



Doctoral Programme in
Agrifood and Environmental Sciences

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Using Polar Organic Chemical Integrated Sampler (POCIS) to
monitor pesticide fluxes in Alpine streams

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ABSTRACT

In recent decades, the issue of water quality has become of great concern worldwide. Anthropogenic pressures threatening freshwater and riparian ecosystems also include agricultural activities, which are often located near watercourses and lead to increased levels of nutrients and pesticides in rivers due to surface runoff from rainwater or from irrigation. One of the most widely used approaches to assessing pesticide concentrations in water is to analyse a single volume of water collected at a specific time, i.e. by “grab” sampling. Although results provided by this sampling method are accurate, they are only representative of the conditions at the time the sampling was carried out. Alternative approaches have been proposed over the past 20 years based on passive samplers, including the Polar Organic Chemical Integrative Sampler (POCIS). POCIS is a simple and robust passive sampler, composed of a receiving phase enclosed between two polymeric membrane sheets, like an Oasis HLB phase and by two polyethersulfone (PES) membranes as used in the present work. The sampler adsorbs pesticides flowing in the stream during its deployment period of time in stream water, which are then extracted with a solvent and analysed by gas chromatography (GC-MS/MS) and liquid chromatography tandem mass spectrometry (LC-MS/MS) systems.

The present Ph.D. thesis focuses on the use of POCIS for pesticides monitoring in Alpine streams. The use of POCIS is relatively recent and several operational and scientific challenges are still posed by its application and data interpretation. In the majority of the works reported in literature, the analytes were extracted only from the receiving phase, considering the membrane only as a physical filter. Instead, recent works show that the PES membrane is able to adsorb some pesticides, but many aspects on its behaviour are still unknown. In addition, the interpretation of the measurements of pesticide concentrations by POCIS in streams still presents several open challenges issues, which limit the samplers’

use in environmental monitoring.

In this context, this Ph.D. thesis addresses three main issues: the study of the functioning of the POCIS and the adsorptive capability of its components (Oasis HLB phase and PES membrane) against a wide number of pesticides, the field validation of a POCIS calibration method, and using POCIS to assess pesticide pollution at a watershed scale and to assess the effectiveness of two pesticides mitigation strategies for running waters.

The first results chapter illustrates a set of laboratory experiments, which showed that the extraction of pesticides from both the sampler compartments (Oasis HLB phase and PES membrane) allows the detection of almost all the investigated compounds (224 over 226), covering a wide range of polarities, from -2 to 7 LogKow units. More than half of these 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.

In the second results chapter, the validation of a POCIS calibration model was reported. The samplings were carried out in the field under real-life conditions of use on alpine streams. The calibration was obtained from the comparison of the total amount of pesticides adsorbed by POCIS with the time-weighted average concentration (TWAc), obtained from several grab samples. The validated model can be used to estimate TWAc concentrations for the studied compounds for future environmental monitoring conducted with POCIS under conditions similar to those under study, such as exposure time, flow velocity, temperature.

The third results chapter reports the study of the effectiveness of two possible pesticide pollution mitigation strategies analysed with POCIS. The case studies were a natural wetland and a washing plant for agricultural equipment serving local farmers. To this end, sampling campaigns were carried out at the wetland tributary and effluent streams and at a manhole of the white wastewater network near the washing plant, before and after its recent opening. In both cases samplings performed using POCIS allowed to quantify the ability of the two mitigation solutions to reduce pesticide concentrations in water for majority of the compounds studied.

In conclusion, the work has improved our knowledge of the POCIS for pesticides monitoring, showing its value for monitoring watercourses, as it is capable of adsorbing a wide number of compounds. In order to optimise the performance of this sampler, the work indicates that it is important to advisable to extract the pesticides also from PES membranes and not only from the phase. The use of POCIS to study the effectiveness of mitigation solutions made it possible to carry out sampling in a simple way, limiting the number of field samplings, without the need for a power supply near the site and ensuring continuous monitoring of pesticide flow; results that would be more difficult to be achieved with the grab sampling method. Finally, the results obtained from this Ph.D. work are able to provide important operational information for the quantitative assessment of pesticides in Alpine watercourses, which can be useful to the environmental protection agencies and stakeholders working in this sector.

CHAPTER 1. INTRODUCTION

The proximity of cultivated fields to surface water courses leads to increased levels of nutrients and pesticides in rivers due to surface runoff from rainwater or irrigation water (Vryzas, Vassiliou, Alexoudis, and Papadopoulou-Mourkidou, 2009). This phenomenon, combined with the use of freshwater for agricultural, industrial and domestic activities results in the presence of organic contaminants that may affect surface water quality (Poulier et al., 2014), which is of crucial relevance for environmental management, with regulatory frameworks that need to continuously adapt to newly detected problems, like those associated with emerging contaminants, to limit the negative effects that anthropogenic pressures have on freshwater and riparian ecosystems (Casari et al., 2023). In this perspective, the European Water Framework Directive (WFD) 2000/60/EC initially required that all water bodies achieve a good chemical and ecological status by 2015 at the latest, with deadlines extended first to 2021 and then to 2027. The WFD defines the environmental quality standards (EQS) and provides a list of priority substances, including several pesticides, to ensure that their concentration in water bodies is kept below an annual average concentration (AA-EQS) and a maximum allowable concentration (MA-EQS) (Directive 2000/60/EC; Directive 2013/39/EC).

A variety of mitigation measures can be implemented to achieve the goals defined by the WFD, adopting both nature-based solutions (NBS) and technical improvements. NBS include buffer strips, hedgerows and wetlands, which take advantage of services provided by specific ecosystems processes. For instance, the vegetative buffer strips and hedgerows limit pesticide transfer by surface runoff (Haddaway et al., 2018; Lauvernet and Helbert, 2020; Lorenz et al., 2022; Reichenberger, Bach, Skitschak, and Frede, 2007) by increasing the distance between the emission source and the surface waters, and by intercepting

spray drift (Haddaway et al., 2018; Reichenberger et al., 2007). Wetlands are defined as areas where water covers the soil for varying periods of time during the year, including the growing season of vegetation. Only a limited number of works in literature have studied the pollution reduction capabilities of natural wetlands: most wetland-related studies examine the abatement capabilities of various pollutants by purpose-built wetlands, either at full or pilot scale. Constructed wetlands (CW) allow the concentration of pesticides in water to be decreased (Tang, Wood, Smith, Thapa, and Aryal, 2021). Processes that allow for concentration reduction include adsorption onto sediment (Cryder, Wolf, Carlan, and Gan, 2021), translocation and degradation within plants (Cryder et al., 2021; Lv et al., 2017) and, in parallel with these processes, photodegradation occurring in the upper 10 cm of the water column (Mathon, Coquery, Miège, Vandycke, and Choubert, 2019) and degradation due to the presence of bacterial cultures, which allow to speed up the overall degradation rate (Chen, Ma, Yao, and Wang, 2023; Ignatowicz, Łozowicki, Łozowicka, and Piekarski, 2023). An advantage of introducing this type of NBS to mitigate the presence of pesticides is that all the mentioned phenomena are more pronounced during the crop production season (spring-summer) with favourable temperature, sunlight irradiation, and microbial activity (Zachary Cryder, Wolf, Carlan, Budd, and Gan, 2022). In parallel with the implementation of these solutions, the input of pesticides into surface waters can be limited, adopting some technical improvements as required by the European Union (Directive 2009/127/EC; Directive 2009/128/EC). These processes include requiring farmers to use anti-drift nozzles to spray crops to reduce the distance between the operator and the pesticide deposition site, managing excess spray solution and cleaning the sprayer to remove the pesticide found on their external surface after spraying the crops, and then collect and properly treat the used water before it is released in the field. This latter aspect has been the subject of several studies, analysing the performance of various decontamination methods, in terms of minimising water consumption, treating wastewater from washing agricultural machinery, minimising costs, etc. (Layman, Ramsey, Freebury, Newman, and

Newman, 2018; Pavlo and Kubai, 2024; Ramwell, Johnson, Boxall, and Rimmer, 2004; Smolyanichenko, Kulik, and Yakovleva, 2021). Among these options, the role of centralised washing plants for vehicles and equipment used to distribute pesticides in a given area to crops does not seem to have been assessed in targeted studies.

In relation to pesticides, compliance with the WFD EQS requires local administrations to do at least four representative water samples per year, which are currently performed by grab sampling, i.e. the collection of a sample of water at a given time (Poulier et al., 2014). Subsequently, analytes extracted from the grab samples are analyzed with the most suitable instrumental analytical approaches. This sampling method provides accurate results, but is only representative of the pesticide concentration present at the time of sampling. Poor temporal representativeness is one of the main limitations of the grab sampling approach, especially when dissolved concentrations vary over time due to changes in hydrological conditions (Allan et al., 2006). To overcome this drawback, alternative approaches based on passive samplers have been proposed in the past 20 years (Alvarez et al., 2004; Vrana et al., 2005). The Polar Organic Chemical Integrative Sampler (POCIS) is a valid device for assessing the presence of a wide variety of organic pollutants like illegal drugs, pesticides, pharmaceuticals contained in surface waters (Wang, Liu, Liu, and Gao, 2020). Its structure is made from a sandwich of two polymeric membranes, containing a given amount of a specific polymeric adsorption phase, all fixed together by stainless steel rings (see Figure 1).

Typically, for the sampling three POCIS are contained in a robust and protective external stainless steel basket provided with numerous holes to allow the free circulation of the water. One of the most widely used adsorption phases for pesticide monitoring is Oasis HLB sorbent which contains both hydrophilic and lipophilic groups. Its chemical structure gives the phase a good wettability and a high absorption capacity of both hydrophobic and

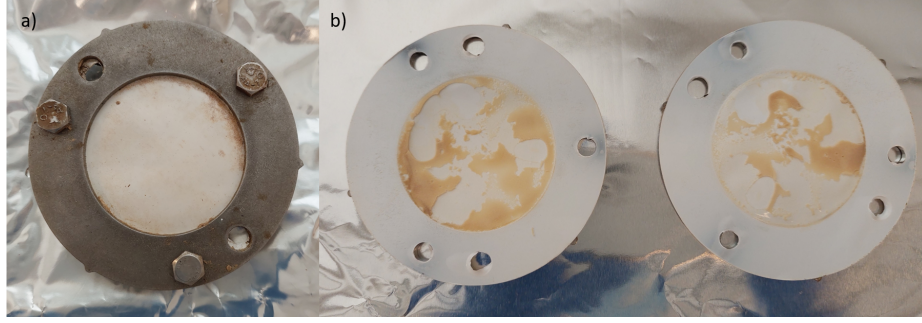


Figure 1 – Illustration of the POCIS layout. a) image of a disk of POCIS made after 3-week sampling in the field. b) picture of a disassembled disk of POCIS, where the adsorbent phase (orange spots) and the two sheets of membrane (the white supporting internal circles) can be seen.

hydrophilic compounds (Godlewska, Stepnowski, and Paszkiewicz, 2021). Sampling accuracy and repeatability are ensured by using simultaneously three separate absorbent packets and keeping the POCIS fully immersed in water for several weeks, allowing the target contaminants dissolved in the flowing water to be gradually absorbed and accumulated over the entire exposure time (Wang et al., 2020). The uptake regime can be described in terms of the temporal variability of the so called “concentration factor in the phase”, CF_{HLB} , which is defined as the ratio between the pesticide amount adsorbed by the Oasis HLB phase (m_{HLB}) and the Time-Weighted Average concentration (TWAc) of the same pesticide in water. Generally, the uptake regime is characterised by an initially linear trend, following a first-order kinetics, and a final equilibrium state, following a zero-order kinetics, in which the adsorbed amount does not vary with time anymore (Godlewska et al., 2021). The linear uptake regime is defined as the one in which a linear relationship between CF_{HLB} and time (t) holds, as follows (Ahrens, Daneshvar, Lau, and Kreuger, 2015; Yabuki et al., 2016):

$$CF_{HLB} = \frac{m_{HLB}}{TWAc} = R_{s,HLB} t \quad (1)$$

The slope of this linear relation is known as sampling rate ($R_{s,HLB}$), which is expressed dimensionally as a volume per time unit. For each pesticide, the $R_{s,HLB}$ represents the calibration parameter of POCIS, because its knowledge, together with the absorbed amount

m_{HLB} , allows to calculate the pesticide concentration in water TWAc (Wang et al., 2020). It follows that, for proper $R_{s,HLB}$ estimation, it is important to simultaneously collect m_{HLB} and TWAc data when the POCIS is uptaking within the linear regime and not beyond.

Previous studies indicate that $R_{s,HLB}$ depends on several environmental factors, on physico-chemical properties of the studied contaminant and sampler design choices. Laboratory experiments suggested a relationship between $R_{s,HLB}$ and water temperature that follows the Arrhenius law (Djomte, Taylor, Chen, Booij, and Chambliss, 2018; Yabuki et al., 2016), although this evidence was not confirmed by field studies (Booij, Chen, and Trask, 2020). In particular, $R_{s,HLB}$ increases with the velocity of the water that skims the sampling device, especially when changing from stagnant to flow conditions (Charlestra, Amirbahman, Courtemanch, Alvarez, and Patterson, 2012), but, once a (relatively small) velocity threshold is exceeded, $R_{s,HLB}$ tends to reach a limit value (Djomte et al., 2018). However, several other physical and chemical factors can also influence the POCIS operation, such as possible suspended inorganic matter, dissolved organic matter and membrane biofouling (Charlestra et al., 2012; Djomte et al., 2018; Djomte, Chen, and Chambliss, 2020; Harman, Allan, and Vermeirssen, 2012; Lissalde, Mazzella, and Mazellier, 2014). Other works explored the possible relationship between $R_{s,HLB}$ and some physico-chemical properties of the studied pollutants, such as polarity (expressed as Log Kow) and molecular mass. Unfortunately, in both cases, it was not possible to define a robust and general expression relating $R_{s,HLB}$ to the known physico-chemical properties of the contaminants (Wang et al., 2020). Furthermore, $R_{s,HLB}$ is also influenced by the polymeric material used as membrane to assemble POCIS and its porosity (MacKeown, Magi, Di Carro, and Benedetti, 2022). Recent studies showed that the polyethersulfone (PES) is able to directly absorb some organic compounds, intercepting them before they reach the internal phase (Casari et al., 2023; Casari et al., 2025; Morin et al., 2018; Silvani et al., 2017; Vermeirssen, Dietschweiler, Escher, Van Der Voet, and Hollender, 2012). Silvani

and colleagues (2017) confirmed that compounds with LogKow higher than 5 (i.e. highly hydrophobic) appear to accumulate more effectively in the PES membrane than in the Oasis HLB phase itself. Unfortunately, polarity alone does not fully predict the affinity of organic compounds towards one of the two materials, and the interaction with the PES membrane seems to imply a more complex relationship with the various physicochemical properties (MacKeown, Benedetti, Scapuzzi, Di Carro, and Magi, 2024).

The literature search conducted has shown the follows aspects. The pesticide pollution mitigation strategies can be valuable aids in achieving the environmental quality standards imposed by the European Communities although for the most part of the results in the literature refer to studies conducted at laboratory or pilot scale. POCIS can be a valuable tool for environmental monitoring of watercourses, although high complexity of the adsorption mechanisms, the high number of involved variables and their interplay. In the current state of knowledge it is still questionable to theoretically propose a universal $R_{s,HLB}$ value that can be adaptable to the high variability of the natural environment and chemical properties of the active principles. For this reason, to implement POCIS in environmental monitoring, the $R_{s,HLB}$ has to be estimated in exposure conditions similar to the real situations (Vrana et al. 2021); but currently, a field POCIS calibration is only available for a limited number of pesticides. Regarding the possibility of extracting pesticides from the PES membrane, although the number of works referring to membrane sampling rates ($R_{s,PES}$) is limited and the rules governing these adsorption processes are not fully understood yet, 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 and Matsuura, 2018; MacKeown et al., 2022; MacKeown et al., 2024; Suchana and 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.

CHAPTER 2. AIM OF THE THESIS AND SPECIFIC OBJECTIVES

This Ph.D. research specifically aims to improve the approaches currently used for the passive environmental monitoring of watercourses and showcase how the use of POCIS can allow the concentration of a wide number of compounds to be estimated. This was also achieved both by optimising the sampling strategy, by reducing the exposure time of POCIS in watercourses, and by improving the extraction strategy, considering as sorbent compartments of POCIS both the Oasis HLB phase and the PES membrane.

Firstly, there were 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 employed as an experimental model were pesticides commonly used in viticulture and fruit farming, and some of their metabolites. This objective is addressed in Chapter 4 of the thesis.

To address the limitations in the quantitative interpretation of the outputs of POCIS analysis, it was assessed the possibility of building quantitative and replicable models for the TWAc by using a passive sampler and considering a large selection of pesticides. To this aim, we compared the outputs of POCIS deployment in an alpine stream with parallel

quantitative measurements from frequent grab samplings, taken from the same location and spanning the entire deployment time. We investigated more than 310 molecules, some of which are used in viticulture and fruit farming and identified as priority substances (Directive 2000/60/EC; Directive 2013/39/EC). The experiments were carried out on a small alpine stream in the Trentino Region (NE Italy), where we also carefully monitored hydraulic and thermal conditions that may affect the functioning of POCIS. The robustness of the calibration models was then verified on the same stream in an additional sampling campaign and their transferability was tested on a different water body, characterised by decidedly different hydraulic conditions and location and found within the same Region. To the best of our knowledge, this work is probably the first to date reporting the POCIS calibration in an alpine setting, following the innovative approach of joint extraction of the two POCIS components (PES membrane and HLB adsorbent phase). Furthermore, at local level, the collected data contribute to the characterisation of the chemical status of two water bodies in intensively cultivated areas, which is relevant for the implementation of the requirements of the EU Water Framework Directive. This objective is addressed in Chapter 5 of the thesis.

Finally, the distribution of pesticides in agricultural-intensive alpine areas using POCIS was studied, looking for a quantitative relationship between the presence of pesticide in watercourses and the characteristics of the watershed upstream of the sampling sites. In parallel, the effectiveness of two mitigation solutions of different types in the studied area was evaluated. These solutions are: a natural wetland surrounded by farmland and a centralise washing plant for agricultural equipment and vehicles that was built for the purpose reducing pesticides transported to watercourses. The pesticide degradation capacity of the wetland was tested and the reduction in the concentration of pesticides in the drainage network (white wastewater) downstream the washing plant for agricultural equipment was evaluated. This objective is addressed in Chapter 6 of the thesis.

CHAPTER 3. MATERIALS AND METHODS

3.1 Chemicals and materials

Pesticide reference standards (331, see Table 8) (purity ranging between 90-99%) were obtained from Merck KGaA (Darmstadt, Germany) and Dr. Ehrendorfer GmbH (Augsburg, Germany); Stock solution of $5000 \mu\text{g L}^{-1}$ 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 ($30 \mu\text{m}$ particle size, $810 \text{ m}^2 \text{ g}^{-1}$, divinylbenzene N-vinyl-pyrrolidone) obtained from Waters (Guyancourt, France); (ii) polyethersulfone (PES) membranes (normal pore size $0.1 \mu\text{m}$, 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 Wetzler (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).

3.2 Samples preparation and analysis

3.2.1 *Procedure for the extraction of pesticides from the two POCIS compartments separately*

After exposure, POCIS compartments were extracted following the procedure described in our previous studies (Casari et al., 2023; Casari et al., 2025), based on the approach pro-

posed by Jeong, Schäffer, and Smith, 2018. 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 minutes 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; 2025). 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.

3.2.2 Procedure for the extraction of pesticides from the two POCIS compartments together

For the extraction of the pesticides from both POCIS compartments together, the procedure described in section 3.2.1 was used in the extraction of the PES membrane; with the difference that both compartments were placed in a single plastic test tubes (PET, 50 mL).

3.2.3 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 Appendix A (Table 6).

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 x 0.18 mmID x 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 (Appendix A, Table 7).

3.2.4 Validation method

Validation data such as recoveries (Rec%), repeatability (RSD%), limits of quantification (LOQ) and matrix effect were evaluated according to *SANTE guidelines 11312*, 2021,

and all details are reported in Appendix C (Tables 9 and 10). 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 $\mu\text{g L}^{-1}$); 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 9 and was calculated according to the indications reported in the SANTE guidelines.

As regards the POCIS, 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 Table 10), 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 (*Eurachem Guide*, 2014).

3.3 Sampling rate (Rs) calculation

Generally, the uptake regime is characterised by an initially linear trend, following a first-order kinetics, and a final equilibrium state, following a zero-order kinetics, in which the adsorbed amount does not vary with time anymore (Godlewska et al., 2021). In accordance with the observations reported by Vrana et al., 2005 in their work, see Figure 2, where the temporal variation of the concentration of a generic compound in a passive sampler is shown. It follows that, in order to be able to derive quantitative information from the passive sampler, it is necessary to make the sampling last long enough for the adsorption to be detectable with the chosen analytical approach but not too long, such that it remains within the linear stretch of the uptake trend.

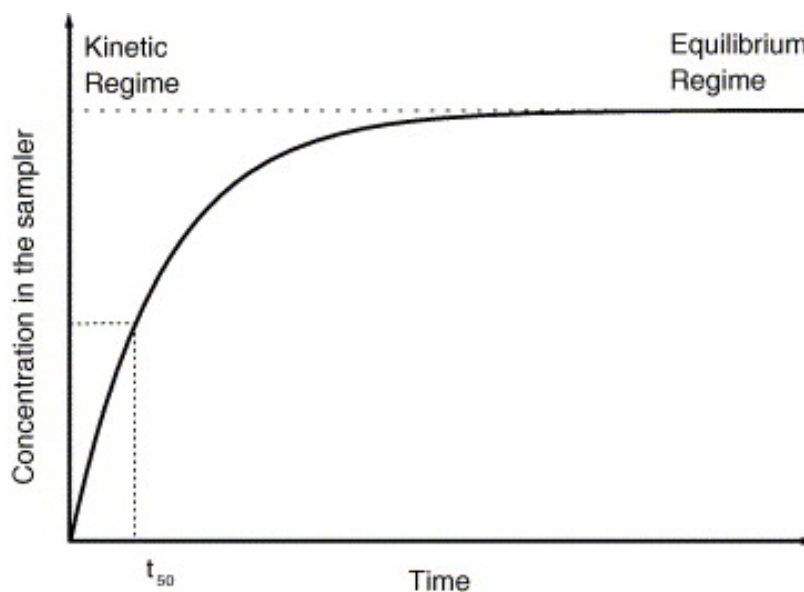


Figure 2 – Passive sampling devices operate in two main regimes: kinetic and equilibrium (Source: Vrana et al., 2005).

Assuming to work in the linear section of the uptake trend on the Oasis HLB phase, the uptake trend can be described in terms of the temporal variability of the so called “concentration factor”, CF (Ahrens et al., 2015; Yabuki et al., 2016), which is defined as the ratio between the pesticide amount adsorbed (m_{ads}) and the Time-Weighted Average concentra-

tion (TWAc) of the same pesticide in water (see eq. 2).

$$R_S = \frac{CF}{t} = \frac{m_{ads}}{TWA_C} \cdot \frac{1}{t} \quad (2)$$

This approach makes the uptake trends of various pesticides easily comparable regardless of their average concentration in water. The slope of the line that links the CF and the exposure time, takes the name of sampling rate (R_S), which is expressed dimensionally as a volume per unit time. For each pesticide, the R_S represents the calibration parameter of the passive sampler, because its knowledge, together with the absorbed amount m_{ads} , allows to calculate the pesticide concentration in water TWA_C (Wang et al., 2020). Besides being the calibration parameter, the R_S reflects the accumulation performance of each pesticide on the studied adsorbent substrate, regardless of the pesticide concentration in the water. Indeed, by knowing the value of R_S for different pesticides, it is easy to understand which compound is adsorbed more efficiently. In fact, a higher value of R_S corresponds to a higher rate of adsorption of the pesticide on the adsorbent substrate.

In addition to the literature evidence, we chose 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 to study the uptake regime on the Oasis HLB phase and on the PES membrane, estimating the $R_{S,HLB}$ and $R_{S,PES}$ as

follows:

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

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 (Equation 4) that is analogous to Equation 3, in which MS 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:

$$R_S = R_{S,HLB} + R_{S,PES} = \frac{CF}{t} = \frac{m_{HLB} + m_{PES}}{TWA_C} \cdot \frac{1}{t} \quad (4)$$

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.

