{S,PES}$ and $R_{S,HLB}$, calculated on a 14-day timeframe, were estimated for 11 and 13 compounds respectively. It was not possible to calculate values of sampling rate for all 20 molecules found in the POCIS sampler because the concentration in water for the following molecules was lower than the LOD for at least 8 days out of 14: cyflufenamid,

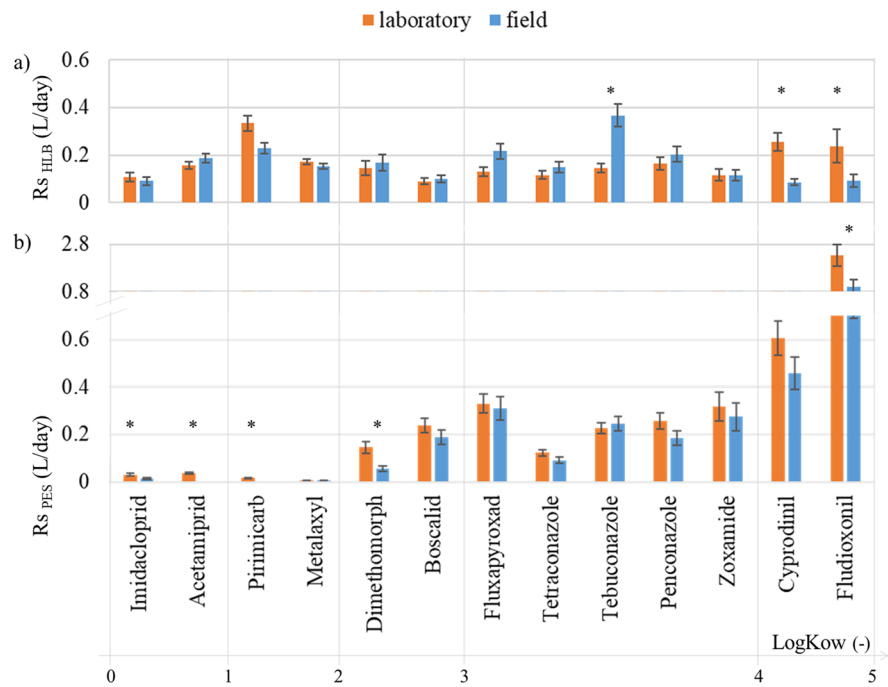

Fig. 7 Value of sampling rates **a**) $R_{S,HLB}$ **b**) $R_{S,PES}$ estimated from laboratory experiments and from the field sampling campaign. * Asterisked molecules indicate that the ratio of field and laboratory sampling rates differs by a factor greater than 2

diphenylamine, mandipropamid, metamitron, spirotetramat, sulfoxaflor and trifloxystrobin.

Comparing the values of the sampling rates ($R_{S,PES}$ and $R_{S,HLB}$) between tests carried out in the laboratory and in the field, it is observed that for tebuconazole, cyprodinil and fludioxonil, adsorbed on the phase and for imidacloprid, acetamiprid, pirimicarb, dimethomorph and fludioxonil adsorbed on the membrane, the relative values of sampling rate differing by a factor greater than 2. As can be seen by comparing Figs. 6 and 7, the largest discrepancies were recorded for the compounds that have the lowest affinity for the considered substrate. This aspect could be due to the different environmental conditions to which the POCIS were exposed, because some environmental variables can affect the adsorption process. Indeed, in the laboratory, the POCIS were immersed in a turbulent environment at a temperature of roughly 21 °C; while, in the field, a mean flow velocity of 2.5 cm s^{-1} was estimated, without accounting for its further likely reduction by the perforated canister (Booij et al., 2020). These different conditions could have determined a reduction of the sampling rates affecting the adsorption process between the laboratory and the field calibration (Charlestra et al., 2012; Djomte et al., 2018; Yabuki et al., 2016). In addition, the laboratory experiment was conducted using tap water which does not possess the same physicochemical properties of river water, an aspect that in turn may affect the uptake (Wang et al., 2020).

4 Conclusion

From the laboratory tests emerged that both the Oasis HLB phase and the PES membrane contribute to the pesticide adsorption. Comparing the amount of pesticide adsorbed by the two sampler compartments it was observed that for 122 of 226 compounds the amount adsorbed by the PES membrane is higher than that adsorbed by the Oasis HLB phase. It follows that to monitor these pesticides, it is possible to use the PES membrane as a single sampler, adopting the same structure of POCIS or increasing the membrane surface to increase its adsorbent capability regarding the moderate polar compounds. The extraction of both sampler compartments allowed us to intercept almost all the compounds which were present in water during the experiment (except four compounds), covering a wide range of polarity (from −2 to 7 units of LogKow). Finally, the operation of the two POCIS compartments studied in an artificial channel was mostly in accordance with the results obtained in the laboratory, the discrepancies may be due to the different environmental conditions to which the POCIS were exposed.

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Author Contribution Anna Casari, Roberto Larcher and Loris Tonidandel conceived and planned the experiments. Material preparation, data collection and analysis were performed by Anna Casari and Alice Barbero. The first draft of the manuscript was written by Anna Casari, Guido Zolezzi, Loris Tonidandel and Roberto Larcher. All other authors provided critical feedback and helped shape the research, analysis and manuscript.

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Data Availability The data are available from the author upon reasonable request.

Declarations

Conflicts of Interest All authors declare that they have no conflicts of interest.

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