3.4 Study area

The sampling campaigns, conducted as part of the PhD project focused on watercourses located in Trentino-Alto Adige, a north-eastern region of Italy. The study area comprises the Non Valley, located in the north-western part of the autonomous province of Trento, and the Adige Valley, the main alluvial plain of the entire region.

The Non Valley is a valley rich in small Alpine watercourses characterised by a nivo-pluvial hydrological regime. Its orography presents a ‘Y’ shaped bifurcation at the northernmost part of the Santa Giustina artificial lake. The construction of this lake for hydro-electric purposes has led to significant microclimatic variations in the entire valley. These variations have strongly favoured agricultural activity, so much so that today the valley’s economy is mainly agricultural, dedicated to the cultivation of apple trees. Descending



Figure 3 – Study area

from the Non Valley, one reaches the largest alluvial plain in the province of Trento, known as the Adige Valley, named after the river of the same name that flows through it. Agricultural activity dedicated to the cultivation of vines and apple trees is also widespread in this area.

The intensive agricultural activities carried out in these areas and their proximity to streams and drainage canals risk compromising the quality of these watercourses due to the use of pesticides and fertilisers. For this reason, the competent authorities are very interested in monitoring the quality status of these watercourses, also using POCIS. In order to identify the most critical areas and evaluate possible mitigation strategies.

CHAPTER 4. INVESTIGATING THE ROLE OF SAMPLER COMPARTMENTS EMPLOYED BY POCIS DEVICES IN PESTICIDES SAMPLING

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4.1 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 adsor-

bent substrates allowed to intercept almost all the studied compounds satisfactorily and this behaviour was also confirmed by a field sampling campaign.

4.2 Materials and methods

4.2.1 Laboratory experimentation

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 $0.1 \mu\text{g L}^{-1}$ (see Table 11 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 ($\text{SD} = 2.8^{\circ}\text{C}$). 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 Figure 30). 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. Finally, both types of samples were extracted and analysed following the procedure reported in Section 3.2.1.

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:

$$f_{PES} = \frac{m_{PES}}{m_{PES} + m_{HLB}} \quad f_{HLB} = \frac{m_{HLB}}{m_{PES} + m_{HLB}} \quad (5)$$

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.

4.2.2 *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 Equation 5, 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.

$$f'_{PES} = \arcsin(\sqrt{f_{PES}}) \quad (6)$$

4.2.3 *Study area and sampling strategy*

A sampling campaign was carried out on the artificial channel called Caldaro's canal, located in Trentino Region, North-East Italy (Figure 4). 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 is 160 km², and it is mainly used for cultivating permanent crops such as apple trees and vines.

At the Caldaro channel 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

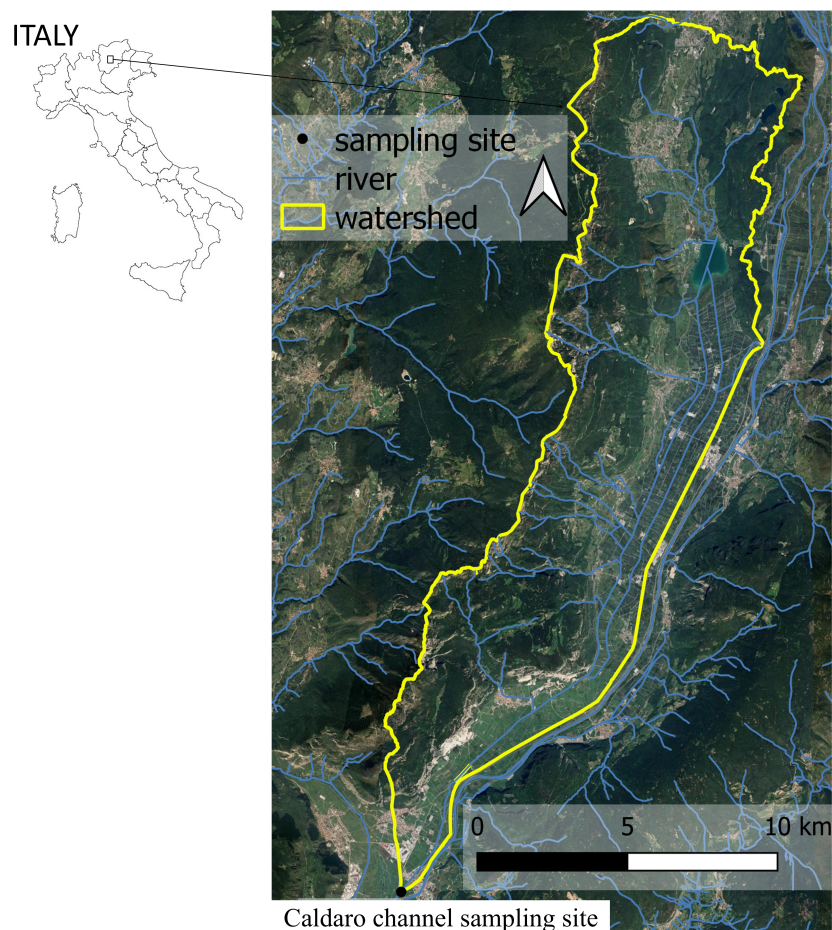


Figure 4 – Map of the Caldaro canal catchment and location of the sampling point.

mL of water every 30 minutes during the 14 days of 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 ($<8^{\circ}\text{C}$) and then analysed at the conclusion of the 14-days sampling campaign, following the procedure explained in Section 3.2.1.

4.3 Results and discussion

4.3.1 Investigation of partition between polyethersulfone 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 (Equation 5) 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 (Vermeirssen et al., 2012; Silvani et al., 2017). As reported in Figure 5, the adsorbent capability of PES membrane is typically weak for the pesticides with LogKow lower than 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 $\text{LogKow} \geq 4$ 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, Pardon, and Budzinski, 2014; Bernard, Boutry, Tapie, Budzinski, and Mazzella, 2018; Endo and Matsuura, 2018; Noro, Endo, Shikano, Banno, and Yabuki, 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 and Matsuura, 2018; MacKeown et al., 2022; MacKeown et al., 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 (Figure 5).

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 (Figure 5) can be justified by the fact that, besides the polarity, other physico-chemical properties of the analytes affect the accumulation in the PES membrane, such as: ionisation of the pollutant (Morin et al., 2018), occurrence of $\pi - \pi$ interactions between aromatic rings of the PES and the aromatic rings of the pesticides (Silvani et al., 2017), and others (Estoppey et al., 2019, Suchana and 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.

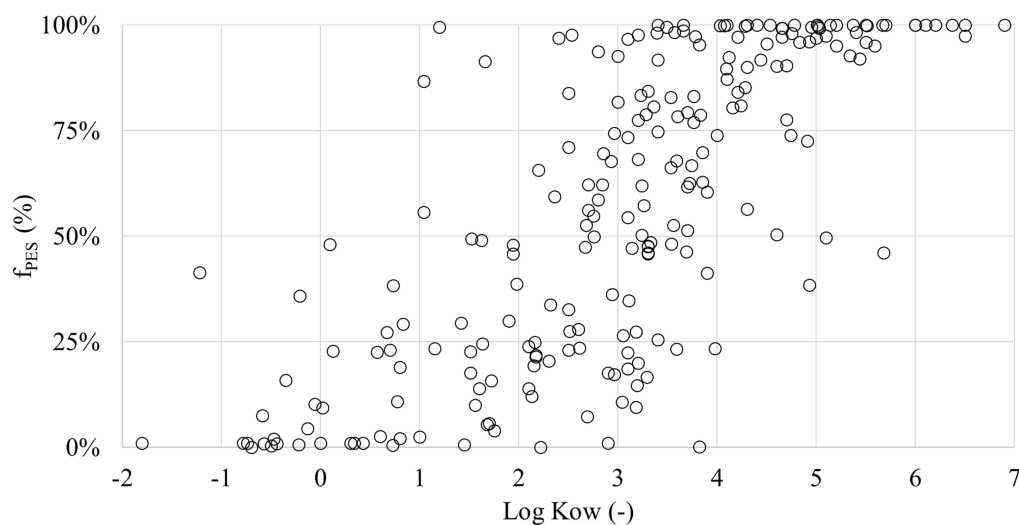


Figure 5 – Fraction (f_{PES}) of the mean accumulated mass of analyte in the PES membrane to that in the total POCIS, for the examined compounds ordered according to their polarity (LogKow). Numerical values are reported in the Table 12.

4.3.2 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 were detected in water at an average concentration higher than LOD and for which the variation of concentration 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 3.3 has been calculated. Figure 6 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, Chepchirchir, Zhou, Paschke, and Schüürmann, 2020, Suchana and 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.

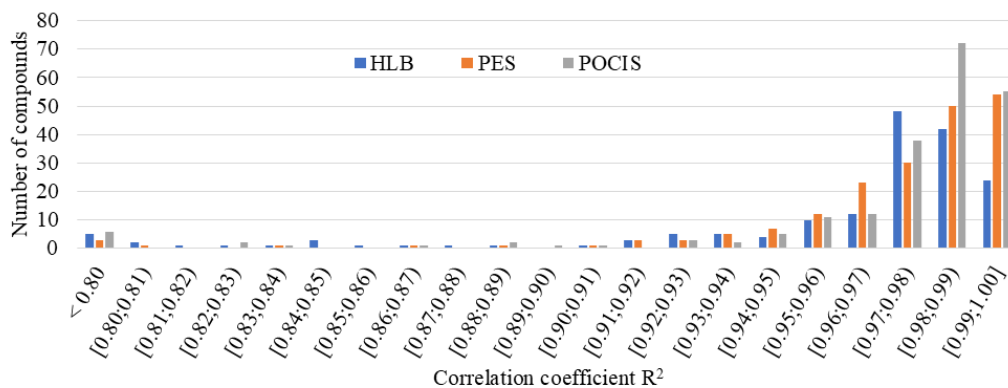


Figure 6 – Distribution of R^2 values for the two sampler compartments and for the entire POCIS

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 Figure 7). The values of $R_{S,PES}$ assumed a median value (5^{th} , 95^{th} percentage) of 0.214 (0.009, 1.172) L day⁻¹, while the $R_{S,HLB}$ assumed a median value (5^{th} , 95^{th} 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 Figure

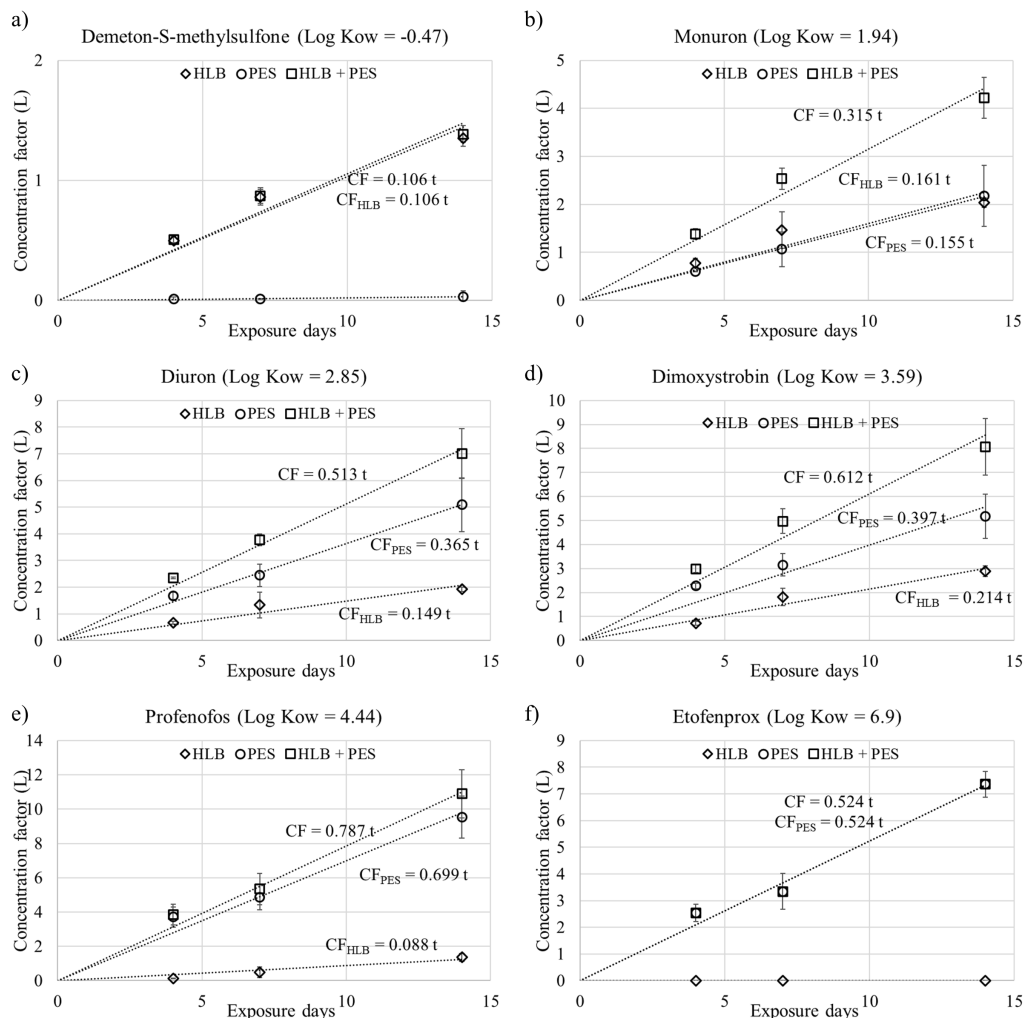


Figure 7 – Uptake trend in terms of concentration factors (CF_{HLB} , CF_{PES} and CF) over time: a) demeton-S-methylsulfone, b) monuron, c) diuron, d) dimoxystrobin, e) profenofos and f) etofenprox.

8(a,b). 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 Figure 8d);
- 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 (5^{th} , 95^{th} percentiles) equals 0.313 (0.062, 1.194) L day⁻¹. Figure 8c 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.

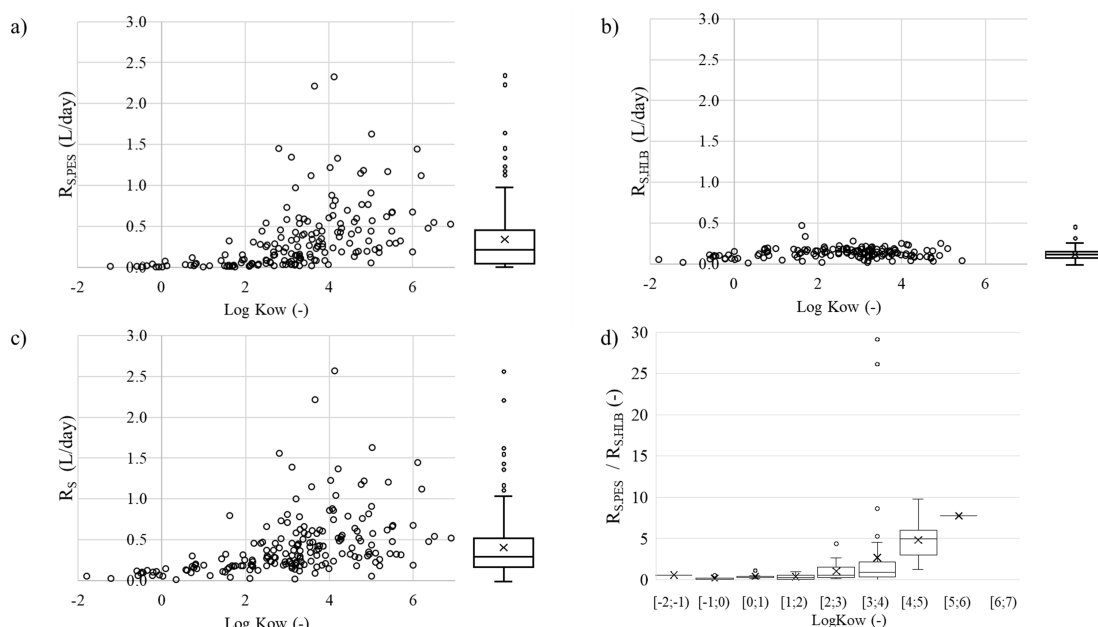


Figure 8 – Values of sampling rate arranged in polarity order, plotted for: a) PES membrane, b) Oasis HLB phase and c) POCIS. d) Ratio between $R_{S,PES}$ and $R_{S,HLB}$ for the molecules which have been adsorbed from both sampler compartments. In the sections a), b) and c) were reported the distribution of sampling rates in boxplots. Numeral values are reported in Appendix D (Table 13).

4.3.3 Polyethersulfone (PES) membrane 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 Figure 9a), 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 Figure 9b). 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 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.

4.3.4 Results from field activities

Here differences between the results obtained in the laboratory and obtained in the field 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,

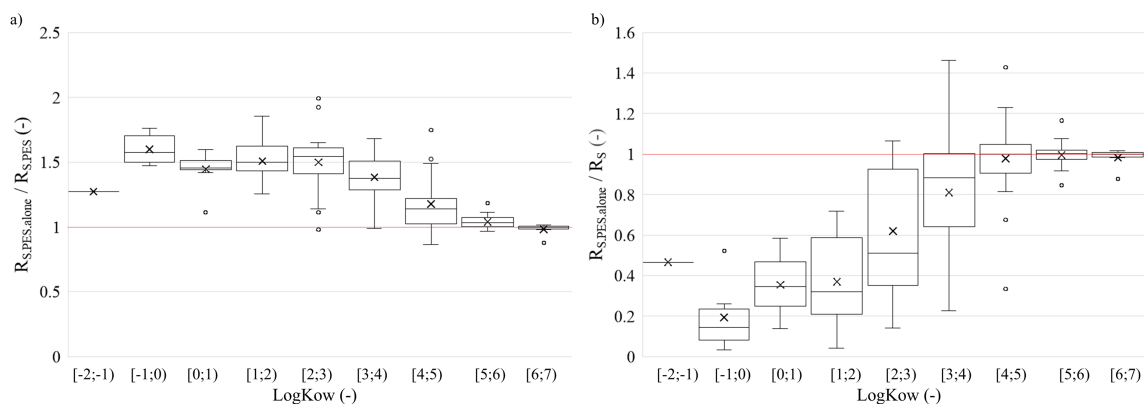


Figure 9 – Distributions of the ratio a) between the $R_{S,PES,alone}$ and the $R_{S,PES}$ and b) between the $R_{S,PES,alone}$ and the R_S . The distributions (boxplots) are arranged in polarity order (LogKow).

was calculated using the data collected from the field (Equation 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 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 Figure 10. A t-test ($\alpha=0.05$) was adopted to evaluate if there were significant differences between the results obtained from laboratory tests and from field sampling following the procedure explained in paragraph 4.2.2. A significant discrepancy was evidenced for 5 compounds, see asterisked molecules in Figure 11. 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

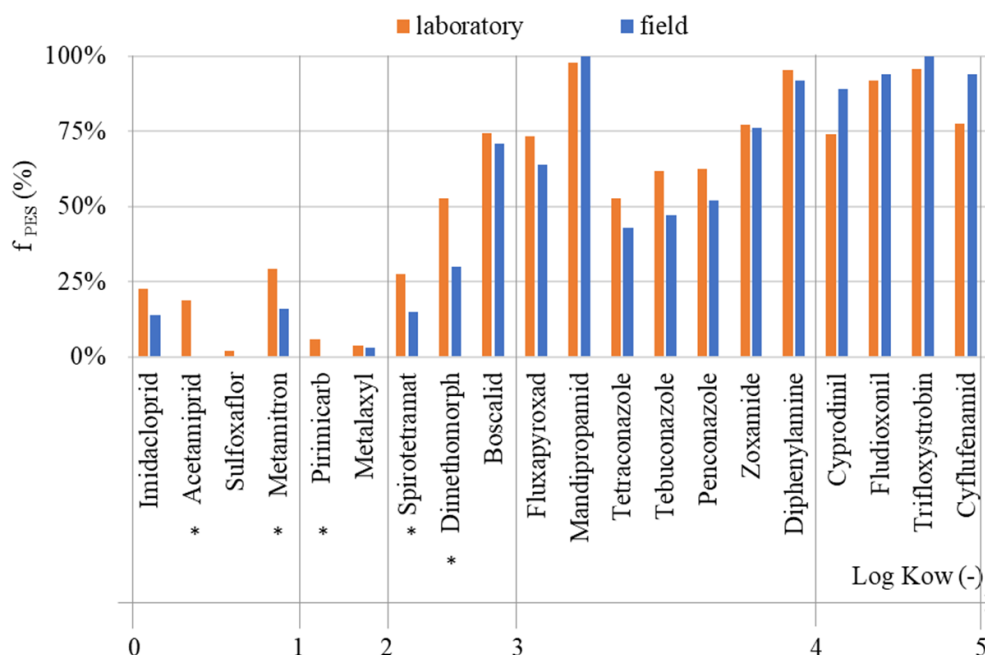


Figure 10 – Percentage of adsorbed amount by PES membrane in laboratory experiments and in the field. Compounds are arranged for increasing value of LogKow. ★ The asterisked molecules exhibited a significant difference between the results obtained in the laboratory and in the field (t-test, $\alpha=0.05$), following the procedure explained in paragraph 4.2.2.

in water for the following molecules was lower than the LOD for at least 8 days out of 14: cyflufenamid, 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 Figures 10 and 11, 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

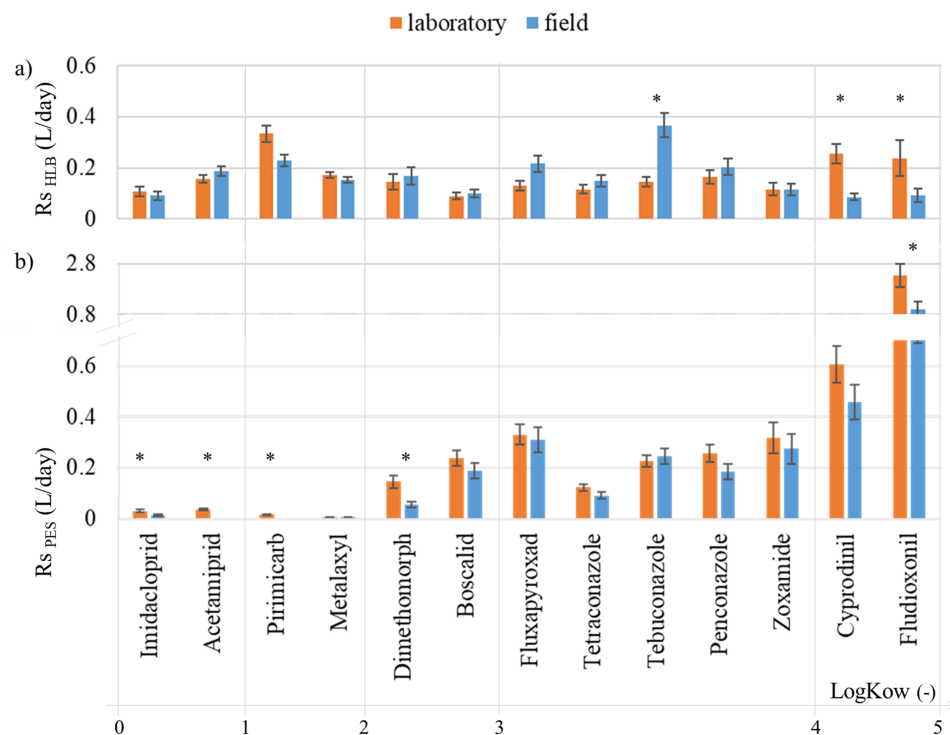


Figure 11 – Value of sampling rates a) $R_{S,HLB}$ b) $R_{S,PES}$ estimated from laboratory experiments and from the field sampling campaign. * Asterisked molecules indicate that the ratio of field and laboratory sampling rates differs by a factor greater than 2.

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).

4.4 Conclusions

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.

CHAPTER 5. VALIDATION OF A CALIBRATION MODEL ABLE TO ESTIMATE THE CONCENTRATION OF PESTICIDES IN AN ALPINE STREAM THROUGH PASSIVE SAMPLING (POCIS) MONITORING

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5.1 Abstract

The Polar Organic Chemical Integrative Sampler (POCIS) is a passive sampler composed of a receiving phase, Oasis HLB, enclosed between two polyethersulfone (PES) membranes. It is used for monitoring organic compounds in surface water and in groundwater. Measurements of pesticides concentration by passive samplers in streams still represents an open challenge, which limits their use in environmental monitoring of the quality status of water bodies in accordance with the EU Water Framework Directive. We addressed these limitations by calibrating a POCIS with concentration measurements performed on samples collected by means of an automatic sampler from the same section of the small alpine river where the passive sampler was deployed. In the majority of published studies, the analytes were extracted only from the phase but recent works show that some compounds were also adsorbed by the PES membrane, suggesting the importance of extracting the analytes from both the phase and the membrane. The POCIS was calibrated for 31 compounds, from the comparison between the total amount of pesticides adsorbed by POCIS (M_s) and the Time-Weighted Average concentration (TWAc) obtained from several grab sampling, through the estimation of the sampling rate (R_s), which allow to link the M_s

with the TWAc over time. The data showed an increasing R_s trend with hydrophobicity for the most hydrophobic and hydrophilic compounds, while compounds with $1.5 \leq \text{LogKow} \leq 3.5$ assumed value of R_s independent of LogKow. The contribution of PES membranes allow to expand the calibration of R_s to the most hydrophobic compounds and allow monitoring of pesticides that would hardly have been detected if they were extracted only from the Oasis HLB phase, such as fluazinam. The calibration was then verified on the same stream and the model extended to a different sampling site; in both cases, this calibration allowed to estimate a value of TWAc which fits with the reality within a factor of 5, and in the majority of cases within a factor of 2. If this level of accuracy is accepted, the R_s reported here can be used to estimate TWAc from sampling with POCIS.

5.2 Materials and methods

5.2.1 Sampling sites

Five sampling campaigns were carried out in two sites, four on the Ribosc stream and one on the Caldaro channel, both located in the Trentino Region (Figures 12 and 13). The Ribosc is a small alpine stream, whose catchment is 31.5% covered by agricultural land. Farmlands mainly consist of apple orchards through intensive agriculture that releases pesticides to the water bodies by runoff and infiltration. The sampling site (coordinates 46°21'5.77"N and 11°02'45.93" E; WGS84) allows monitoring of the surface runoff that drains a catchment area of 12.5 km². The fifth sampling campaign was conducted on the Caldaro artificial channel, which is the main canal draining a large network of agricultural ditches, and a few local springs, at the floor of the Adige valley, which is the main floodplain of the entire region. The sampling site in the Caldaro channel (coordinates 46°11'34.7"N and 11°07'18.9"E; WGS84) allows monitoring of the drainage contribution of a catchment area of 160 km², chiefly used for intensive cultivation of apples and grapes.

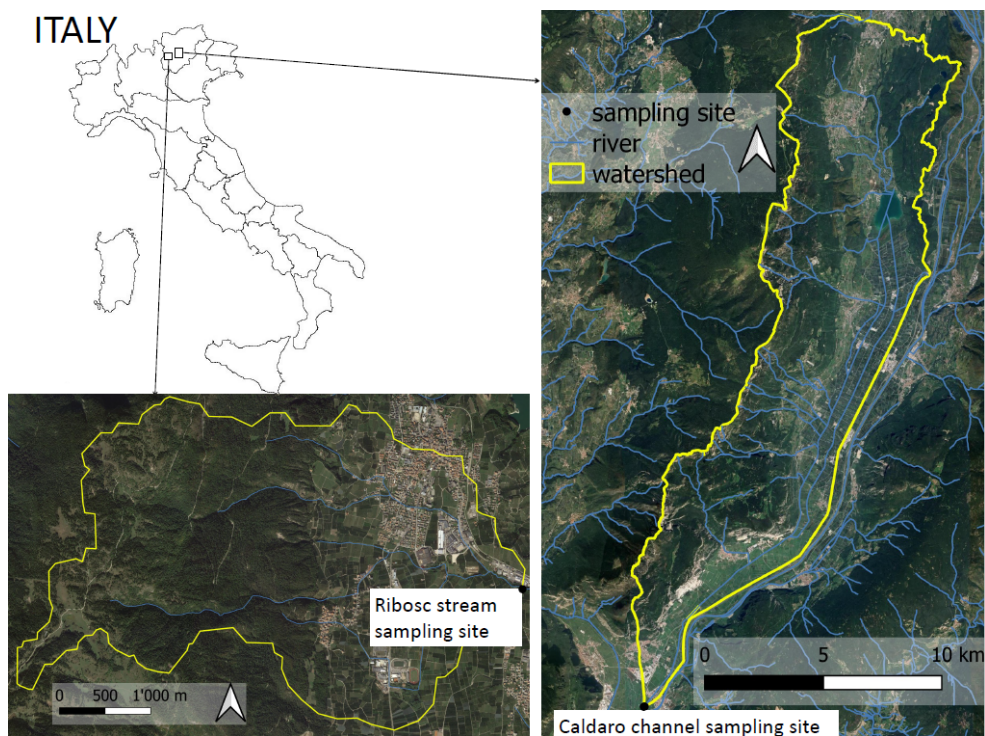


Figure 12 – Map of the draining catchments with location of the sampling sites (Google Maps 2023).

5.2.2 Sampling strategy

During the period from May 2021 to June 2022, four sampling campaigns were conducted on the Ribosc stream. The sampling campaigns were performed using two sampling systems synchronously (frequent grab method and POCIS deployment), two campaigns in 2021 with each for a duration of 28 days (from 13/05 to 10/06/2021 and from 10/06 to 8/07/2021) and two campaigns in 2022 with each for a duration of 21 days (from 06/05/2022 to 27/05/2022 and from 27/05/2022 to 17/06/2022). The sampling by POCIS followed the scheme reported in figure 14: four (in 2021) and three (in 2022) triplicates of POCIS were immersed in water simultaneously at the beginning of each sampling campaign and at the end of each week one of them was collected, leaving the remaining in the stream. The automated sampling equipment was set to collect 100 mL of water every 30 minutes throughout the sampling period and the collected volume was stored in one litre glass bottles which were drawn and replaced every 2 days. The collected water samples and



Figure 13 – Illustrative photos of the sampling sites. a) Ribosc stream, b) Caldaro channel.

POCIS were kept on ice in a thermal box and transported to the laboratory refrigerator ($< 10\text{ }^{\circ}\text{C}$). Then, methanol was added (1% v/v final) to the water samples to avoid the proliferation of algae and bacteria. Finally, the water samples and POCIS were analysed within 10 days from their collection. In parallel, the sampling campaign on the Caldaro channel was carried out following the same procedure explained above, but using three replicates of POCIS for a period of 21 days (from 13/05/2022 to 03/06/2022).

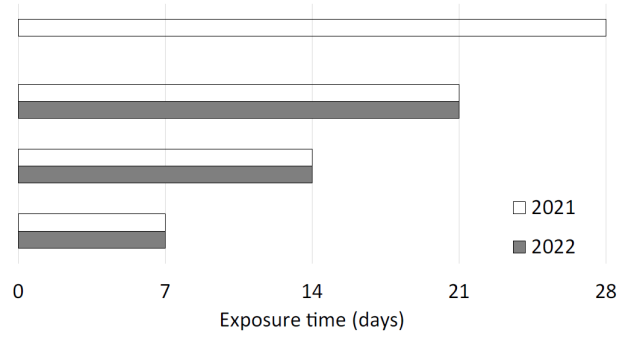


Figure 14 – Deployment period of POCIS triplets on the Ribosc stream, during the sampling campaigns carried out in 2021 and 2022.

5.2.3 Characterization of the streamflow and temperature regimes

During all the sampling campaigns on the Ribosc stream, field conditions were monitored using a multiparametric sensor, which continuously recorded river water temperature and water surface level at the sampling site at time steps of 1 hour and 5 minutes, respectively. To convert continuous flow depth data into discharge data, a stage-discharge rating curve was reconstructed (see Figure 15). To this aim, fourteen discharge measurements were performed at different flow conditions through the salt dilution method (Kilpatrick and Cobb, 1984). This allowed to estimate the stage (Y) - discharge (Q) rating curve, by fitting the measured data with a power law of the type:

$$Q(Y) = a Y^m \quad (7)$$

where the dimensionless coefficients a and m (>1) are determined by fitting the measured data.

The salt dilution method (ISO-9555-1, 1994) is an indirect method which allows an accurate estimation of the flow rate without requiring knowledge of the cross-section bathymetry, which is particularly convenient in small mountain streams with complex morphology and roughness (Farò, Politti, Speltoni, Bertoldi, and Zolezzi, 2021). Briefly, the method con-

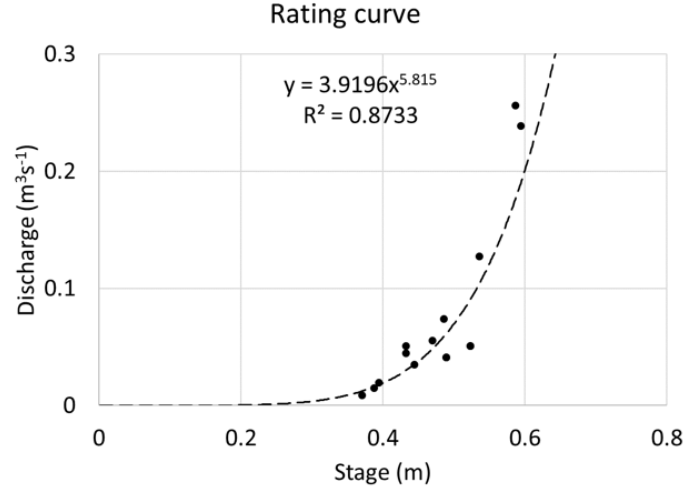


Figure 15 – Stage-discharge rating curve reconstructed on the Ribosc sampling station through instream measurements with the salt dilution method.

sists of releasing a known amount of NaCl (M_{salt}) into the watercourse, which generates an increase in conductivity that propagates downstream. Two conductimeters are deployed close to the left and right banks on the channel bed to record the variation of the electrical conductivity ($C(t)$), at a suitable downstream distance from the release section to ensure complete transverse mixing. Such distance is typically of the order of several tens of channel widths (Fischer, 1966), depending on the river morphological and roughness characteristics. The discharge can finally be computed through the following equation:

$$Q = \frac{M_{salt}}{k \int C_{net}(t) dt} \quad (8)$$

where k is the calibration coefficient and $C_{net}(t)$ is the net conductivity, that is the difference between the conductivity recorded and the base conductivity of the watercourse, and the integral is extended between the time of release and the end of the experiment, when the measures $C(t)$ returns to the initial value prior to the salt release. A standard value of k equal to 0.5 has been used, which has been verified in the field by measuring the conductivity of the stream water samples to which known amounts of salt have been progressively added. For the Caldaro channel, the discharge series was provided by the

local authorities and the water temperature was measured manually two times a day.

5.3 Results and discussion

The presentation and discussion of the results of the analysis is organised as follows: first the outcomes of the POCIS calibration models for the investigated compounds are presented (5.3.1), then the models are validated to assess their robustness (5.3.2) and the model transferability to a different water body is assessed (5.3.3). Finally, the relevance of the present investigation for the assessment of the chemical status of the study sites is discussed (5.3.4).

5.3.1 *In situ* POCIS calibration

First the variability of field conditions and of R_s among samplings was assessed. During the sampling campaigns no significant changes in the streamflow were observed except during a few short flooding events lasting two hours or less. The three sampling campaigns were conducted under similar environmental and hydraulic conditions with the water as shown by the little variability of water discharge. During the three sampling, the discharge took median values (5th, 95th percentiles) of: 0.041 (0.023, 0.089), 0.020 (0.011, 0.071) and 0.021 (0.010, 0.63) $m^3 s^{-1}$, respectively; while temperature recorded median values (5th, 95th percentiles) of: 12.3 (9.4, 15.8), 13.8 (11.1, 17.8) and 14.1 (10.9, 18.3) °C, respectively (see Figure 16).

Each sample was then investigated for the presence of 319 compounds, which were selected taking into account the large differences in agronomic and physicochemical properties, and to cover a wide range of polarities, from -2 to 7 of LogKow units. The POCIS calibration was performed by considering the analytical results achieved in the first three sampling campaigns (Ribosc stream) and to the pesticides that were detected by both sampling methods. The number of compounds detected using POCIS ranged from 38 to 45,

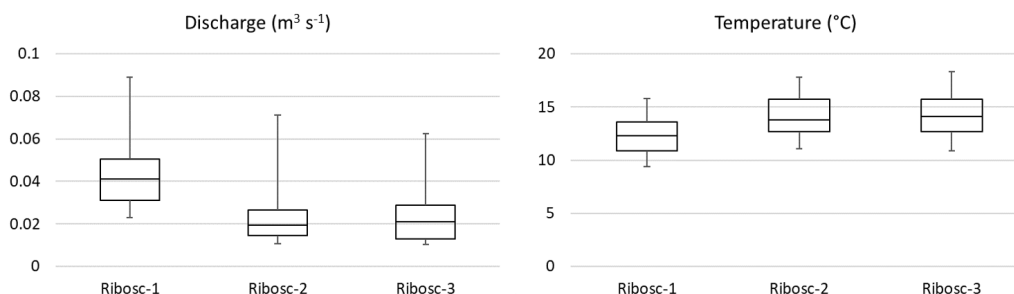


Figure 16 – Range of variability of discharge and water temperature during the sampling periods on the Ribosc stream; expressed in terms of boxplots indicating the 5th, 25th, 50th, 75th and 95th percentiles.

while, using the grab sampling method, their number in the weekly average water samples ranged from 36 to 40. The compounds satisfying the above criteria were 31 and covered a polarity range from 0.3 to 4.91 Log Kow units (see Table 1). Among the compounds that did not satisfy these criteria there were carbaryl and chlorpyrifos methyl, which could be frequently detected using POCIS, but not by means of the grab sampling. In general, most of the compounds were detected at a TWA concentration over 21 days (TWAc21d) lower or equal to $0.010 \mu\text{g L}^{-1}$ and often just above the LOD. Instead, the amount of pollutants adsorbed by POCIS after 21 days of exposure ranged from 0.001 to $1.644 \mu\text{g}$, being fluazinam the most adsorbed.

The sampling carried out in 2021 have been performed over 28 days because Silvani et al (2017) observed a linear absorption regime for alkylphenol over 28 days of exposure, both on the Oasis HLB phase and on the PES membrane. However, in our experiments it was observed that the Concentration Factor (CF, Figure 17) seems to vary linearly over the 28 days of exposure only for 5 compounds (fluazinam, metamitron, piperonyl-butoxide, pyraclostrobin and terbutryn), while for the others compounds the CF seems to have a fairly linear trend if only 21 sampling days were considered. Consequently, for the POCIS calibration it was choose to use a linear model over 21 days, which allow to obtained the trend that better mime the available data. The calibration model was developed with the data

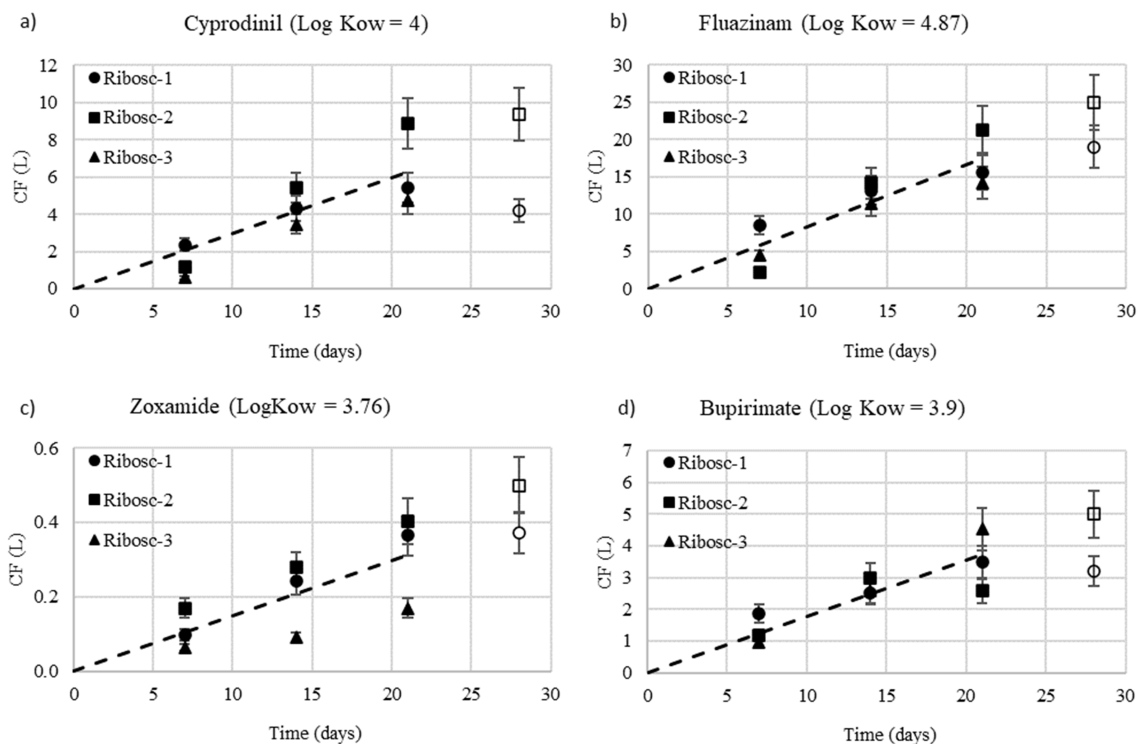


Figure 17 – Four examples of uptake regimes by POCIS; Concentration Factor (CF, litre) after 7, 14 and 21 exposure days. The CF after 28 exposure days, data that are not used for the calibration, are reported as open symbols. The dashed line represents the calibration straight line, calculated using the three sampling campaigns together. All similar plots for each calibrated compound are reported in Appendix E (Figure 31).

collected up to day 21 in 2021 and a shorter POCIS exposure time was then adopted in the following spring 2022 campaigns. On the basis of this evidence, we suggest to limit the exposure time of POCIS during field monitoring to 14 or 21 days, to avoid the underestimation of the pesticide TWA concentration in water, which would result from assuming a longer linear uptake regime, in agreement with what suggested by other authors (Challis, Stroski, Luong, Hanson, and Wong, 2018; Mathon et al., 2022). A longer exposure may be desirable for increasing sensitivity, but it may reduce the accuracy due to the change in the accumulation rate in the last part of the exposure.

Some differences are also expected among the field campaigns, because of the possible interference of the suspended inorganic matter, the dissolved organic matter or biofouling, on the adsorption mechanism, which may influence the uptake regime (Charlestra et

al., 2012; Djomte et al., 2018; Djomte et al., 2020; Harman et al., 2012; Lissalde et al., 2014). Therefore, the statistical differences of the R_s of the investigated compounds in the three campaigns were tested. Analysis of variance (ANOVA; $\alpha = 0.05$) evidenced significant differences in R_s for 9 compounds (cyflufenamid, difenoconazole, dimethomorph, propiconazole, pyraclostrobin, spirotetramat-ketohydroxy, tetraconazole, triflumuron and zoxamide), confirming for them a not negligible impact of the aforementioned phenomena on the normal absorption conditions, even without identifying any dominant environmental factor that affects the R_s values. For other 22 compounds, the ANOVA test did not identify statistical differences between the R_s recorded in the three sampling campaigns. Therefore, for all the 31 compounds, a single value of R_s was estimated on the basis of data from the three in situ campaigns (as described in section 2.5) and the existing uncertainty of the field data was accepted. The estimated values of R_s are reported in table 1 and varied from 0.015 to 0.836 L day⁻¹ with a median value at 0.106 L day⁻¹. From the estimation of the linear regression lines were calculated the relative standard deviation (RSD) of the R_s which varied between 7% and 30%, while the correlation coefficients (R^2) of the regression linear models were generally higher than 0.80 (except for pyraclostrobin, $R^2 = 0.76$). The compounds that showed the most divergent absorption regime were fluazinam and zoxamide (Figures 17b,c) with the highest and lowest R_s values being respectively 7.9 times higher and 7.1 times lower than the overall median R_s (0.106 L day⁻¹).

We also investigated whether R_s was correlated to hydrophobicity, plotting R_s against LogKow (see Figure 18) and investigating the regression lines that best fit the data. The polarity domain can be divided into three intervals within which a similar trend is observed. In the first case, the most hydrophilic compounds, with a LogKow lower than 1.5, displayed R_s values lower than the median R_s value, referred to the entire dataset. In addition, it was seen that for these compounds the R_s followed a weakly increasing trend with the LogKow. For compounds with LogKow values between 1.5 and 3.5, the R_s seem to be independent

Table 1 – Calibrated compounds with their: usage, polarity (Log Kow), estimated R_s , relative standard deviation (RSD) of R_s and correlation coefficient R^2 (n=9).

Compound	Use	Log Kow	R_s (L day ⁻¹)	RSD ¹	R^2
6-Benzyladenine	PGR	2.16	0.091	26%	0.81
Acetamiprid	I	0.8	0.097	9%	0.97
Boscalid	F	2.96	0.113	14%	0.93
Bupirimate	F	3.9	0.177	11%	0.96
Carbendazim	F	1.51	0.131	14%	0.94
Chlorantranilprole	I	2.76	0.099	7%	0.98
Cyflufenamid	F	4.7	0.192	15%	0.92
Cyprodinil	F	4	0.298	15%	0.92
Difenoconazole	F	4.4	0.487	19%	0.89
Dimethomorph	F	2.68	0.068	23%	0.84
Ethirimol	F	2.22	0.053	15%	0.92
Flonicamid	I	0.3	0.03	15%	0.93
Fluazinam	F	4.87	0.836	11%	0.96
Fluopyram	F	2.06	0.072	17%	0.9
Fluxapyroxad	F	3.1	0.108	14%	0.93
Imidacloprid	I	0.57	0.054	20%	0.87
Metamitron	F	0.83	0.045	16%	0.91
Penconazole	F	3.72	0.144	15%	0.92
Penthiopyrad	F	3.9	0.113	9%	0.97
Piperonyl-Butoxide	I	4.75	0.226	7%	0.98
Pirimicarb	I	1.7	0.094	9%	0.97
Propiconazole	F	3.72	0.104	26%	0.8
Pyraclostrobin	F	3.99	0.084	30%	0.76
Pyrimethanil	F	2.84	0.208	8%	0.98
Spirotetramat-ketohydroxy	I	N.F.	0.132	21%	0.86
Sulfoxaflor	I	0.8	0.064	14%	0.94
Tebuconazole	F	3.7	0.207	13%	0.94
Terbutryn	H	3.65	0.162	12%	0.95
Tetraconazole	F	3.56	0.068	14%	0.94
Triflumuron	I	4.91	0.166	19%	0.89
Zoxamide	F	3.76	0.015	19%	0.89
F = fungicides; H = herbicide; I = insecticide; PGR = plant growth regulator; N.F. = not found					
¹ relative standard deviation of the regression line calculated by the least squares regression line method.					

of LogKow, with a median value of 0.099 L day⁻¹ (similar to the median value of the entire dataset) and a narrow range of variability (from 0.053 to 0.208 L day⁻¹). It follows that for the compounds within this polarity range a single value of R_s (such as the median value) can reasonably be assumed. Finally, the most hydrophobic compounds, with a LogKow higher than 3.5, tended to display a R_s value larger than the entire dataset median, and which followed an increasing trend with LogKow. This behaviour is probably due to the adsorption capability of the PES membrane that increases for the most hydrophobic compounds, as reported by Silvani et al. (2017). Unfortunately, the fitting was too poor to

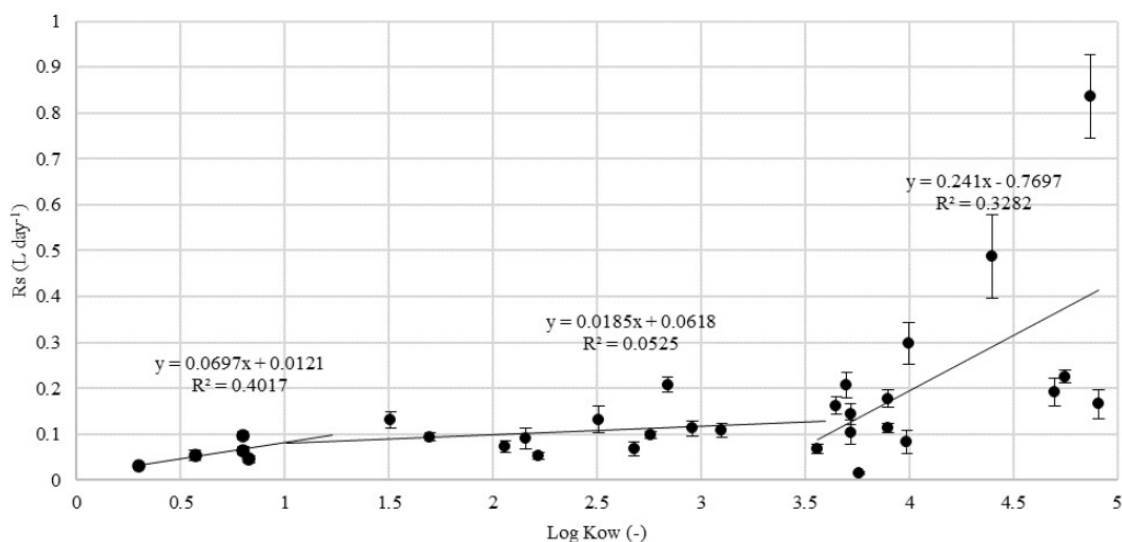


Figure 18 – Correlation between R_s and Log Kow. Each dot represents a compound, the error bars correspond to the SD, the continuous lines represent three possible regression lines.

predict the R_s value based on the polarity of the compound; indeed, zoxamide and bupirimate have a similar value of LogKow but markedly different values of R_s (Figure 17c,d). For these reasons we conclude that defining a robust, general relationship between R_s and the polarity of compounds may not be appropriate, as also pointed out by Wang et al., 2020.

Unfortunately, to the best of our knowledge, no previous work addressed this topic for these compounds by extracting these pesticides from both the Oasis HLB phase and the PES membrane. For this reason, it was chosen to compare the estimated value of R_s with $R_{s,HLB}$ data reported by previous studies (Ahrens et al., 2015; Bernard et al., 2019; Berton, Brugnera, and Does, 2018; Ibrahim, Togola, and Gonzalez, 2013b), which were obtained from laboratory (instead of field) calibrations and from the extraction only from Oasis HLB phase. The comparison was done for 13 compounds, using values of sampling rates appropriately normalised on the basis of the Oasis HLB quantity used in the POCIS sampler (Table 2). The comparison highlights two behaviours. A first group of compounds shows a R_s lower than $R_{s,HLB}$ by a factor in the range 1.5 – 12. A similar phenomenon was also

observed by Ibrahim, Togola, and Gonzalez, 2013a when comparing the $R_{s,HLB}$ estimated in field and laboratory conditions. This reduction of sampling rate passing from laboratory to field conditions could be related to different hydraulic and environmental conditions. An opposite behaviour was noticed instead for the most hydrophobic compounds, especially with $\text{Log Kow} \geq 3.99$; which have shown a R_s value higher than $R_{s,HLB}$ by a factor 2.05 - 70. Silvani et al. (2017) reported that the accumulation on the PES membrane increases with the hydrophobicity, so this phenomenon can be due to the PES membrane contribution. In addition, it is worth noting that the proposed POCIS total extraction (phase plus membrane) made it possible to detect and quantify compounds that were not found in previous POCIS-based studies. Some of these studies, for instance, extracted only the POCIS phase (Oasis HLB), and could not detect compounds such as fluazinam, which were instead detected using the direct grab sampling (Ahrens et al., 2015). The presented update on the POCIS method has therefore significantly enhanced sampling sensitivity, in terms of R_s , and expanded the number of compounds that can be monitored.

Table 2 – Comparison of R_s estimated in this study with $R_{s,HLB}$ values available in the literature (the data was normalised with respect to the amount of Oasis HLB phase used and expressed in terms of $\text{mL g}^{-1} \text{day}^{-1}$).

Compound	LogKow	R_s	literature $R_{s,HLB}$ ($\text{mL g}^{-1} \text{day}^{-1}$)				$R_s/R_{s,HLB}$ mean ratio
			Ahrens et al. 2015	Berton et al. 2018	Ibrahim et al. 2013a	Bernard et al. 2019	
Imidacloprid	0.57	0.27	0.818	-	-	1.13	0.28
Acetamiprid	0.8	0.485	1.727	0.909	-	-	0.37
Carbendazim	1.51	0.655	1	-	-	1.52	0.52
Pirimicarb	1.7	0.47	1.682	-	-	1.18	0.33
Dimethomorph	2.68	0.34	-	-	-	1.205	0.28
Terbutryn	3.65	0.81	9.636	-	-	-	0.08
Tebuconazole	3.7	1.035	-	-	-	0.895	1.16
Penconazole	3.72	0.72	0.773	-	1.395	-	0.66
Propiconazole	3.72	0.52	0.8	-	-	-	0.65
Pyraclostrobin	3.99	0.42	0.136	-	-	-	3.08
Cyprodinil	4	1.49	0.727	-	-	-	2.05
Difenoconazole	4.4	2.435	0.273	-	-	-	8.93
Cyflufenamid	4.7	0.96	0.014	-	-	-	70.4

As it was reported at the beginning of this section, not all the compounds could be

detected using both sampling approaches, but interestingly 2 compounds (carbaryl and chlorpyrifos methyl) were detected exclusively with the proposed POCIS sampling. This phenomenon was explained by studying the stability of these compounds in water and observing that their concentration in the water samples stored before the analysis halved in only 2 days, while the same pesticides adsorbed on POCIS phase or membranes were preserved. Obviously, optimal results could also be obtained with direct sampling, provided that these unstable compounds are extracted immediately after having sampled the water, which however does not allow the production of the weekly average, thereby requiring a larger number of instrumental analyses in order to evaluate the weekly average.

5.3.2 Calibration model robustness

The calibration model robustness was verified using data collected from a fourth sampling campaign carried out on the Ribosc stream from 27/05/2022 to 17/06/2022. During this sampling, the field conditions, both in terms of discharge and water temperature, were similar to those recorded in the previous sampling campaigns. From the analysis of the samples collected during this last campaign it appears that all the 31 calibrated substances were still present and available for the comparison. For each compound, the TWA concentration was calculated from the adsorbed pesticide found using the passive samplers (M_s), using Equation (9) and assuming integrative sampling during the entire exposure ($TWAc_{POCIS}$).

$$TWAc_{POCIS} = \frac{M_s}{R_s t} \quad (9)$$

The standard deviation of $TWAc_{POCIS}$ was calculated from estimated standard deviation of R_s derived from in situ calibration campaigns, and from the analytical uncertainty, by applying the law of error propagation (Brown and Hambley, 2002). The calculated values of $TWAc_{POCIS}$ were compared with those measured in the same period but using the grab sampling ($TWAc$) and results are reported in figure 19a. It can be observed

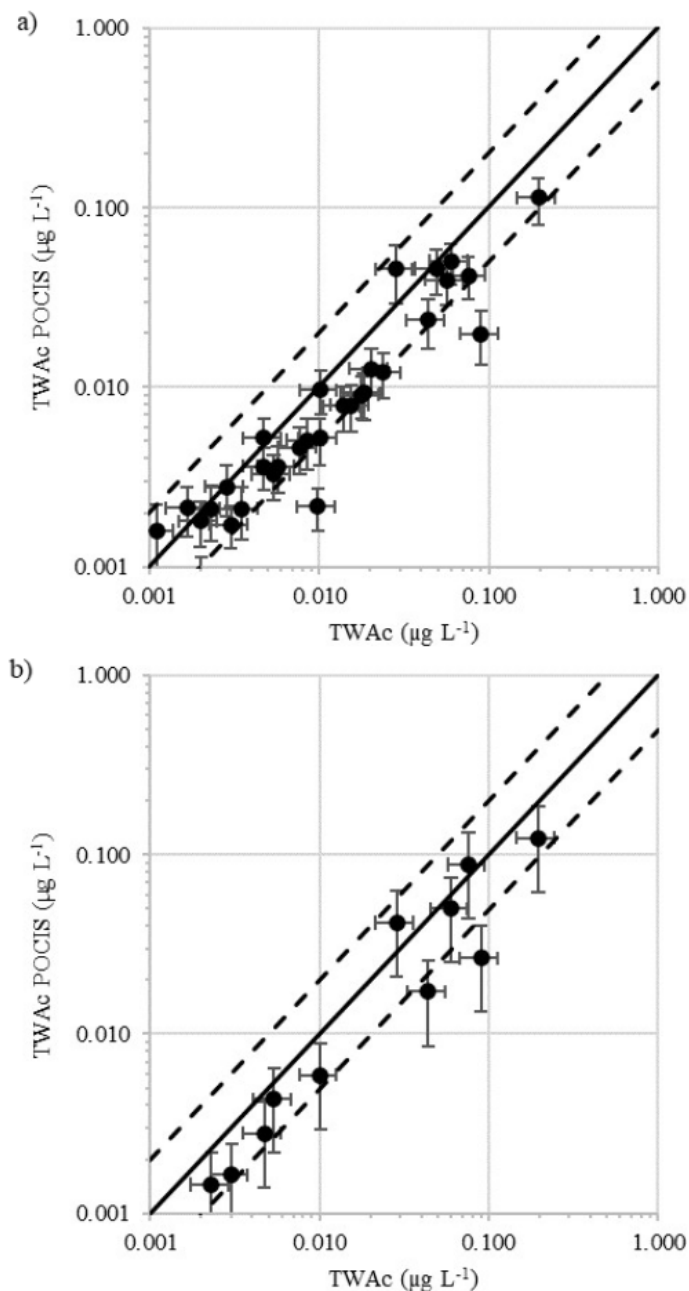


Figure 19 – Comparison between TWAcPOCIS (calculated from POCIS sampling and using the calibrated R_s) and TWAc (measured by frequent grab sampling) on the Ribosc stream, reported in a bi-logarithmic graph. a) TWAcPOCIS calculated using the R_s specific for each compound. b) Comparison between the TWAcPOCIS calculated using the R_s specific for each compound (circle) and TWAcPOCIS calculated using the median value of R_s (square), only for the compounds with $1.5 \leq \text{LogKow} \leq 3.5$. Each dot represents a compound, the error bars correspond to the SD, the continuous line represents perfect equality and the area between the parallel dashed lines delimits the range in which both compared values differ by a factor of less than 2.

that the large majority of the studied compounds (28 of 31) are characterised by a ratio TWAcPOCIS/TWAc falling within the range 0.5 - 2, while acetamiprid (TWAcPOCIS/TWAc = 0.22; TWAc = 0.010 $\mu\text{g L}^{-1}$), propiconazole (0.41; 0.002 $\mu\text{g L}^{-1}$) and spirotetramat-ketohydroxy (0.22; 0.090 $\mu\text{g L}^{-1}$) fell outside such range. Excluding acetamiprid and spirotetramat-ketohydroxy, for which the discrepancy between the two methods reached 78%, the calibration modelling demonstrated satisfactory robustness for more than 90% of the tested compounds. Previous work considered a good match between pesticide measurements derived from passive and active samplings when the ratio between TWAcPOCIS and TWAc was in the range between 2 and 3 (Ahrens, Daneshvar, Lau, and Kreuger, 2018; Criquet et al., 2017; Ibrahim et al., 2013a). Coherently with these results, it can be stated that the proposed calibration performed through in-situ field experiments allows a good estimation of the TWA values for a large selection of pesticides. A good match was also found for the majority of the molecules for which R_s was more sensitive to changes in environmental conditions (via ANOVA test, section 5.3.1).

Finally, for those compounds with LogKow values between 1.5 and 3.5, it was tested the possibility to use their R_s median value (0.099 $\mu\text{g L}^{-1}$) to estimate the TWA concentration, as proposed in section 5.3.1 (figure 19b). From the comparison between the TWAcPOCIS, calculated in this way, and the TWAc, estimated by frequent grab sampling, it can be observed that the large majority of the studied compounds (9 of 11) showed a TWAcPOCIS/TWAc falling in the range 0.5 - 2, while for two compounds (fluopyram and spirotetramat-ketohydroxy) this ratio was in the range 0.5 - 0.29. This further confirms that for the majority of the compounds this approach allows a good estimation of the TWA concentration.

5.3.3 Model transferability to different contexts

The applicability of the proposed POCIS calibration model for the estimation of pesticide concentration was assessed for the Caldaro channel, the main canal of a dense network

Table 3 – Value of TWA concentration calculated for the Ribosc site from the sampling by POCIS (TWAc POCIS), estimated by frequent grab sampling (TWAc) and the ratio between the two amounts. Compounds for which the ratio between the two values is larger than 2 or lower than 0.5 are reported in **bold**.

Compounds	TWAcPOCIS $\pm$ SD ($\mu\text{g L}^{-1}$)	TWAc $\pm$ SD ($\mu\text{g L}^{-1}$)	ratio (-)
6-Benzyladenine	0.046 $\pm$ 0.026	0.029 $\pm$ 0.014	1.6
Acetamiprid	0.002 $\pm$ 0.001	0.010 $\pm$ 0.005	0.22
Boscalid	0.005 $\pm$ 0.003	0.010 $\pm$ 0.005	0.51
Bupirimate	0.01 $\pm$ 0.005	0.010 $\pm$ 0.005	0.95
Carbendazim	0.003 $\pm$ 0.002	0.005 $\pm$ 0.003	0.61
Chlorantranilprole	0.05 $\pm$ 0.025	0.060 $\pm$ 0.030	0.84
Cyflufenamid	0.008 $\pm$ 0.004	0.016 $\pm$ 0.008	0.51
Cyprodinil	0.005 $\pm$ 0.002	0.008 $\pm$ 0.004	0.6
Difenoconazole	0.005 $\pm$ 0.003	0.009 $\pm$ 0.004	0.6
Dimethomorph	0.002 $\pm$ 0.001	0.002 $\pm$ 0.001	0.92
Ethirimol	0.005 $\pm$ 0.003	0.005 $\pm$ 0.002	1.1
Flonicamid	0.004 $\pm$ 0.002	0.006 $\pm$ 0.003	0.63
Fluazinam	0.04 $\pm$ 0.020	0.056 $\pm$ 0.028	0.7
Fluopyram	0.024 $\pm$ 0.012	0.044 $\pm$ 0.022	0.54
Fluxapyroxad	0.113 $\pm$ 0.059	0.196 $\pm$ 0.098	0.58
Imidacloprid	0.002 $\pm$ 0.001	0.003 $\pm$ 0.002	0.6
Metamitron	0.013 $\pm$ 0.007	0.02 $\pm$ 0.010	0.63
Penconazole	0.009 $\pm$ 0.005	0.018 $\pm$ 0.009	0.51
Penthiopyrad	0.009 $\pm$ 0.005	0.018 $\pm$ 0.009	0.51
Piperonyl-Butoxide	0.004 $\pm$ 0.002	0.005 $\pm$ 0.002	0.77
Pirimicarb	0.002 $\pm$ 0.001	0.003 $\pm$ 0.002	0.57
Propiconazole	0.001 $\pm$ 0.000	0.002 $\pm$ 0.001	0.41
Pyraclostrobin	0.002 $\pm$ 0.001	0.001 $\pm$ 0.001	1.44
Pyrimethanil	0.042 $\pm$ 0.021	0.076 $\pm$ 0.038	0.55
Spirotetramat-ketohydroxy	0.020 $\pm$ 0.011	0.090 $\pm$ 0.045	0.22
Sulfoxaflor	0.046 $\pm$ 0.024	0.049 $\pm$ 0.025	0.93
Tebuconazole	0.012 $\pm$ 0.006	0.024 $\pm$ 0.012	0.5
Terbutryn	0.002 $\pm$ 0.001	0.002 $\pm$ 0.001	0.9
Tetraconazole	0.008 $\pm$ 0.004	0.014 $\pm$ 0.007	0.56
Triflumuron	0.002 $\pm$ 0.001	0.002 $\pm$ 0.001	1.28
Zoxamide	0.003 $\pm$ 0.001	0.003 $\pm$ 0.001	0.98

of agricultural ditches draining roughly 160 km² of the Adige river agricultural floodplain. The Caldaro channel is characterised by markedly different hydro-morphological conditions (flow regime, cross-sectional morphology, longitudinal slope, etc.) with respect to the Ribosc stream used for the calibration. Measured water temperature of Caldaro channel varied within a similar interval as in the Ribosc stream; the hydraulic conditions were

almost constant over the sampling period of 21 days, with a streamflow median value (5th, 95th percentiles) of 0.307 (0.271, 0.348) m³ s⁻¹. Although in the sampling period the discharge of Caldaro channel was higher than that of the Ribosc stream, the average flow velocity was comparable, because of the wider cross-section of the latter with respect to the former.

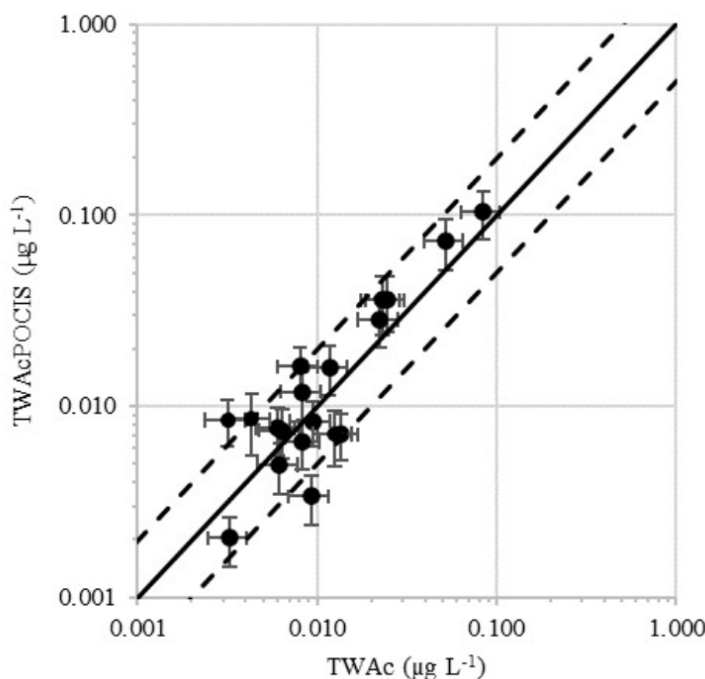


Figure 20 – Comparison between TWAcPOCIS (calculated by POCIS sampling) and TWAc (measured by frequent grab sampling) on the Caldaro channel, reported in a bi-logarithmic graph. Each dot represents a compound, the error bars correspond to the s.d., the continuous line represents the bisector and the area between the parallel dashed lines delimits the range in which both compared values differ by a factor of less than 2.

Following the same approach proposed in section 5.3.2, the TWAcPOCIS values calculated with the calibration model were compared with the TWAc directly measured within the Caldaro channel using grab sampling. Due to the different abundance of pesticides at detectable content in the Caldaro channel, only 19 of the 31 molecules previously found in the Ribosc stream were detected and available for the comparison: acetamiprid, boscalid, carbendazim, chlorantranilprole, cyflufenamid, cyprodinil, dimethomorph, ethirimol, floni-

camid, fluazinam, fluxapyroxad, imidacloprid, penconazole, pirimicarb, propiconazole, spirotetramat-ketohydroxy, tebuconazole, terbutryn and tetraconazole. Figure 20 reports in a bi-logarithmic graph their concentration values, showing that the majority of them (17 of 19) fell within the range $0.5 < \text{TWAcPOCIS}/\text{TWAc} < 2$. The compounds that fall outside this range are (TWAc; TWAcPOCIS/TWAc): acetamiprid ($0.003 \mu\text{g L}^{-1}$; 2.67) and cyprodinil ($0.009 \mu\text{g L}^{-1}$; 0.36). The comparison confirmed that the R_s values, computed from the model are in good agreement with the observations, on the Caldaro channel for the majority of compounds, resulting in acceptable TWAcPOCIS values. Unfortunately, for acetamiprid the estimates were unsatisfactorily for both sites. It is worth highlighting that within the investigated compounds, the proposed approach has made it possible to detect and properly quantify terbutryn, a molecule classified as priority substance by the European WFD and which was present in the Caldaro channel at a TWAc21d from 0.002 to $0.015 \mu\text{g L}^{-1}$, values in any case lower than the limits established by current European regulations.

5.3.4 *Results' implications for the WFD chemical status of the study sites*

Besides allowing the development and validation of POCIS calibration models for a set of relevant pesticides, the sampling campaigns carried out in this study contributed to the assessment of the chemical quality of the two investigated streams in relation to the pressure due to the agricultural activities in the catchment. The Italian legislation “Legislative Decree 152/2006” that implements the Water Framework Directive at the national level sets specific limits for the priority substances (such as terbutryn) and for some other specific pollutants, while for all the other pesticides it fixes a precautionary annual average concentration limit of $0.1 \mu\text{g L}^{-1}$. In addition, it prescribes that the total concentration of pesticides, obtained as the sum of the concentrations of each individual pesticide, must keep below an annual average of $1 \mu\text{g L}^{-1}$. From the comparison of these limits with the detected pesticides concentration in the streams, it was seen that the majority of the com-

pounds had a lower concentration compared to the limits set by the national legislation. Only three compounds, on the Ribosc sampling site, had a TWAc21d that exceeded the limits: fluazinam, during the third sampling campaign; fluxapyroxad, in all the sampling campaigns, and sulfoxaflor, during the second sampling campaigns. The total concentration of pesticides instead exceeded the $1 \mu\text{g L}^{-1}$ limit in the second and the third sampling campaigns in the Ribosc stream. Although higher concentrations than the regulatory limits were recorded for specific periods, it should be remembered that these values refer to the peak of the agricultural season, and not to an entire year, which is the timeframe to which the cumulative legislative limit refers. As the presence of pesticides in water typically follows the trend of farmland activities, the annual average concentration of pesticides is expected to be lower than the values reported here.

It is finally worth mentioning that the presence of compounds whose use is forbidden in Trentino province was also investigated. From the samplings, it emerged that six of the detected compounds are forbidden according to the local environmental regulations of the Trentino Province. Three of these substances can not be used as pesticides (carben-dazim, ethirimol and terbutryn), but they are also the metabolites of allowed pesticides that are currently used. Their presence can therefore be due to degradation processes of other pesticides. Under the assumption that the local environmental regulations are duly respected, the presence of the other three compounds (carbaryl, chlorpyrifos methyl and imidacloprid), can be explained from their accumulation in the agricultural soil that might have occurred in previous years, when their use was permitted and which are now being released in streams through subsurface runoff, especially as a consequence of rainfall and snowmelt events.

5.4 Conclusions

Three field sampling campaigns were performed and the collected data used for developing the POCIS calibration model for 31 pesticides. The choice of extracting the analytes from both the Oasis HLB phase and the PES membrane turned out to be advantageous, because some of these compounds might be not detected if they were extracted only from the Oasis HLB phase. Although the used analytical approach may investigate more than 310 pesticides, the results of this work are limited to the number of compounds which were present in water of the analysed sites.

The field verification demonstrated that the proposed calibration model is able to estimate the value of Time-Weighted Average (TWA) concentration within a factor of 5, but in the majority of cases within a factor of 2, both in the alpine stream used to calibrate the model and a channel draining one of the main agricultural valley floor in the Italian Alps with contrasting hydraulic and environmental conditions. Our work shows that POCIS can be applied in environmental monitoring programs aimed at assessing the temporal and spatial variability of contaminants and pesticides in streams or for comparison with concentration limits set for environmental pollutants if such accuracy is acceptable. Finally, this work suggests extending the use of POCIS for monitoring hydrophobic compounds using the PES membrane as sorbent, and provides environmental agencies with the optimal operating conditions to use POCIS and practical, cheap and transferable tools to estimate the value of TWA concentration.

CHAPTER 6. PESTICIDES MITIGATION IN ALPINE STREAMS: EFFECTIVENESS OF NATURE-BASED AND CONVENTIONAL TREATMENT SOLUTIONS ASSESSED THROUGH POCIS

6.1 Abstract

The reduction of pesticide concentrations in watercourses in agricultural areas is an open challenge. At the European level, the European Union's Water Framework Directive raises awareness of this issue and pushes for the improvement of water quality also through the introduction of technical and nature-based solutions (NBS). Firstly, this work looked for possible relationships between the presence of pesticides in watercourses and the characteristics of the catchments upstream of the sampling sites, such as total area, percentage of land used for agriculture; secondly, it evaluated the effectiveness of one nature-based and one more conventional mitigation solutions in reducing the presence of pesticides in watercourses. For this purpose, sampling was carried out using the Polar Organic Chemical Integrative Sampler (POCIS), a simple and robust passive sampler, which adsorbs increasing amounts of pesticide during a period of time of exposure to stream water. No significant relationship was found between the presence of pesticides in water and upstream catchment characteristics. The examined NBS is a wetland surrounded by agricultural areas, and the more conventional technical solution is a washing plant for agricultural equipment and vehicles coupled with a conventional wastewater treatment plant, serving local farmers. In the case of the NBS, the amount of pesticide adsorbed by POCIS was compared, for the same exposure time, on the tributary and on the emissary of the wetland, recording that overall, after passing through the wetland, the presence of most pesticides compounds in the stream decreases significantly. In fact, the adsorbed amounts of 67.9% of the compounds decreased by more than 50%, with an average decrease of about 77% in the entire

period of sampling. This result shows analogous performance with the few cases that could be found in literature, where similar studies refer to constructed instead of natural wetlands. Finally, as far as the washing plant is concerned, sampling was carried out on the white sewer before and after the work was commissioned. This comparison showed that for 79% of the compounds studied in 2023 and for 84% of the compounds studied in 2024, their adsorbed amount decreased by more than 50% after the starting of operation of the agricultural equipment washing plant.

6.2 Materials and methods

6.2.1 Study areas and sampling strategies

The sampling campaigns were carried out in seven sites all located in Trentino Region in NE Italy. Data from four monitoring sites which were used for investigating the pesticides distribution in the studied area (see open dots in figure 21), while data from the other three sites were used to assess the performance of the two mitigation solutions (see triangles in figure 21).

6.2.1.1 Studied area

The samplings were carried out in spring, during which the peak of the agricultural productive season occurs. Pesticide pollutants was compared between watersheds characterised by different basin area and lengths, distance between the sampling sites and the farmlands centroid, land use and crop types, such as permanent orchards or arable land. In most cases, agricultural land in the region is used for apple or grape production, with the exception of the Moscabio stream, where the percentage of land used for permanent crops, relative to the total area, is only 0.2%. Table 4 shows key characteristics of the monitored river catchments.

At each site, the sampling campaign was carried out for about three months (between

May and July) by three triplets of POCIS, each one immersed in water for approximately 28 days. Finally, the POCIS were stored in a refrigerator ($<8^{\circ}\text{C}$) and then analysed at the end of each sampling campaign.

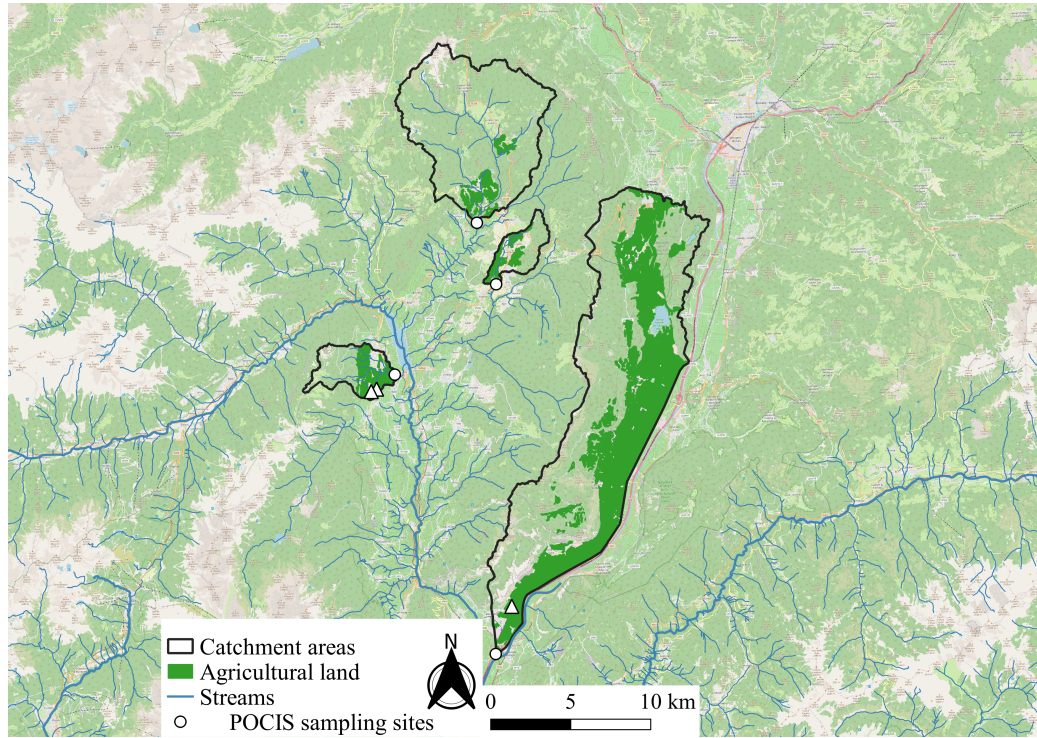


Figure 21 – Map of the draining catchments, areas used for agricultural purposes and sampling points.

6.2.1.2 Environmental data analysis

The collected data were normalised before being further processed, as the POCIS samplers were immersed in the waters of the considered watercourses for different periods of time, because of different sampling strategies, management choices and weather conditions. On this basis, and assuming a linear accumulation regime over time (Godlewska, Stepnowski, and Paszkiewicz, 2020), it was chosen to divide the amount adsorbed by each POCIS (M_s) by its exposure time (t); to calculate the amount of pesticide adsorbed per time unit (m).

$$m = M_s/t \quad (10)$$

Table 4 – Characteristics of the monitored catchment areas.

	Streams			
	Ribosc	Novella	Moscabio	Caldaro channel
Predominant crop	apple production	-	arable land	apple and grapes production
Monitored catchment area surface (km ²)	12.5	68.7	8.6	160
Farmland surface (km ²)	3.94	3.4	2.4	54.4
Surface used for permanent crops (km ²)	3.85	1.37	0.02	50
% farmlands	31.5%	5%	28%	34%
% permanent farmland	30.8%	2%	0.2%	31%
Distance between sampling point and centroid of farmland (km)	1.7	2.7	1.8	16
Watershed length (km)	3.94	11.1	5.5	29.1
Ratio between watershed length and the distance of farmland centroid (-)	0.36	0.24	0.33	0.55

Meteorological data, such as air temperature and precipitation, are collected and made freely available to the public by the local environmental monitoring agencies through meteorological stations located near the sampling points, and they were downloaded from the related website (<https://www.meteotrentino.it/index.html#!/home>). Samplings were conducted in the same months but in different years, so therefore the amounts of pesticides adsorbed during the samplings could have been affected by the inter-annual variability of meteorological conditions. For this reason, the non-parametric Kruskal-Wallis test ($\alpha = 0.05$) was used to check the similarity of the median rainfall values recorded at the various locations during the samplings.

The same approach was adopted, for each compound, to study the variability in the amount of pesticide adsorbed at the various sampling sites. If a compound occurs in similar

amounts at the sites, the search for a relationship linking that adsorbed amount with the characteristics of the basin becomes meaningless. For this reason, compounds whose adsorbed amounts per time unit (m) did not show significant differences between sampling sites were excluded from the subsequent study. For the other compounds, the relationship between the physical parameters of the catchment area and adsorbed amount of each pesticide per unit of time was conducted by means of a Principal Component Analysis (PCA). Finally, all pesticides were studied together, normalising the amount adsorbed by POCIS against the maximum amount adsorbed by all POCIS for each individual pesticide. Then, the relationship between the physical parameters of the catchment area and the normalised adsorbed amount was studied by a linear mixed effects model using RStudio software.

6.2.2 *Mitigation solutions*

The sampling sites adopted to study the effectiveness of the mitigation solutions were located upstream and downstream of a natural wetland and in a manhole of the white wastewater network. The wetland studied is located in the upper part of the Ribosc stream catchment, and closes a catchment area of 1.15 km². Before entering the wetland, the stream flows for roughly 1.7 km surrounded by permanent apple crops that cover 44.5% of the upstream catchment area. The wetland has a surface area of 8560 m² at an elevation of 671 m, a water depth ranging from 1.5 metres to a few tens of centimetres, and it has only one tributary and one outlet showing the same discharge under steady flow conditions. This marsh also belongs to the "Natura 2000" nature reserve network (see Figure 22). This special protection was assigned to protect the population of aquatic bird species living in this area. The wetland looks like a completely or partially submerged reed bed (*Phragmites australis*) and a few willow bushes (*Salix* sp.).

Both the tributary and the outlet of the wetland were sampled synchronously by POCIS during the period between 09/04/2021 and 23/09/2022, using 34 triplets of POCIS exposed

in the watercourses for periods of approximately 28 days. Finally, the POCIS were stored in a refrigerator ($<8^{\circ}\text{C}$) and then analysed at the end of each sampling campaign.

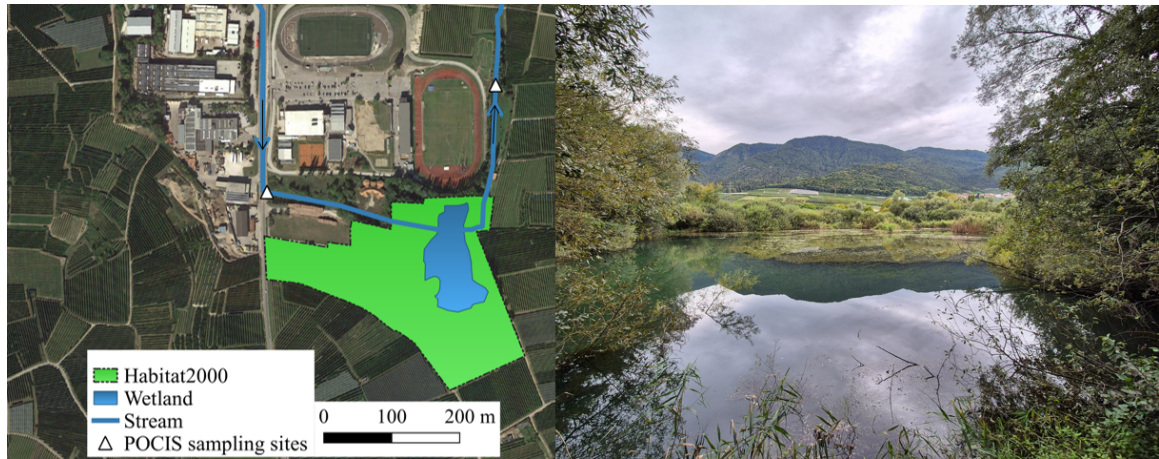


Figure 22 – Map with the location of the two sampling sites (Google Maps 2024) and a picture of the wetland.

The second studied mitigation solution is a washing plant for farm vehicles and equipment constructed by the local drainage board, near the town of Mezzocorona. Farmers working on roughly 1000 ha of nearby farmland have joined this project, agreeing to exploit the possibility to clean their equipment in a controlled system where the wastewater was collected and treated on site. In this way, the pesticides which are present on the external surface of the farm equipment doesn't flow in the watercourses draining the farmland or in the white sewage system. After washing, the wastewater from such a process is treated by means of an oil separator, desander, ultrafiltration and passage through activated carbon, after which the water is ready to be reused within the plant.

To evaluate if there is a reduction of pesticides concentration in the white sewage due to the coming into operation of this plant, a manhole with the follow characteristics was identified: (i) located on one of the major branches of the white sewage downstream Mezzocorona town (see Figure 23), where the majority of the farmers live, and (ii) having a permanently non-vanishing hydraulic head and high enough to cover the POCIS canister. The white sewage was sampled by six triplets of POCIS, ante opera, for an exposure time

of roughly a month in the period between 30/04 and 22/07/2020, 06/05 and 27/07/2021 and by six triplets of POCIS, post opera, for an exposure time of roughly 21 days in the period between 11/05 and 07/08/2023 and for an exposure time of roughly a month in the period between 24/04 and 17/07/2024. Finally, the POCIS were stored in a refrigerator ($<8^{\circ}\text{C}$) and then analysed at the end of each sampling campaign.



Figure 23 – Map of the major branches of the Mezzocorona white sewage system, with the location of the washing plant and the monitoring point (Open Street Map 2024).

6.2.2.1 Environmental data analysis

The data collected with the POCIS in the Mezzocorona manhole were affected by a significant difference in terms of exposure days, due to different sampling strategies, management choices and field conditions. For this reason, assuming a linear accumulation regime over time and adopting a law of proportionality through the pesticide adsorbed amount and the exposure time, it was chosen to normalize all data at an exposure time of 21 days (m_{21d}).

The weather data such as air temperature and precipitation were recorded by a meteorological station located close to Mezzocorona and collected by the local administration. These data were used to study the year variability of weather conditions during the sampling campaigns, adopting the Kruskal-Wallis test ($\alpha = 0.05$).

6.2.3 *Samples preparation and analysis*

After exposure, POCIS sorbent compartments were extracted following the procedure described Section 3.2.2 and then analysed by GC-MS/MS and LC-MS/MS systems.

6.3 **Results and discussion**

6.3.1 *Spatial distribution of pesticides*

We first investigated possible relationships between the presence of pesticides in the studied streams and the physical characteristics of their upstream catchment area. First of all, it was found that 16 compounds were detected in at least 3 sites out of 4 (boscalid, bupirimate, chlorantranilprole, chlorpyrifos, cyflufenamid, cyprodinil, difenoconazole, fluazinam, imidacloprid, penconazole, penhiopyrad, pirimicarb, piperonyl-butoxide, tebuconazole, terbutryn and tetraconazole). First of all, it was evaluated if weather conditions had been significantly different during the sampling periods. To this aim the Kruskal-Wallis test ($\alpha = 0.05$) highlighted that the mean air temperature, the daily average precipitation and the number of rainfall days did not exhibit significant differences through the sampling sites. For this reason, it wasn't investigated a relationship between these variables and the pesticides pollution. The same approach was adopted, per each compound, to evaluate if there were significant differences in terms of concentration through the sampling sites; for four compounds (fluazinam, imidacloprid, pirimicarb and piperonyl-butoxide) a p-value higher than 0.05 was obtained, for this reason these compounds were excluded from the rest of the study. For the other compounds, the relationship between the physical parameters of the catchment area upstream the sampling sites (see Table 4) and adsorbed amount

of pesticide per unit of time was studied. The biplots reported in Figure 24 give an overview of the phenomenon. First of all no overlap of the response of the sampling sites is evident, and it can be noticed that each pesticides has its own specific trend, which often seem to be better explained by different parameters or by none, as in the case of difenoconazole.

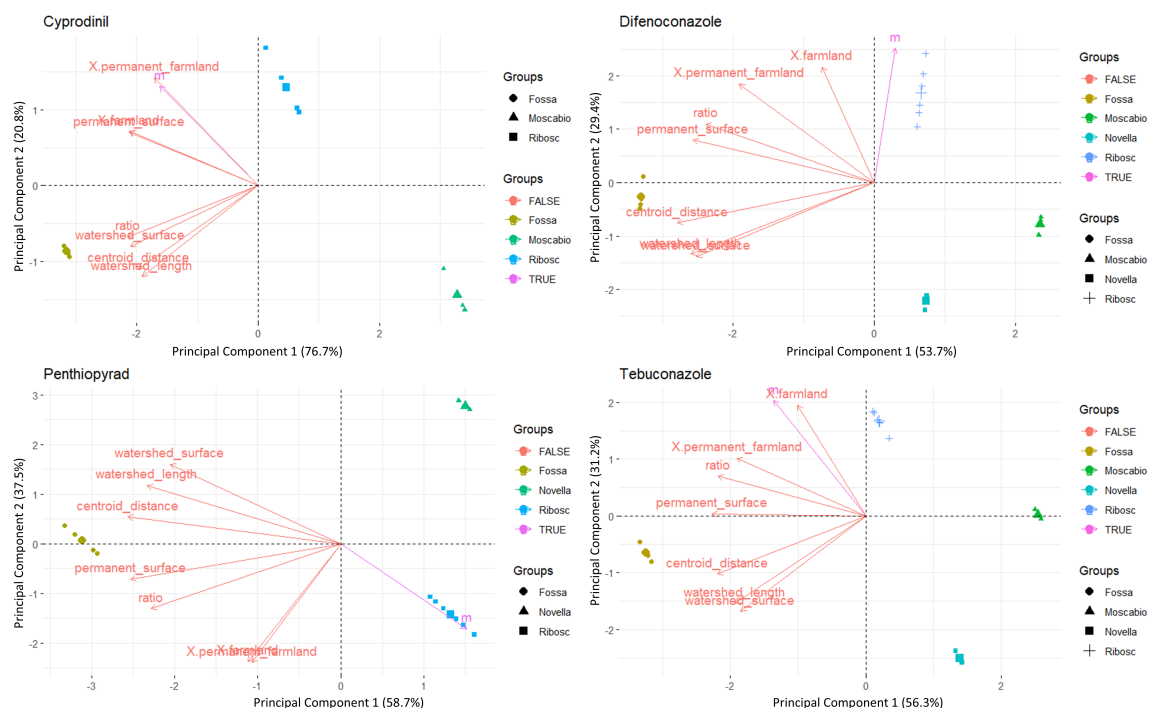


Figure 24 – Four examples of PCA biplot. The plots for the other studied compound are reported in Appendix F (Figure 32).

Given the difficulty of finding a robust statistical relationship between the presence of pesticides and site characteristics using the PCA method, this relationship was studied by normalising the amount adsorbed by POCIS against the maximum amount adsorbed by all POCIS for each individual pesticide and using a linear mixed-effects model. For the same reason it was chosen to study the pesticides all together and not separately in this analysis. This approach did not find a significant relationship either.

6.3.2 *Nature based solution for pesticides mitigation (wetland)*

In this section, the amounts of pesticides adsorbed by POCIS on the tributary and emissary stream of the wetland were compared (see Figure 22). A total of 56 compounds were detected by POCIS in either the upstream and downstream sampling points. First, the total amount of each pesticide adsorbed by POCIS over the entire sampling period (from April 2021 to September 2022) on the tributary and effluent was compared. As Figure 25 shows, in 67.9% of the compounds, the total adsorbed amount is higher in the tributary than in the emissary with a ratio of more than 2. Nearly one fourth (25%) of the compounds appear to be unaffected by the presence of the wetland, with similar amounts adsorbed in the effluent as those found in the tributary. The remaining 7.1% (four compounds) show the opposite behaviour to the previous ones, such as terbutryn and piperonyl butoxide, for which an increase in concentration was recorded passing through the wetland, and such as myclobutanil, terbumeton, which were only detected downstream of the wetland. The source of these four compounds, in most cases, is difficult to identify as these pesticides occurred sporadically throughout the year, often in quantities slightly above the LOD (as shown in fig 26). It is reasonable to assume that these compounds originate not only from the agricultural area, but also from other sources such as the lawn maintenance of the football pitch located downstream of the wetland. Terbutryn, for example, is an herbicide used to prevent the growth of broadleaf weeds within the football pitch and its recorded values do not follow the dominant pattern of agricultural activity in the upstream catchment, and, generally, in the regional area. Despite these peculiarities, which could be investigated in other studies, most of the comports show that the wetland positively interacts with the flow of pesticides in the stream by reducing their downstream concentration.

In addition to a total comparison referred to the 17 months of monitoring, the monthly trend of adsorbed pesticide fluxes was investigated. From the comparison between the upstream and downstream amounts adsorbed by POCIS, the monthly variability of the wet-

land mitigation performance could be detected over time. In particular, a sharp decline in pesticide mitigation yield was observed in the winter months. This type of response suggests that the vegetation and microbiological activity present in the wetland play a central role in the degradation of pesticides; which slow down or might even cease their activity in the winter months due to lower temperatures and the advent of vegetative rest.

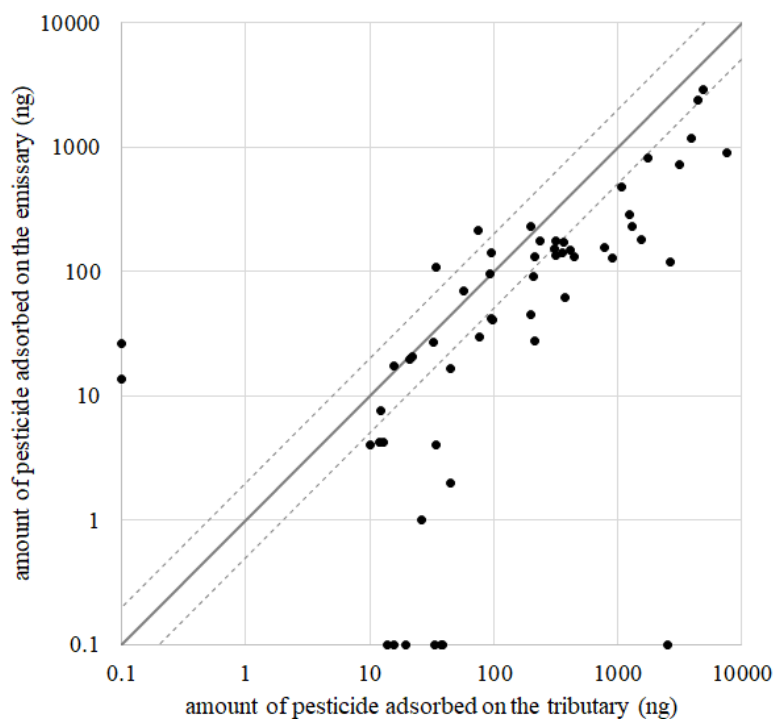


Figure 25 – Comparison between the total amount of each adsorbed pesticide by POCIS on the upstream tributary and on the downstream emissary over the entire sampling period from April 2021 to September 2022, reported in a bi-logarithmic graph. Each dot represents one compound, the continuous line represents the bisector and the area between the parallel dashed lines delimits the range in which both compared values differ by a factor of less than 2.

Reported wetlands in literature to investigate their ability to mitigate pesticide pollution are usually constructed wetlands on a laboratory or pilot scale, characterised by special planting, recirculation systems and multiple layers of bed substrate designed to optimise the degradation process (Moore, Schulz, Cooper, Smith Jr, and Rodgers Jr, 2002; Agudelo, Penuela, Aguirre, Morató, and Jaramillo, 2010; Sadaria, Supowit, and Halden, 2016; Papaevangelou, Gikas, Vryzas, and Tsihrintzis, 2017; Lyu et al., 2018; Jing et al., 2021). In

general, these types of wetlands are much more complex than the one studied here. An interesting outcome of the present study is that also the natural wetland studied here, in addition to protecting aquatic avifauna, is able to reduce pesticide concentrations with a performance in line with other CWs. Table 5 reports the detected, compound-specific mitigation performance of several constructed wetlands as found in literature, together with the reference and the key features of each wetland, in comparison with the one presented in this study.

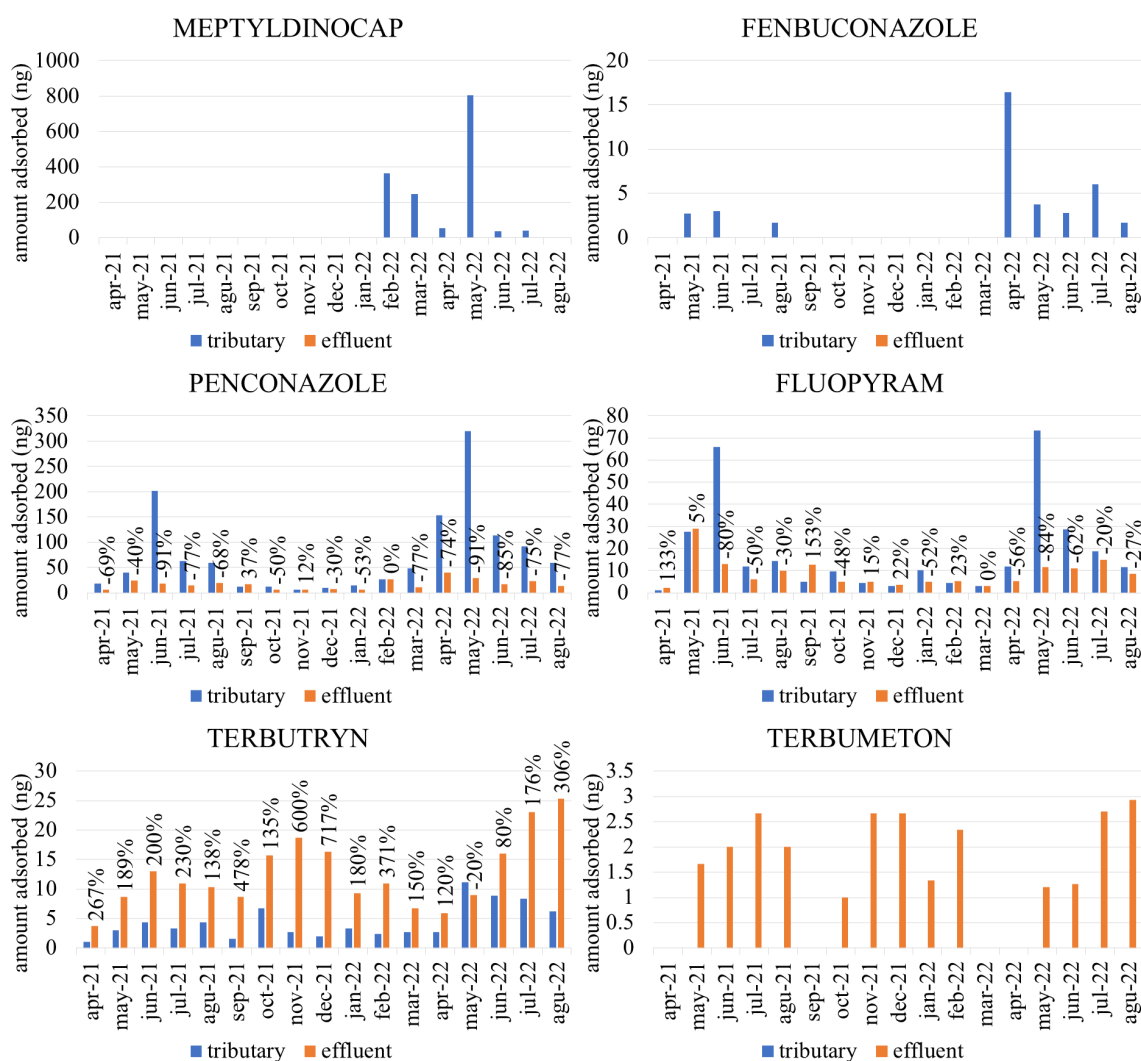


Figure 26 – Six examples of monthly absorbed pesticides amounts by POCIS during the sampling period, with indication of the monthly abatement yield for compounds that were detected both upstream and downstream. All data for each compound are reported in Appendix G (Table 14).

Table 5 – Key characteristics of wetland (natural or constructed) for which the ability to reduce pesticide concentration in streams has been investigated.

	This work	Jing et al 2021	Sadaria et al 2016	Aguedo et al 2010
Surface	8560 m ²	90*15 cm	-	1*0.6 m ²
Water depth	< 1.5 m	0.27 m	1.5 m	0.2 m
Typology	Natural wetland	CW, lab scale	CW	CW, lab scale
Plant	Phragmites australis and a few willow bushes (Salix sp.).	Phalaris arundinacea		Phragmites australis (reed) and Igneous rock
Country	Italy	-	South-western region of the United States	-
HRT	N.A.	8-12 days	4.7 days	1.1 cm/d
pesticide concentration abatement yield (%)				
Propiconazole	88%	>83%	-	-
Imidacloprid	58%	46-98%	negligible	-
Acetamiprid	84%	-	negligible	-
Chlorpyrifos	60%	-	-	96.2%
Boscalid	45%	-	-	-
Tebuconazole	71%	-	-	-
	This work	Papaevangelou et al 2017	Moore et al 2002	Lyu et al 2018
Surface	8560 m ²	3*0.75 m ²	660 m ²	20 cm of diameter
Water depth	< 1.5 m	-	0.24 m	0 cm
Typology	Natural wetland	CW	CW	CW
Plant	Phragmites australis and a few willow bushes (Salix sp.).	Phragmites australis	Juncus effusus, Leersia sp., and Ludwigia sp.	Juncus effusus, Typha latifolia, Berula erecta, Phragmites australis and Iris pseudacorus.
Country	Italy	Greece	Mississippi, USA	-
HRT	N.A.	6-8 days	N.A.	2-0.25 days
pesticide concentration abatement yield (%)				
Propiconazole	88%	-	-	-
Imidacloprid	58%	-	-	-
Acetamiprid	84%	-	-	-
Chlorpyrifos	60%	-	>83%	-
Boscalid	45%	72.5-75.1%	-	-
Tebuconazole	71%	-	-	99.80%
1: for our work, the percentage of reduction for the entire period was reported, using all the available data for each compound. HRT = Hydraulic Residence Time				

6.3.3 *Conventional treatment solution for pesticides mitigation (washing plant)*

In this section it was to compare the amounts of pesticides adsorbed by POCIS in the white sewage before and after the coming into operation of the carwash plant for farm equipment and vehicles. For this sampling point, 34 compounds were detected by POCIS in all the four sampling campaigns. Firstly, we evaluated the weather conditions, in particular the precipitation and the daily averaged air temperature recorded during the POCIS exposure period. Figure 27 shows a gradual decrease in cumulative rainfall from 2020 to 2023, which may have caused both a decrease in the amount of pesticides used in agriculture and a decrease in their dilution factor in white sewage water. In addition, during the sampling period in spring 2024, a peak in precipitation was recorded, which may have resulted in a higher use of pesticides in agriculture and a parallel higher dilution factor in watercourses. In both cases, these factors would play in opposite directions in the way they affect the concentration of pesticides in the streams. The Kruskal-Wallis test ($\alpha = 0.05$) showed that there aren't significant differences in weather conditions both in terms of average daily air temperature and average monthly precipitation, so it is reasonable to assume that the variations in cumulative rainfall did not lead to appreciable changes in water pesticide concentration.

Following this preliminary analysis, we studied the variability of the data in the two years before the coming into operation of the carwash for farm equipment and of its related wastewater treatment plant, to identify those compounds that were more consistently present over time. The ratio between the adsorbed amounts spring 2021 and 2020 assume a median (5^{th} ; 95^{th} percentile) value of 0.74 (0.13; 14.4), showing that not all the compounds were present consistently over time. For 15 out of 34 compounds this ratio was either higher than 2 or lower than 0.5, with the majority of cases showing higher concentration in water for 2021 compared to 2020. While exploring the reasons for such variability is out of the scope of the present work, we focused on the 19 compounds for which the 2021 to 2020

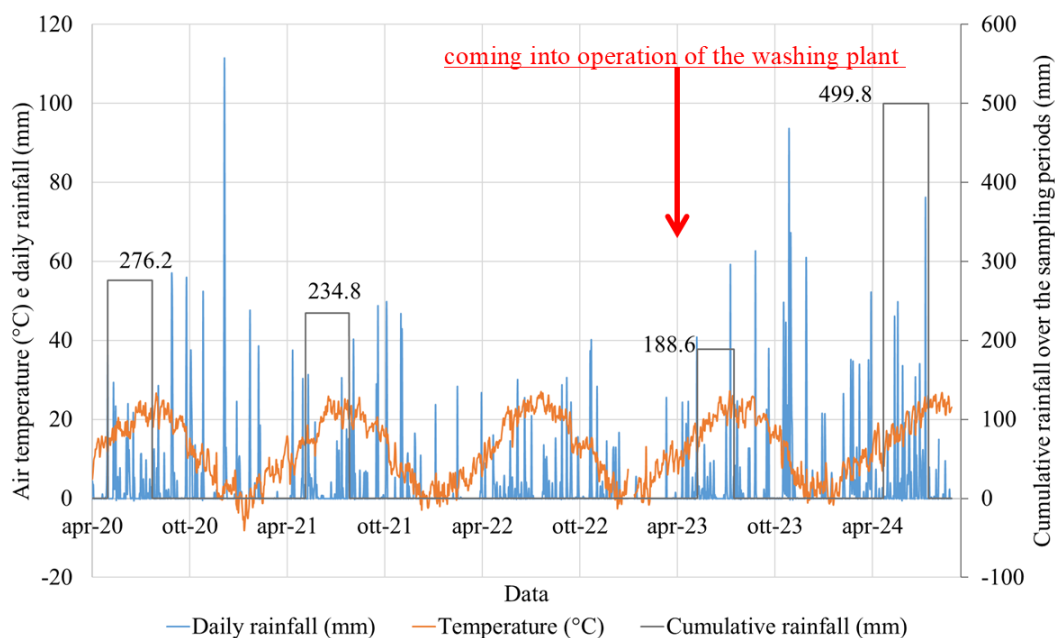


Figure 27 – Time series of air temperature and daily rainfall pattern between 2020 and 2024 and indication of cumulative rainfall over the sampling periods.

ratio of absorbed amounts on POCIS was within the 0.5 - 2.0 range, indicating a consistent presence over time before the coming into operation of the carwash for farm equipment and related treatment plant (see dark squares in figure 28).

For these 19 compounds, the amounts of pesticides adsorbed by the POCIS in the white sewage were compared before (2020) and after the Mezzocorona plant became operational (2023 and 2024: Figure 29). Ratios of the adsorbed amount after and the coming into operation of the plant to that absorbed in 2020 have a median (5^{th} ; 95^{th} percentile) value of 0.09 (0.03; 1.11) for 2023 and 0.10 (0.01; 0.72) for 2024, showing that the presence of pesticides in the white sewage after the coming into operation of the Mezzocorona plant is, in median, one tenth than before. More in detail for 15 of 19 compounds in 2023 and for 16 of 19 compounds in 2024 the ratio is lower than a factor 0.5, i.e., the absorbed amount is less than half, while the other compounds maintained an almost constant concentration even after the coming into operation of the carwash for farm equipment plant. This result proves that the introduction of this plant positively affects the quality of this white sewage

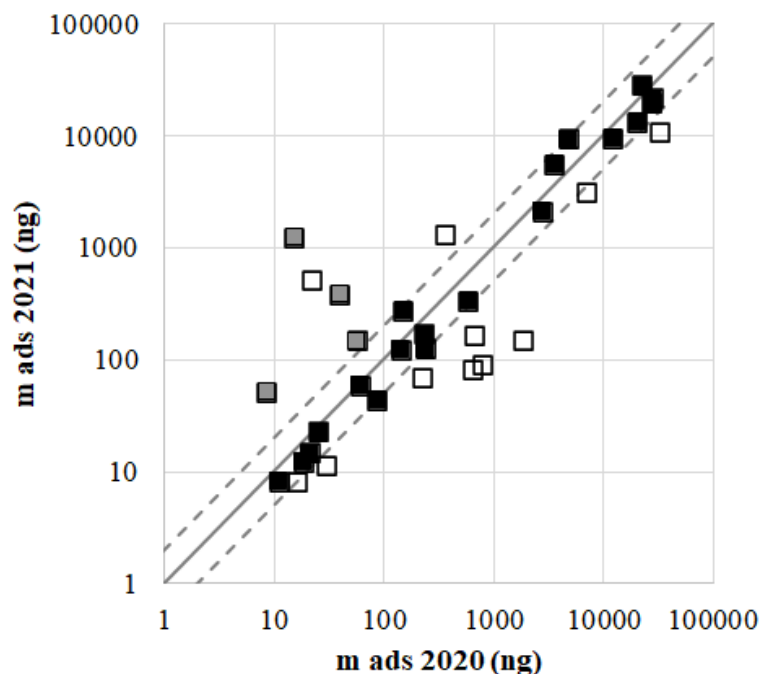


Figure 28 – Comparison between the amount of each pesticides adsorbed by POCIS in the 2020 and 2021, reported in a bi-logarithmic graph. Each square represents a compound, the continuous line represents the bisector and the area between the parallel dashed lines delimits the range in which both compared values differ by a factor of less than 2.

track in relation to at least 79% of the consistently present pesticides compounds.

The behavior of the few compounds that did not show such behavior can be visualized, by comparing the three bi-log graphs of Figure 28 and Figure 29. It can be seen that there are four compounds (piperonyl butoxide, pirimicarb, tebuconazole and terbutryn), identified with grey squares, for which the ratio between the amounts of pesticides adsorbed by POCIS in the year studied and those in 2020 was always exceeding unity. The presence of these compounds in white sewage water peaks in the years 2021 and 2023, while there is a considerable decrease for pirimicarb, tebuconazole and terbutryn from 2023 to 2024, possibly due to the washing plant. The causes of these fluctuations may be multiple and independent of the washing plant in Mezzocorona.

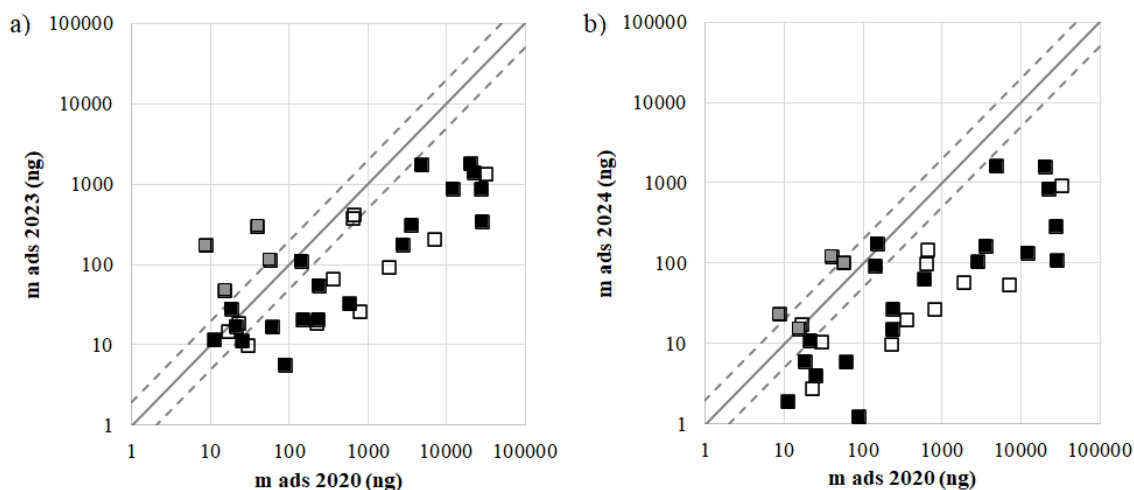


Figure 29 – Comparison between the amount of each pesticides adsorb by POCIS in the 2020 and (a) 2023 and (b) 2024, reported in a bi-logarithmic graph. Each square represents a compound, the continuous line represents the bisector and the area between the parallel dashed lines delimits the range in which both compared values differ by a factor of less than 2. All data for each compound are reported in Appendix H (Table 15).

6.4 Conclusions

Comparison of the amounts of pesticides adsorbed by POCIS in watercourses upstream and downstream of a wetland showed a high ability to reduce pesticide concentrations in the watercourse, in line with the efficiencies reported in the literature for much more complex, purpose-built wetlands. Similar results were found following the construction of a washing plant for agricultural equipment, which significantly reduced the concentration of pesticides in the white sewer network. These two types of mitigation solutions have proven to be excellent strategies to address pesticide pollution in watercourses affected by high agricultural pressure. In the case of the nature-based solution, the study suggests a novel perspective in the use and management of analogous small-scale natural wetlands, which are often present across the territory, and whose potential for the reduction of emerging contaminants in streams might have been underrated. In the case of the more conventional solution, its proven effectiveness through this study can support upscaling their construction in several parts of the agricultural territory.

CHAPTER 7. CONCLUSIONS

A review of the available literature found that, at present, POCIS has been extensively studied as a passive sampler for qualitative monitoring of various organic compounds in watercourses streams, with only a limited number of studies focusing on calibrating this device for a large number of compounds. Regarding the use of this sampling system, essentially consisting of an adsorbent polymeric phase enclosed by two PES membranes, most of the studies seen in literature are based on the verification of the content of pesticides adsorbed only on the phase. Only recent studies have shown that the membrane is not only a "container of the adsorbent phase" that puts the water in contact with the adsorbent, but it plays an active role in the adsorption itself. Starting from this evidence and before trying to propose a sort of calibration that allows to interpret the data that the POCIS produces also from a quantitative point of view, it was decided to study in a completely independent way the behaviour of the phase and the membrane towards a large number of pesticides dissolved in waters. The literature review also showed a growing international interest in reducing pesticide pollution in watercourses; many studies have focused on identifying nature-based or technological mitigation solutions created for this purpose, though this remains an evolving area. In an effort to expand knowledge of POCIS compartments and these mitigation solutions, several laboratory experiments and field sampling efforts were conducted during this doctoral work. Before studying the performance of POCIS, the chemical analysis methods of both POCIS and water samples collected by grab sampling were perfected and validated as reported in sections 3.2.1 and 3.2.4.

Laboratory experiments were performed to study the partitioning of pesticides between the two compartments of POCIS with respect to a large number of pesticides and to investigate their calibration parameter (sampling rate) under laboratory conditions; field sampling

was conducted to develop a robust calibration model of POCIS and to assess whether there is correspondence between laboratory and field results; and finally, POCIS was used to study two pesticide pollution mitigation strategies.

The study carried out in laboratory demonstrated that extracting pesticides from both sampler compartments (Oasis HLB phase and PES membrane) allows for the detection of almost all investigated compounds (224 out of 226), covering a wide range of polarities, from -2 to 7 LogKow units. As a result of this experimentation, it was possible to compare the amounts of pesticide adsorbed by the two POCIS compartments, noting that more than half of the pesticides were more effectively adsorbed by the PES membrane than by the Oasis HLB phase. In particular, compounds exhibiting this type of behaviour were the most hydrophobic ones, i.e. those characterised by high LogKow values. This means that the commonly used approach of extracting pesticides solely from the adsorbent phase is limiting and does not allow for effective monitoring of the most hydrophobic compounds. Based on this evidence and due to the linearity of accumulation trends recorded for most compounds, the sampling rate was estimated for both POCIS compartments and for total POCIS. Although predicting the sampling rate values from the polarity (LogKow) of the compounds for all molecules is challenging, certain patterns emerged: $R_{S,PES}$ was typically higher than $R_{S,HLB}$ for compounds with LogKow values above 3; for compounds with LogKow values higher than 6, only the values of $R_{S,PES}$ and R_S could be estimated, as they would have been undetectable if extracted solely from the Oasis HLB phase. For the adsorbent phase R_S , instead, HLB was less affected by polarity than $R_{S,PES}$ and R_S (with a coefficient of variation equal to 45%). This result supports the traditional POCIS extraction method, because if one chooses to extract pesticides from the Oasis HLB phase alone, it makes it possible to estimate the average concentration in water of the detected compounds, as a first approximation, using a single $R_{S,HLB}$ value for all pesticides (e.g. the median value), instead of having to use the compound-specific $R_{S,HLB}$ value. However,

this method excludes a large number of compounds, especially the more hydrophobic ones, against which the PES membrane is much more effective, achieving higher sampling rates. Therefore, to increase the range of compounds that can be monitored with POCIS and improve its accumulation performance, it is preferable to study the overall POCIS sampling rate (R_S) rather than using either compartment individually.

Furthermore, a comparison between the results obtained from the laboratory experiment and those obtained from a field sampling campaign showed that, for 15 of the 20 pesticides available for comparison, the partitioning between the two POCIS compartments remained constant under varying environmental conditions. Greater variability was observed, however, in terms of $R_{S,HLB}$ and $R_{S,PES}$, especially for compounds with a lower affinity for the substrate in question. This could be due to the different environmental conditions to which POCIS was exposed, as other researchers have also reported in their work. This highlights another reason why, in order to implement POCIS in environmental monitoring, the sampling rate should ideally be estimated under exposure conditions similar to those in real life. These initial results showed that the potential of POCIS is far greater than those used so far, opening up the possibility of also considering the PES membrane as an adsorptive component of POCIS. At this point, further studies would need to be carried out to understand how the $R_{S,PES}$ is affected by environmental conditions (such as water temperature, the presence of biofouling on the outer surface of the POCIS, etc.) and proceed to calibrate the POCIS as a whole in the field.

From the sampling tests carried out on the Ribosc torrent aimed at proposing a calibration model it was seen that, for quantitative results from POCIS monitoring, it is optimal to sample for 14 - 21 days, as there was a progressive loss of linearity in the accumulation trend after 21 days of exposure for many compounds. By using data collected within 21 days, the R_S sampling rate for 31 compounds was estimated, covering a polarity range

from 0.3 to 4.91 LogKow units. A comparison of estimated Rs values in the field and the polarity of the compounds also showed a very similar relationship to that obtained from the previous laboratory test. That is, a weak or absent dependence between Rs and polarity for hydrophilic and moderately hydrophilic compounds, and a stronger dependence as the hydrophobicity of the compounds increases.

To assess the robustness of the model and its transferability to another stream, concentrations measured in water by frequent grab sampling were compared with corresponding estimates from the calibration model. In both cases, results were very satisfactory, showing a good match between measured and estimated values for more than 89% of compounds. This suggests that for future environmental monitoring with POCIS under similar conditions (such as exposure time, flow velocity, and temperature), the validated model can be used to estimate the average concentrations of these pesticides in watercourses. This represents an important achievement for agencies using POCIS for environmental monitoring, as this model allows estimating the average concentration of nearly 30 pesticides. To enable this approach to be used on a larger scale and on a number of pesticides in line with those used in the field, it would be appropriate to repeat this study on different streams on whose watersheds different crops are grown and different pesticides are used than those calibrated here.

Finally, part of this PhD work employed POCIS to monitor various alpine watercourses and study two possible pesticide pollution mitigation strategies. A relationship was sought between the physical parameters of the catchment area upstream of sampling sites and the amount of pesticide adsorbed per unit time; however, no strong relationship was found between the variables considered and the amount of pesticide adsorbed by POCIS.

Regarding the two mitigation strategies, the results are highly satisfactory. The case

studies included a natural wetland and a washing plant for agricultural equipment and vehicles, coupled with a conventional water treatment, used by local farmers. To assess the ability of these two mitigation solutions to reduce pesticide concentrations in water, POCIS sampling campaigns were conducted at the wetland tributary and emissary streams and at a manhole in the whitewater network near the washing plant before and after its opening. A comparison of the total amount of pesticide adsorbed by POCIS over a 17-month period at the wetland tributary and effluent showed that, in 67.9% of cases, the total amount adsorbed was higher in the tributary than in the effluent, with a ratio of more than 2. For 25% of compounds, there appeared to be no impact from the wetland, while for the remaining 7.1% (four compounds), the behaviour was opposite. Despite these peculiarities, which could be further investigated, most compounds showed that the wetland positively affects pesticide levels by reducing their concentrations downstream. Studying monthly reductions showed these were highest in spring summer season and lowest in the winter, highlighting the role of wetland vegetation and microbiological activity in pesticide degradation, which decreases or halts in colder months due to lower temperatures and vegetative dormancy. Wetlands typically studied for pesticide mitigation are constructed wetlands (CWs) on laboratory or pilot scales, with specific planting, recirculation systems, and multiple substrate layers designed to optimise degradation processes. In general, these types of wetlands are more complex than the one studied here. However, the natural wetland studied, in addition to protecting aquatic avifauna, is able to reduce pesticide concentrations with a performance comparable to CWs. Concerning the agricultural equipment washing plant, data showed that the presence of pesticides in whitewater after the Mezzocorona plant became operational was generally lower than before. Indeed, for 15 (16) of 19 compounds in 2023 (2024), the ratio was lower than 0.5, while the other compounds maintained almost constant concentrations even after the plant became operational. This result indicates that the introduction of this plant positively affects the quality of this white sewage track. This final study, in addition to evaluating the effectiveness of these mitigation solutions, revealed to

us how the use of a passive sampler to carry out this type of study was a winning choice. In fact, the peculiarities of POCIS made sampling simple and dynamic, enabling continuous monitoring with a limited number of field samplings and without the need for a power supply near the site; performance that would have been more difficult to achieve with the grab sampling method.

In conclusion, the work carried out as part of this PhD project has deepened knowledge of POCIS for pesticide monitoring, discovering new features that may be useful for users of this device. This study demonstrated the value of POCIS for environmental monitoring of watercourses, thanks to its ability to adsorb a wide variety of organic compounds with very different chemical and physical properties and thanks to its ability to adapt well to situations where grab or automated sampling would be more difficult to use. Finally, the results obtained from this PhD work are able to provide important operational information for the quantitative assessment of pesticides in Alpine watercourses, which may be useful to environmental protection agencies and stakeholders working in this field.

APPENDIX A. INSTRUMENTAL SETTINGS

Table 6 – Instrument acquisition data for pesticides analysed by LC-MS/MS.

* = sum of isomers

	Compound	Ion mode	CV (V)	Quant. trace	CE (eV)	Qual. trace	CE (eV)
1	3-Hydroxycarbofuran	ES+	30	238 > 163	16	238 > 181	10
2	3-Ketocarbofuran	ES+	22	236 > 161	24	236 > 179	15
3	6-Benzyladenine	ES+	30	226.1 > 91	26	226.1 > 65	36
4	Abamectin (B1a)	ES+	74	895.52 > 751.48	44	895.52 > 183.1	52
5	Acephate	ES+	8	184.1 > 143	8	184.1 > 125.1	18
6	Acetamiprid	ES+	32	223 > 126	22	223 > 56	14
7	Acibenzolar-S-methyl	ES+	40	211 > 135.93	28	211 > 91.06	20
8	Aldicarb	ES+	26	208.1 > 89	15		
9	Aldicarb sulfone	ES+	15	240.1 > 86.2	20	240.1 > 148.2	13
10	Aldicarb sulfoxide	ES+	12	207.1 > 132.1	10	207.1 > 89.1	14
11	Allethrin	ES+	15	303.2 > 90.9	40	303.2 > 107	20
12	Ametocradin	ES+	68	276.223 > 149.0999	36	276.223 > 176.213	36
13	Ametryn	ES+	28	228.1 > 186.1	18	228.1 > 96	36
14	Amidosulfuron	ES+	20	370.1 > 69	50	370.1 > 261.1	15
15	Amisulbron	ES+	15	466 > 227	20	468 > 229	20
16	Atrazine	ES+	29	216.1 > 174	18		23
17	Azaconazole	ES+	30	300 > 159	28	300 > 231	18
18	Azinphos-methyl	ES+	12	318 > 261	8	318 > 160	8
19	Azoxystrobin	ES+	17	404 > 372	15	404 > 329	30
20	Beflubutamid	ES+	25	356.1 > 91.1	35	356.1 > 65.1	40
21	Benalaxyl	ES+	17	326.1 > 148	20	326.1 > 91	34
22	Bendiocarb	ES+	15	224.1 > 109	20	224.1 > 167.1	10
23	Bensulfuron-methyl	ES+	28	411 > 149	22	411 > 182	20

	Compound	Ion	CV	Quant. trace	CE	Qual. trace	CE
		mode	(V)		(eV)		(eV)
24	Benthiavalicarb Iso-propyl	ES+	20	382 > 180	30	382 > 116	20
25	Benzoximate	ES+	9	364>199	8	364>105	26
26	Benzoylprop-ethyl	ES+	16	366 > 105	14	366 > 77	45
27	Bifenazate	ES+	16	301.159 > 198.112	10	301.159 > 170.089	20
28	Bifenthrin	ES+	16	440.25 > 181.125	14	440.25 > 165.96	44
29	Bitertanol	ES+	12	338.1>99.1	16	338.1>70.1	8
30	Boscalid	ES+	32	342.9 > 307	20	342.9 > 139.9	20
31	Bromacil	ES+	20	261 > 205	14	261 > 188	28
32	Bromophos-methyl	ES+	30	365 > 229	24	365 > 291	30
33	Bromoxynil	ES-	38	275.8 > 78.9	30	275.8 > 80.8	30
34	Bromuconazole *	ES+	32	376 > 158.9	35	378 > 159	25
35	Bupirimate	ES+	31	317 > 108	28	317 > 166	28
36	Buprofezin	ES+	22	306.1 > 201	12	306.1 > 57.4	20
37	Cadusafos	ES+	17	271 > 159	15	271 > 97	32
38	Carbaryl	ES+	19	202 > 145	22	202 > 117	28
39	Carbendazim	ES+	26	192.1 > 160.07	16	192.1 > 132.1	28
40	Carbofuran	ES+	20	222.1 > 165.1	12	222.1 > 123	22
41	Carbosulfan	ES+	25	381 > 118	22	381 > 76	34
42	Carfentrazone Ethyl	ES+	36	412.096 > 345.999	24		14
43	Chlorantranilprole	ES+	20	482.07 > 450.99	18	482.07 > 283.95	12
44	Chlorfenvinphos	ES+	18	358.9 > 155	12	358.9 > 99	30
45	Chlorpyrifos	ES+	27	349.9 > 97	32	349.9 > 198	20
46	Chlozolinate	ES+	34	331 > 268	24	331 > 81	28
47	Chromafenozide	ES+	15	395 > 175	18	395 > 339	10
48	Clofentezine	ES+	19	303 > 138	22	303 > 102	35
49	Cloquintocet	ES+	30	238>179	22	238>192	20
50	Cloquintocet-mexyl	ES+	25	336 > 192	35	336 > 238	18
51	Clothianidin	ES+	20	250.03 > 168.99	12	250.03 > 131.98	14
52	Coumaphos	ES+	30	363 > 227	25	363 > 307	16

	Compound	Ion mode	CV (V)	Quant. trace	CE (eV)	Qual. trace	CE (eV)
53	Cyanazine	ES+	27	241 > 214	17		20
54	Cyantraniliprole	ES+	24	474.99 > 285.89	18	474.99 > 111.97	62
55	Cyazofamid	ES+	17	325 > 107.9	20	325 > 261	10
56	Cyflufenamid	ES+	24	413.09 > 295.05	14	413.09 > 241.01	22
57	Cyflumetofen	ES+	21	465 > 173	22	465 > 249	12
58	Cymoxanil	ES+	14	199 > 128	8	199 > 111	18
59	Cyproconazole	ES+	27	292.2 > 70.2	18	292.2 > 125.1	24
60	Cyprodinil	ES+	47	226 > 93	33	226 > 108	25
61	Demeton-S- methylsulfone	ES+	30	263 > 169	17	263 > 121	17
62	Desethyl-Atrazine	ES+	30	188 > 146	16	188 > 79	26
63	Desisopropyl-Atrazine	ES+	34	174 > 96	18	174 > 78.9	18
64	Desmedipham	ES+	18	318 > 182	10	318 > 136	22
65	Desmethyl-pirimicarb	ES+	25	225 > 72	20	225 > 168	16
66	Diazinon	ES+	20	305.1 > 169	22	305.1 > 96.9	35
67	Dichlorvos	ES+	23	221 > 109	22	221 > 79	34
68	Dicrotophos	ES+	17	238 > 112	10	238 > 193	10
69	Diethofencarb	ES+	16	268.1596 > 124.0039	30	268.1596 > 152.0901	22
70	Difenoconazole	ES+	37	406 > 251.1	25	406 > 111.1	60
71	Diffubenzuron	ES-	20	309 > 289	9	309 > 156	11
72	Dimethoate	ES+	12	230.1 > 125	20	230.1 > 199	10
73	Dimethomorph	ES+	30	388.1 > 300.9	20	388.1 > 165	30
74	Dimoxystrobin	ES+	15	327.1 > 116	21	327.1 > 205	10
75	Diniconazole	ES+	37	326.1 > 70.2	25	328 > 70	25
76	Diphenamid	ES+	30	240.1 > 134.1	20	240.1 > 167.1	25
77	Diuron	ES+	22	233 > 72.1	18	233 > 46.1	15
78	Dodemorph	ES+	30	282 > 116	21	282 > 98	28
79	Emamectin Benzoate	ES+	52	886.59 > 158.11	34	886.59 > 82.01	50
	B1a						

	Compound	Ion mode	CV (V)	Quant. trace	CE (eV)	Qual. trace	CE (eV)
80	Epoxiconazole	ES+	25	330 > 121	25	330 > 101	25
81	Etaconazole Isomer	ES+	16	328.1 > 159	25	328.1 > 205	13
82	Ethirimol	ES+	30	210 > 140	23	210 > 98	25
83	Ethofumesate	ES+	25	287.1 > 121.1	15	287.1 > 259.1	10
84	Ethoprophos	ES+	18	243.2 > 131	20	243.2 > 97	31
85	Ethoxyquin	ES+	30	218>148	22	218>160	32
86	Etofenprox	ES+	17	394.3 > 177	15	394.3 > 106.9	43
87	Etiozazole	ES+	34	360.2744 > 141.0321	30	360.2744 > 113.0764	58
88	Etrimfos	ES+	30	293 > 125	25	293 > 265	18
89	Fenamidone	ES+	22	312.1 > 92	25	312.1 > 236.1	14
90	Fenamiphos	ES+	27	304.1 > 217.1	24	304.1 > 202.1	36
91	Fenarimol	ES+	37	331 > 268	22	331 > 81	34
92	Fenazaquin	ES+	27	307.2 > 57.2	25	307.2 > 161	19
93	Fenbuconazole	ES+	29	337 > 125	36	337 > 70.1	20
94	Fenbutatin-oxide	ES+	52	519.15 > 90.99	44	519.15 > 196.89	52
95	Fenhexamid	ES+	32	302.1 > 97.2	22	302.1 > 55.3	38
96	Fenothiocarb	ES+	15	270 > 95	25	270 > 242	12
97	Fenoxaprop	ES+	26	334<288	20	334>70	20
98	Fenoxycarb	ES+	22	302.22 > 88	20	302.22 > 116.04	10
99	Fenpropidin	ES+	50	274 > 147	30	274 > 86	30
100	Fenpropimorph *	ES+	45	304 > 147	28	304 > 117	28
101	Fenpyrazamine	ES+	26	332.16 > 230.412	18	332.16 > 216.117	28
102	Fenpyroximat	ES+	23	422.2 > 366.1	15	422.2 > 138.1	32
103	Fenpyroximate	ES+	23	422.2 > 366.1	15	422.2 > 138.1	32
104	Fenthion-sulfoxide	ES+	30	295 > 109	32	295 > 280	18
105	Fipronil	ES-	22	435 > 330	15	435 > 250	25
106	Fipronil-sulfone	ES-	25	451 > 415	15	451 > 282	26
107	Flazasulfuron	ES+	23	408.1 > 181.9	20		44
108	Flonicamid	ES+	36	230.03 > 203.01	18	230.03 > 147.96	28

	Compound	Ion mode	CV (V)	Quant. trace	CE (eV)	Qual. trace	CE (eV)
109	Florasulam	ES+	30	360 > 129	22	360 > 192	25
110	Fluazifop	ES+	30	328.1 > 282.1	20	328.1 > 255.1	23
111	Fluazifop-P-Butyl	ES+	32	384.16 > 282.107	22		16
112	Fluazinam	ES-	34	462.9 > 415.98	22	462.9 > 397.97	14
113	Fludioxonil	ES-	42	247 > 180	28	247 > 126	35
114	Flufenacet	ES+	15	364.1 > 152.1	23	364.1 > 194.1	11
115	Flufenoxuron	ES+	31	489.12 > 158.02	22	489.12 > 141	46
116	Fluopicolide	ES+	30	383.05 > 173	22	383.05 > 144.9	54
117	Fluopyram	ES+	32	397.096 > 173.008	32	397.096 > 145.051	52
118	Flupyradifurone	ES+	25	289 > 126	25	289 > 99	40
119	Fluquinconazole	ES+	32	376.0319 > 349.079	20	376.0319 > 107.999	48
120	Fluroxypyr	ES+	74	254.102 > 91.04	28		34
121	Fluroxypyr-1- methylheptyl ester	ES+	15	367 > 255	11	367 > 181	32
122	Flusilazole	ES+	27	316 > 247	18	316 > 165	28
123	Flutriafol	ES+	28	302.16 > 69.99	16	302.16 > 123.06	28
124	Fluxapyroxad	ES+	20	382.1 > 362.1	15	382.1 > 342.1	22
125	Fonofos	ES+	15	247.1 > 109	20	247.1 > 137	10
126	Formetanate - hy- drochloride	ES+	16	222 > 165	15	222 > 46	23
127	Fosthiazate	ES+	15	284 > 104	22	284 > 228	10
128	Fuberidazole	ES+	35	185 > 157	22	185 > 65	22
129	Furalaxyl	ES+	20	302.1 > 95	29	302.1 > 242.1	16
130	Furathiocarb	ES+	20	383.2 > 195.1	18	383.2 > 252.1	13
131	Heptenophos	ES+	15	251 > 127	14	251 > 125	14
132	Hexaconazole	ES+	31	314 > 70.1	22	316 > 70	25
133	Hexythiazox	ES+	21	353 > 228.1	14	353 > 168.1	26
134	Imazalil	ES+	30	297 > 159	23	297 > 69	22
135	Imazaquin	ES+	35	312.1 > 128	45	312.2 > 267.2	20

	Compound	Ion mode	CV (V)	Quant. trace	CE (eV)	Qual. trace	CE (eV)
136	Imazosulfuron	ES+	22	413 > 155.9	22	413 > 152.8	12
137	Imidacloprid	ES+	23	256.1 > 175.1	20	256.1 > 209.1	15
138	Indoxacarb	ES+	25	528 > 203	40	528 > 150	22
139	Ipconazole Isomer	ES+	28	334.2 > 70	20	334.2 > 125	35
140	Iprovalicarb	ES+	19	321.1 > 119.06	16	321.1 > 203.1	10
141	Isofetamid	ES+	15	360.1 > 125	30	360.1 > 210	10
142	Isopropalin	ES+	30	310.2 > 226.2	20	310.2 > 268.2	15
143	Isoproturon	ES+	26	207.2 > 72.1	22		
144	Isopyrazam	ES+	25	360.2 > 244.1	22	360.2 > 340.2	19
145	Lenacil	ES+	20	235.1 > 153.1	16	235.1 > 136.1	32
146	Linuron	ES+	26	249.1 > 160	20	249.1 > 182.1	15
147	Malaoxon	ES+	15	315 > 98.9	24	315 > 127	12
148	Mandipropamid	ES+	20	412.16 > 328.16	16	412.16 > 125.01	34
149	Mecarbam	ES+	12	330 > 227.1	8	330 > 97	35
150	Mefentrifluconazole	ES+	34	398 > 70	20	398 > 182	20
151	Mepanipyrim	ES+	37	224.1 > 106	25	224.1 > 77	40
152	Mepronil	ES+	30	270.1 > 119.1	28	270.1 > 91	44
153	Mepthylidinocap	ES-	46	295.16 > 193.24	30	295.16 > 134.06	52
154	Metalaxyl	ES+	15	280.1 > 220.1	13	280.1 > 192.1	17
155	Metamitron	ES+	30	203 > 175	15		20
156	Metazachlor	ES+	15	278 > 134.1	22		10
157	Metconazole *	ES+	30	320.1 > 70	22	320.1 > 125	36
158	Methamidophos	ES+	17	142 > 93.9	13	142 > 124.9	13
159	Methidathion	ES+	10	303 > 145	10	303 > 85.1	20
160	Methiocarb-sulfone	ES+	20	258 < 122	19	258 < 107	38
161	Methiocarb-sulfoxyde	ES+	22	242.1 > 185	14	242.1 > 122	28
162	Methomyl	ES+	10	163 > 106	10	163 > 88	10
163	Methoxyfenozide	ES+	25	369.1 > 149.1	18	369.1 > 313.2	8
164	Metolachlor	ES+	18	284.1 > 252.1	15		25

	Compound	Ion mode	CV (V)	Quant. trace	CE (eV)	Qual. trace	CE (eV)
165	Metrafenone	ES+	19	409 > 209.1	14	409 > 226.9	16
166	Metribuzin	ES+	33	215 > 187	20		20
167	Mevinphos	ES+	13	225.1 > 127.1	15	225.1 > 193.1	8
168	Monocrotophos	ES+	25	224 > 127	15	224 > 98	10
169	Monolinuron	ES+	22	215.1 > 126.1	20	215.1 > 99	30
170	Monuron	ES+	20	199 > 72	16	199 > 126	25
171	Myclobutanil	ES+	25	289.1 > 70.2	18	289.1 > 125.1	32
172	Napropamide	ES+	25	272.15 > 129	16	272.15 > 171.1	18
173	Nicosulfuron	ES+	26	411.1 > 106	32	411.1 > 182	22
174	Nuarimol	ES+	37	315 > 252	22	315 > 81.1	28
175	Omethoate	ES+	16	214.1 > 183.1	11	214.1 > 125.1	22
176	Oxadiazon	ES+	32	345.15 > 220	18	345.15 > 177	27
177	Oxadixyl	ES+	31	279 > 219	10	279 > 132	34
178	Oxamyl	ES+	15	237 > 72	12	237 > 90	10
179	Oxathiapiprolin	ES+	35	540.4 > 480.4	25	540.4 > 350.3	28
180	Oxycarboxin	ES+	22	268.1 > 174.8	16	268.1 > 146.9	25
181	Paclobutrazol	ES+	27	294.1 > 125.1	38	294.1 > 70.2	20
182	Paraoxon	ES+	20	276 > 220	20	276 > 94	20
183	Penconazole	ES+	25	284 > 70.1	16	284 > 159	34
184	Pencycuron	ES+	40	329.1 > 124.98	20	329.1 > 218	15
185	Pendimethalin	ES+	12	282.2 > 212.2	10		17
186	Penoxsulam	ES+	40	484>195	29	484>164	29
187	Penthiopyrad	ES+	24	360.2 > 276.2	15	360.2 > 256.1	22
188	Permethrin *	ES+	16	408.175 > 183	25	408.175 > 355.2	8
189	Pethoxamid	ES+	20	296 > 131.1	20	296 > 250.1	14
190	Phoxim	ES+	15	299 > 129	13	299 > 153	7
191	Picoxystrobin	ES+	15	368.1 > 145.1	22	368.1 > 205.1	10
192	Piperonyl Butoxide	ES+	16	356.2873 > 177.109	14	356.2873 > 119.117	34
193	Pirimicarb	ES+	25	239.1 > 72	18	239.1 > 182.1	15

	Compound	Ion mode	CV (V)	Quant. trace	CE (eV)	Qual. trace	CE (eV)
194	Pirimiphos-methyl	ES+	25	306.1 > 108.1	32	306.1 > 164.1	22
195	Prochloraz	ES+	20	376 > 308	15	376 > 266	15
196	Profenofos	ES+	25	372.9 > 302.6	20	372.9 > 127.9	40
197	Promecarb	ES+	15	208.1 > 151	10	208.1 > 109	16
198	Prometon	ES+	30	226.1 > 184.3	28	226.1 > 86.3	18
199	Prometryn	ES+	27	242 > 200.1	17		24
200	Propamocarb	ES+	30	189.1596 > 101.9647	16	189.1596 > 74.0084	24
201	Propanil	ES+	30	218 > 162	16	218 > 127	22
202	Propaquizafop	ES+	26	444>299	22	444>100	18
203	Propargite	ES+	20	368.22 > 231.21	10	368.22 > 175.15	14
204	Propham	ES+	5	180 > 138	8		16
205	Propiconazole	ES+	37	342 > 159	34	342 > 69	22
206	Propoxur	ES+	12	210 > 111	16	210 > 168	10
207	Propyzamide	ES+	22	256.1 > 190	16	256.1 > 173	23
208	Proquinazid	ES+	18	373 > 289	22	373 > 272	32
209	Prosulfocarb	ES+	22	252.1 > 90.9	22	252.1 > 127.9	13
210	Prosulfuron	ES+	26	420 > 141	20	420 > 167	21
211	Prothioconazole- desthio	ES+	30	312>70	22	312>125	35
212	Pyraclostrobin	ES+	20	388.1 > 163	25	388.1 > 193.9	12
213	Pyraflufen Ethyl	ES+	40	413 > 339	20	413 > 253	30
214	Pyrazophos	ES+	33	374 > 222.1	22	374 > 194	32
215	Pyrethrins	ES+	18	317.16 > 149.016	8	317.16 > 106.998	20
216	Pyridaben	ES+	22	365.16 > 147.12	24	365.16 > 309.1	12
217	Pyridaphenthion	ES+	31	341 > 189	22	341 > 92	34
218	Pyrifenox *	ES+	29	295 > 93.1	22	297 > 93	20
219	Pyrimethanil	ES+	42	200 > 107	24	200 > 82	24
220	Pyriofenone	ES+	35	366 > 184.1	25	366 > 209	25
221	Pyriproxyfen	ES+	28	322.16 > 96.06	14	322.16 > 227.1	14

	Compound	Ion mode	CV (V)	Quant. trace	CE (eV)	Qual. trace	CE (eV)
222	Quinalphos	ES+	15	299 > 96.9	30	299 > 162.9	24
223	Quinoxifen	ES+	52	308 > 197	32	308 > 161.9	44
224	Quizalofop Ethyl	ES+	30	373 > 299	22		32
225	Simazine	ES+	32	202 > 96	22		17
226	Spinetoram *	ES+	40	748.4 > 142.12	32	760.4 > 98.05	52
227	Spinosad D	ES+	42	746.52 > 142	31	746.52 > 98.1	53
228	Spirodiclofen	ES+	22	411.1 > 313	13	411.1 > 71.2	13
229	Spirotetramat	ES+	28	374.35 > 216.18	34	374.35 > 302.27	16
230	Spirotetramat-enol- glucoside	ES+	19	464>302	20	464>216	45
231	Spirotetramat- ketohydroxy	ES+	20	318.1 > 300.1	12	318.1 > 214.1	28
232	Spiroxamine	ES+	27	298 > 144	20	298 > 100	32
233	Sulfotep	ES+	17	323 > 97	32	323 > 171	15
234	Sulfoxaflor	ES+	25	276 > 213	15	276 > 261	15
235	Tebuconazole	ES+	31	308 > 125	40	308 > 70.1	22
236	Tebufenozide	ES+	12	353.1 > 133	20	353.1 > 297.1	8
237	Tebufenpyrad	ES+	43	334 > 117	34	334 > 145	28
238	Tebupirimifos	ES+	22	319.1 > 153	29	319.1 > 277	15
239	Terbumeton	ES+	30	226.2 > 170.1	15	226.2 > 114.1	25
240	Terbuthylazine	ES+	28	230 > 174	16		28
241	Terbutryn	ES+	28	242.1 > 186.1	19		20
242	Tetrachlorvinphos	ES+	30	366.8 > 127	16	366.8 > 240.9	23
243	Tetraconazole	ES+	32	372 > 159	30	372 > 70.1	20
244	Tetramethrin *	ES+	20	332 > 164	25	332 > 135	15
245	Thiabendazole	ES+	35	202.1 > 175	28	202.1 > 131	32
246	Thiacloprid	ES+	32	253 > 126	20	253 > 90.1	40
247	Thiamethoxam	ES+	19	292 > 211.2	12	292 > 132	22
248	Thifensulfuron-methyl	ES+	22	388 > 167	15	388 > 56	40

	Compound	Ion mode	CV (V)	Quant. trace	CE (eV)	Qual. trace	CE (eV)
249	Thiobencarb	ES+	20	258 > 125	15	258 > 89	35
250	Thiodicarb	ES+	15	355 > 88	20	355 > 108	15
251	Tolcofos methyl	ES+	30	301.1 > 174.9	29	301.1 > 125	17
252	Triadimefon	ES+	22	294.1 > 197.2	15	294.1 > 69.3	20
253	Tri-allate	ES+	30	304 > 142.9	28	304 > 86	18
254	Triasulfuron	ES+	28	402.05 > 167.05	18	402.05 > 141.05	30
255	Triazamate	ES+	20	315.1 > 72	20	315.1 > 226.1	11
256	Triazophos	ES+	22	314.1 > 161.9	18	314.1 > 118.9	35
257	Trichlorfon	ES+	19	257 > 109	18	257 > 79	30
258	Triclopyr	ES-	12	256 > 198	15	254 > 196	15
259	Tricyclazole	ES+	42	190 > 136	27	190 > 163	18
260	Trifloxystrobin	ES+	25	409 > 186	16	409 > 145	40
261	Triflumizole	ES+	13	346 > 277.9	10	346 > 73	15
262	Triflumuron	ES+	23	359 > 156.1	16	359 > 139.1	35
263	Triticonazole	ES+	15	318.1 > 70.1	18	318.1 > 124.9	40
264	Tritosulfuron	ES+	30	446 > 145	34	446 > 195	18
265	Valifenalate	ES+	23	399 > 116	25	399 > 155	25
266	Vamidothion	ES+	30	288 > 118	28	288 > 146	10
267	Zoxamide	ES+	27	336 > 187.1	25	336 > 159	38

Table 7 – Instrument acquisition data for pesticides analysed by GC-MS/MS

* = sum of isomers

	Compound	Quant. trace	CE (eV)	Qual. trace	CE (eV)
268	Acetochlor	146.0 → 131.1	10	174.0 → 146.1	10
269	Acrinathrin	181.0 → 152.0	30	207.8 → 181.1	10
270	Alachlor	188.1 → 160.1	10	160.1 → 132.1	15
271	Aldrin	262.9 → 192.9	35	254.9 → 220.0	20
272	Benfluralin	292.0 → 264.0	5	292.0 → 206.0	10
273	Bromophos-ethyl	302.8 → 284.7	15	358.7 → 302.8	15
274	Bromopropylate	185.0 → 157.0	15	183.0 → 155.0	15
275	Captan (THPI)	151.0 → 79.0	15	151.0 → 122.0	10
276	Chinomethionate	206.0 → 148.1	15	233.9 → 206.1	10
277	Chlorfenapyr	137.0 → 102.0	15	247.1 → 227.1	20
278	Chlorfenson	175.0 → 111.0	10	111.0 → 75.0	15
279	Chlormephos	121.1 → 65.0	10	153.9 → 121.1	0
280	Chlorpropham	127.0 → 65.0	25	213.0 → 127.0	10
281	Chlorpyrifos-methyl	78.9 → 47.0	10	286.0 → 93.0	15
282	Cyfluthrin *	162.9 → 90.9	15	162.9 → 127.0	5
283	Cyhalofop-butyl	120.1 → 91.0	15	256.2 → 120.1	10
284	Cyhalothrin (Lambda)	181.1 → 152.1	30	208.1 → 181.1	10
285	Cypermethrin *	163.0 → 91.0	10	163.0 → 127.0	5
286	DDT (sum of DDT- o,p'; DDT-p,p'; DDE-o,p'; DDE- p,p'; DDD-o,p'; DDD-p,p')	235.0 → 165.1	25	235.0 → 200.1	10
287	Deltamethrin	252.9 → 93.0	15	181.0 → 152.1	25
288	Dichlobenil	171.0 → 100.0	20	171.0 → 136.0	20
289	Dichlofenthion	223.0 → 204.9	15	279.0 → 223.0	15
290	Dichloran	206.1 → 176.0	10	160.1 → 124.1	10

	Compound	Quant. trace	CE (eV)	Qual. trace	CE (eV)
291	Dichloroaniline, 3,5-	161.0 → 99.0	20	161.0 → 90.0	20
292	Dicofol *	139.0 → 75.0	30	139.0 → 111.0	10
293	Dieldrin	262.9 → 193.0	35	277.0 → 241.0	5
294	Diphenylamine	169.0 → 168.2	15	168.0 → 167.2	15
295	Endosulfan I (alpha isomer)	194.9 → 159.0	5	194.9 → 160.0	5
296	Endosulfan II (beta isomer)	194.9 → 158.9	10	206.9 → 172.0	15
297	Endosulfan sulfate	273.8 → 238.9	15	271.9 → 237.0	20
298	EPN	169.0 → 141.1	5	169.0 → 77.1	25
299	Ethalfuralin	275.9 → 202.1	15	315.9 → 275.9	10
300	Etridiazole	183.0 → 140.0	15	211.1 → 183.0	10
301	Famoxadone	197.0 → 141.1	15	223.9 → 196.2	10
302	Fenclorim	189.1 → 104.1	15	224.1 → 189.1	15
303	Fenitrothion	125.1 → 47.0	15	125.1 → 79.0	5
304	Fenpropathrin	181.1 → 152.1	25	207.9 → 181.0	5
305	Fenson	141.0 → 77.1	5	267.9 → 77.1	20
306	Fenvalerate *	167.0 → 125.1	5	208.9 → 141.1	15
307	Flucythrinate *	156.9 → 107.1	15	198.9 → 157.0	10
308	Heptachlor	271.7 → 236.9	15	273.7 → 238.9	15
309	Hexachlorobenzene	283.8 → 213.9	30	283.8 → 248.8	15
310	Hexaflumuron	176.0 → 148.0	15	277.0 → 176.0	15
311	Iprodione	316.0 → 247.0	10	314.0 → 271.0	10
312	Kresoxim-methyl	116.0 → 89.0	15	116.0 → 63.0	30
313	Malathion	126.9 → 99.0	5	172.9 → 99.0	15
314	Methoxychlor	121.1 → 91.1	15	227.1 → 121.1	15
315	Orthophenilphenol	170.0 → 141.0	15	141.0 → 115.0	15
316	Paraoxon-methyl	108.9 → 79.0	5	229.9 → 106.1	15
317	Parathion-ethyl	139.0 → 109.0	5	109.0 → 81.0	15
318	Parathion-methyl	125.0 → 47.0	10	262.9 → 109.0	10

	Compound	Quant. trace	CE (eV)	Qual. trace	CE (eV)
319	Permethrin *	183.1 → 153.1	15	183.1 → 168.1	10
320	Phosalone	182.0 → 111.0	15	121.1 → 65.0	10
321	Phosmet	160.0 → 77.1	20	160.0 → 133.1	10
322	Phthalimide	147.0 → 103.1	5	104.0 → 76.1	10
323	Procymidone	96.0 → 67.1	10	96.0 → 53.1	15
324	Profluralin	318.1 → 199.1	15	318.1 → 55.1	15
325	Prothiofos	113.0 → 94.9	10	266.9 → 239.0	5
326	Tecnazene	214.9 → 179.0	10	260.9 → 203.0	10
327	Tefluthrin	177.1 → 127.1	15	197.0 → 141.1	10
328	Thiometon	125.0 → 47.0	15	125.0 → 79.0	10
329	Triadimenol	128.0 → 65.0	25	168.0 → 70.0	10
330	Trifluralin	264.0 → 206.0	5	306.1 → 264.0	5
331	Vinclozolin	187.0 → 124.0	20	197.9 → 145.0	15

APPENDIX B. PESTICIDES STUDIED

Table 8 – List of investigated compounds with their CAS number, methodology of analyses and polarity expressed as LogKow. (N.F. = not found; * = sum of isomers)

Compound	CAS number	Log Kow	Compound	CAS number	Log Kow
3-Hydroxycarbofuran	16655-82-6	1.45	Mevinphos	7786-34-7	0.127
3-Ketocarbofuran	16709-30-1	N.F.	Monocrotophos	6923-22-4	-0.22
6-Benzyladenine	1214-39-7	2.16	Monolinuron	1746-81-2	2.2
Abamectin (B1a)	65195-55-3	4.4	Monuron	150-68-5	1.94
Acephate	30560-19-1	-0.89	Myclobutanil	88671-89-0	2.94
Acetamiprid	135410-20-7	0.8	Napropamide	15299-99-7	3.3
Acibenzolar-S-methyl	135158-54-2	3.1	Nicosulfuron	111991-09-4	-1.8
Aldicarb	116-06-3	1.15	Nuarimol	63284-71-9	3.18
Aldicarb sulfone	1646-88-4	-0.57	Omethoate	1113-02-6	-0.74
Aldicarb sulfoxide	1646-87-3	-0.78	Oxadiazon	19666-30-9	4.91
Allethrin	584-79-2	4.96	Oxadixyl	77732-09-3	0.725
Ametocradin	865318-97-4	4.155	Oxamyl	23135-22-0	-0.44
Ametryn	834-12-8	2.63	Oxathiapiprolin	1003318-67-9	3.66
Amidosulfuron	120923-37-7	1.63	Oxycarboxin	5259-88-1	0.772
Amisulbron	348635-87-0	4.4	Paclobutrazol	76738-62-0	3.2
Atrazine	1912-24-9	2.5	Paraoxon	311-45-5	1.98
Azaconazole	60207-31-0	2.17	Penconazole	66246-88-6	3.72
Azinphos-methyl	86-50-0	2.96	Pencycuron	66063-05-6	4.7
Azoxystrobin	131860-33-8	2.5	Pendimethalin	40487-42-1	5.2
Beflubutamid	113614-08-7	4.28	Penoxsulam	219714-96-2	-0.354
Benalaxyl	71626-11-4	3.54	Penthiopyrad	183675-82-3	3.9
Bendiocarb	22781-23-3	1.72	Permethrin *	52645-53-1	6.1
Bensulfuron-methyl	83055-99-6	0.79	Pethoxamid	106700-29-2	2.96
Benthiavalicarb Iso-propyl	177406-68-7	2.6	Phoxim	14816-18-3	4.104

Compound	CAS number	Log Kow	Compound	CAS number	Log Kow
Benzoximate	29104-30-1	2.4	Picoxystrobin	117428-22-5	3.6
Benzoylprop-ethyl	22212-55-1	N.F.	Piperonyl Butoxide	51-03-6	4.75
Bifenazate	149877-41-8	3.4	Pirimicarb	23103-98-2	1.7
Bifenthrin	82657-04-3	6	Pirimiphos-methyl	29232-93-7	4.2
Bitertanol	55179-31-2	4.095	Prochloraz	67747-09-5	3.53
Boscalid	188425-85-6	2.96	Profenofos	41198-08-7	4.44
Bromacil	314-40-9	1.88	Promecarb	2631-37-0	3.1
Bromophos-methyl	2104-96-3	5.21	Prometon	1610-18-0	2.69
Bromoxynil	1689-84-5	1.04	Prometryn	7287-19-6	3.1
Bromuconazole *	116255-48-2	3.24	Propamocarb	24579-73-5	1.12
Bupirimate	41483-43-6	3.9	Propanil	709-98-8	3.3
Buprofezin	69327-76-0	4.93	Propaquizafop	111479-05-1	4.78
Cadusafos	95465-99-9	3.9	Propargite	2312-35-8	5.7
Carbaryl	63-25-2	2.36	Propham	122-42-9	2.6
Carbendazim	10605-21-7	1.51	Propiconazole	60207-90-1	3.72
Carbofuran	1563-66-2	1.52	Propoxur	114-26-1	1.56
Carbosulfan	55285-14-8	5.4	Propyzamide	23950-58-5	3.3
Carfentrazone Ethyl	128639-02-1	3.36	Proquinazid	189278-12-4	5.5
Chlorantranilprole	500008-45-7	2.76	Prosulfocarb	52888-80-9	4.65
Chlorfenvinphos	470-90-6	3.85	Prosulfuron	94125-34-5	-0.21
Chlorpyrifos	2921-88-2	4.7	Prothioconazole- desthio	120983-64-4	1.9
Chlozolate	84332-86-5	3.3	Pyraclostrobin	175013-18-0	3.99
Chromafenozide	143807-66-3	2.7	Pyraflufen Ethyl	129630-19-9	3.49
Clofentezine	74115-24-5	4.1	Pyrazophos	13457-18-6	3.8
Cloquintocet	88349-88-6	-0.7	Pyrethrins	8003-34-7	5.9
Cloquintocet-mexyl	99607-70-2	5.03	Pyridaben	96489-71-3	6.37
Clothianidin	210880-92-5	0.7	Pyridaphenthion	119-12-0	3.2
Coumaphos	56-72-4	4.13	Pyrifenox *	88283-41-4	3.7
Cyanazine	21725-46-2	2.1	Pyrimethanil	53112-28-0	2.84

Compound	CAS number	Log Kow	Compound	CAS number	Log Kow
Cyantraniliprole	736994-63-1	1.94	Pyriofenone	688046-61-9	3.2
Cyazofamid	120116-88-3	3.2	Pyriproxyfen	95737-68-1	5.37
Cyflufenamid	180409-60-3	4.7	Quinalphos	13593-03-8	4.44
Cyflumetofen	400882-07-7	4.3	Quinoxifen	124495-18-7	4.66
Cymoxanil	57966-95-7	0.67	Quizalofop Ethyl	76578-14-8	4.28
Cyproconazole	94361-06-5	3.1	Simazine	122-34-9	2.1
Cyprodinil	121552-61-2	4	Spinetoram *	935545-74-7	4.29
Demeton-S-methylsulfone	17040-19-6	-0.47	Spinosad D	131929-63-0	4.5
Desethyl-Atrazine	6190-65-4	1.51	Spirodiclofen	148477-71-8	5.1
Desisopropyl-Atrazine	1007-28-9	1.15	Spirotetramat	203313-25-1	2.51
Desmedipham	13684-56-5	3.39	Spirotetramat-enol-glucoside	1172614-86-6	N.F.
Desmethyl-pirimicarb	30614-22-3	1	Spirotetramat-ketohydroxy	1172134-11-0	N.F.
Diazinon	333-41-5	3.3	Spiroxamine	118134-30-8	2.885
Dichlorvos	62-73-7	1.66	Sulfotep	3689-24-5	3.99
Dicrotophos	141-66-2	-0.5	Sulfoxaflor	946578-00-3	0.802
Diethofencarb	87130-20-9	3.02	Tebuconazole	107534-96-3	3.7
Difenoconazole	119446-68-3	4.4	Tebufenozide	112410-23-8	4.25
Diflubenzuron	35367-38-5	3.89	Tebufenpyrad	119168-77-3	4.93
Dimethoate	60-51-5	0.704	Tebupirimifos	96182-53-5	4.93
Dimethomorph	110488-70-5	2.68	Terbumeton	33693-04-8	3.04
Dimoxystrobin	149961-52-4	3.59	Terbuthylazine	5915-41-3	3.4
Diniconazole	83657-24-3	4.3	Terbutryn	886-50-0	3.65
Diphenamid	957-51-7	2.17	Tetrachlorvinphos	22248-79-9	3.53
Diuron	330-54-1	2.85	Tetraconazole	112281-77-3	3.56
Dodemorph	1593-77-7	4.14	Tetramethrin *	7696-12-0	4.6
Emamectin Benzoate	138511-97-4	5	Thiabendazole	148-79-8	4.6
B1a					

Compound	CAS number	Log Kow	Compound	CAS number	Log Kow
Epoxiconazole	133855-98-8	3.33	Thiacloprid	111988-49-9	0.73
Etaconazole Isomer	60207-93-4	3.1	Thiamethoxam	153719-23-4	-0.13
Ethirimol	23947-60-6	2.22	Thifensulfuron-methyl	79277-27-3	0.02
Ethofumesate	26225-79-6	2.7	Thiobencarb	28249-77-6	4.23
Ethoprophos	13194-48-4	3.59	Thiodicarb	59669-26-0	1.62
Ethoxyquin	91-53-2	3.979	Tolcofos methyl	57018-04-9	4.56
Etofenprox	80844-07-1	6.9	Triadimefon	43121-43-3	3.11
Etoxazole	153233-91-1	5.59	Tri-allate	2303-17-5	4.6
Etrimfos	38260-54-7	2.94	Triasulfuron	82097-50-5	-0.59
Fenamidone	161326-34-7	2.8	Triazamate	112143-82-5	2.15
Fenamiphos	22224-92-6	3.3	Triazophos	24017-47-8	3.34
Fenarimol	60168-88-9	3.69	Trichlorfon	52-68-6	0.43
Fenazaquin	120928-09-8	5.51	Triclopyr	55335-06-3	-0.45
Fenbuconazole	114369-43-6	3.23	Tricyclazole	41814-78-2	1.42
Fenbutatin-oxide	13356-08-6	5.2	Trifloxystrobin	141517-21-7	4.5
Fenhexamid	126833-17-8	3.51	Triflumizole	68694-11-1	5.1
Fenothiocarb	62850-32-2	3.28	Triflumuron	64628-44-0	4.91
Fenoxaprop	95617-09-7	1.04	Triticonazole	131983-72-7	3.29
Fenoxycarb	79127-80-3	4.07	Tritosulfuron	142469-14-5	2.93
Fenpropidin	67306-00-7	2.9	Valifenalate	283159-90-0	3.05
Fenpropimorph *	67564-91-4	4.1	Vamidothion	2275-23-2	0.16
Fenpyrazamine	473798-59-3	3.52	Zoxamide	156052-68-5	3.76
Fenpyroximat	111812-58-9	5.01	Acetochlor	34256-82-1	4.14
Fenpyroximate	111812-58-9	5.01	Acrinathrin	101007-06-1	5.6
Fenthion-sulfoxide	3761-41-9	N.F.	Alachlor	15972-60-8	3.09
Fipronil	120068-37-3	4	Aldrin	309-00-2	6.5
Fipronil-sulfone	120068-36-2	N.F.	Benfluralin	1861-40-1	5.29
Flazasulfuron	104040-78-0	-0.06	Bromophos-ethyl	4824-78-6	6.15
Flonicamid	158062-67-0	0.3	Bromopropylate	18181-80-1	5.4
Florasulam	145701-23-1	-1.22	Captan (THPI)	1469-48-3	0.3

Compound	CAS number	Log Kow	Compound	CAS number	Log Kow
Fluazifop	69335-91-7	3.18	Chinomethionat	2439-01-2	3.78
Fluazifop-P-Butyl	79241-46-6	4.95	Chlorfenapyr	122453-73-0	4.83
Fluazinam	79622-59-6	4.03	Chlorfenson	80-33-1	4.21
Fludioxonil	131341-86-1	4.12	Chlormephos	24934-91-6	3.04
Flufenacet	142459-58-3	3.2	Chlorpropham	101-21-3	3.76
Flufenoxuron	101463-69-8	4	Chlorpyrifos-methyl	5598-13-0	4.24
Fluopicolide	239110-15-7	3.26	Cyfluthrin *	68359-37-5	5.9
Fluopyram	658066-35-4	3.3	Cyhalofop-butyl	122008-85-9	3.32
Flupyradifurone	951659-40-8	1.2	Cyhalothrin (Lambda)	91465-08-6	5.5
Fluquinconazole	136426-54-5	3.24	Cypermethrin *	52315-07-8	5.55
Fluroxypyr	69377-81-7	1.2	DDT (sum of DDT-o,p'; DDT-p,p'; DDE-o,p'; DDE-p,p'; DDD-o,p'; DDD-p,p')	8017-34-3	6.91
Fluroxypyr-1-methylheptyl ester	81406-37-3	4.53	Deltamethrin	52918-63-5	4.6
Flusilazole	85509-19-9	3.74	Dichlobenil	1194-65-6	2.7
Flutriafol	76674-21-0	2.3	Dichlofenthion	97-17-6	5.14
Fluxapyroxad	907204-31-3	3.1	Dichloran	99-30-9	2.8
Fonofos	944-22-9	3.94	Dichloroaniline, 3,5-	626-43-7	2.9
Formetanate - hydrochloride	23422-53-9	-0.0014	Dicofol *	10606-46-9	5.02
Fosthiazate	98886-44-3	1.68	Dieldrin	60-57-1	3.7
Fuberidazole	3878-19-1	2.67	Diphenylamine	122-39-4	3.82
Furalaxyl	57646-30-7	2.61	Endosulfan I (alpha isomer)	959-98-8	4.74
Furathiocarb	65907-30-4	4.6	Endosulfan II (beta isomer)	33213-65-9	3.83
Heptenophos	23560-59-0	2.32	Endosulfan sulfate	1031-07-8	3.66
Hexaconazole	79983-71-4	3.9	EPN	2104-64-5	5.02
Hexythiazox	78587-05-0	2.53	Ethalfuralin	55283-68-6	5.11

Compound	CAS number	Log Kow	Compound	CAS number	Log Kow
Imazalil	35554-44-0	3.82	Etridiazole	2593-15-9	3.37
Imazaquin	81335-37-7	0.34	Famoxadone	131807-57-3	4.65
Imazosulfuron	122548-33-8	1.59	Fenclorim	3740-92-9	4.17
Imidacloprid	138261-41-3	0.57	Fenitrothion	122-14-5	3.32
Indoxacarb	144171-61-9	4.65	Fenpropathrin	64257-84-7	6
Ipconazole Isomer	125225-28-7	4.21	Fenson	80-38-6	3.57
Iprovalicarb	140923-17-7	3.19	Fenvalerate *	51630-58-1	5.01
Isofetamid	875915-78-9	2.5	Flucythrinate *	70124-77-5	4.74
Isopropalin	33820-53-0	4.69	Heptachlor	76-44-8	5.44
Isoproturon	34123-59-6	2.5	Hexachlorobenzene	118-74-1	3.93
Isopyrazam	881685-58-1	4.1	Hexaflumuron	86479-06-3	5.68
Lenacil	2164-08-1	2.31	Iprodione	36734-19-7	3
Linuron	330-55-2	3	Kresoxim-methyl	143390-89-0	3.4
Malaoxon	1634-78-2	N.F.	Malathion	121-75-5	2.75
Mandipropamid	374726-62-2	3.2	Methoxychlor	72-43-5	5.83
Mecarbam	2595-54-2	2.29	Orthophenilphenol	90-43-7	3.09
Mefentrifluconazole	1417782-03-6	3.4	Paraoxon-methyl	950-35-6	1.33
Mepanipyrim	110235-47-7	3.28	Parathion-ethyl	56-38-2	3.83
Mepronil	55814-41-0	3.66	Parathion-methyl	298-00-0	3
Mepthyldinocap	131-72-6	4.54	Permethrin *	52645-53-1	6.1
Metalaxyl	57837-19-1	1.75	Phosalone	2310-17-0	4.01
Metamitron	41394-05-2	0.83	Phosmet	732-11-6	2.95
Metazachlor	67129-08-2	2.13	Phthalimide	85-41-6	1.15
Metconazole *	125116-23-6	3.85	Procymidone	32809-16-8	3.14
Methamidophos	10265-92-6	-0.8	Profluralin	26399-36-0	5.58
Methidathion	950-37-8	2.2	Prothiofos	34643-46-4	5.67
Methiocarb-sulfone	2179-25-1	N.F.	Tecnazene	117-18-0	4.38
Methiocarb-sulfoxyde	2635-10-1	0.7	Tefluthrin	79538-32-2	6.5
Methomyl	16752-77-5	0.093	Thiometon	640-15-3	3.15
Methoxyfenozide	161050-58-4	3.7	Triadimenol	55219-65-3	2.9

Compound	CAS number	Log Kow	Compound	CAS number	Log Kow
Metolachlor	51218-45-2	2.9	Trifluralin	1582-09-8	5.34
Metrafenone	220899-03-6	4.3	Vinclozolin	50471-44-8	3
Metribuzin	21087-64-9	1.6			

**APPENDIX C. VALIDATION PARAMETERS OF THE ANALYTICAL
METHOD**

Table 9 – Limit of detection¹ (LOD_W , $\mu g L^{-1}$) and limits of quantification² (LOQ_W , $\mu g L^{-1}$) for the analytes extracted from water samples, recoveries and their relative standard deviation at different level of concentration, range of calibration, the correlation coefficient of the calibration and matrix effect (%). ¹: limit of detection (LOD) was estimated as one third quantification limit; ²: limit of quantification (LOQ) was assessed in accordance with the SANTE/11312/2021 guideline

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
1	3-Hydroxycarbofuran	0.003	0.009	97%	11%	91%	19%	98%	7%	0.5-100	0.993	12%
2	3-Ketocarbofuran	0.003	0.009	106%	14%	114%	1%	113%	15%	0.5-100	0.983	14%
3	6-Benzyladenine	0.003	0.009	84%	18%	90%	7%	90%	16%	0.5-100	0.984	1%
4	Abamectin (B1a)	0.005	0.015	49%	25%	108%	10%	114%	2%	1-100	0.981	9%
5	Acephate	0.003	0.009	34%	1%	38%	14%	37%	7%	0.5-100	0.988	11%
6	Acetamiprid	0.003	0.009	114%	1%	106%	9%	120%	6%	0.5-100	0.999	-6%
7	Acibenzolar-S-methyl	0.003	0.009	35%	19%	34%	15%	35%	8%	0.5-100	0.980	0%
8	Aldicarb	0.015	0.045	57%	29%	115%	15%	113%	10%	2-100	0.980	12%
9	Aldicarb sulfone	0.003	0.009	94%	15%	95%	17%	95%	5%	0.5-100	0.982	-5%
10	Aldicarb sulfoxide	0.003	0.009	32%	7%	37%	1%	35%	14%	0.5-100	0.988	2%
11	Allethrin	0.005	0.015	126%	6%	110%	12%	111%	4%	1-100	0.999	-8%
12	Ametocradin	0.003	0.009	107%	8%	102%	18%	110%	9%	0.5-100	0.997	7%
13	Ametryn	0.003	0.009	105%	20%	107%	7%	106%	2%	0.5-100	0.991	-8%
14	Amidosulfuron	0.003	0.009	95%	15%	95%	7%	91%	2%	0.5-100	0.986	-5%
15	Amisulbrom	0.015	0.045	135%	3%	98%	18%	105%	14%	2-100	0.986	-7%
16	Atrazine	0.003	0.009	97%	18%	93%	17%	103%	17%	0.5-100	0.998	4%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
17	Azaconazole	0.003	0.009	108%	11%	94%	2%	105%	19%	0.5-100	0.984	2%
18	Azinphos-methyl	0.005	0.015	67%	31%	101%	7%	106%	12%	1-100	0.997	-7%
19	Azoxystrobin	0.003	0.009	112%	8%	106%	6%	107%	15%	0.5-100	0.989	-1%
20	Beflubutamid	0.003	0.009	101%	7%	97%	2%	105%	12%	0.5-100	0.981	10%
21	Benalaxyl	0.003	0.009	107%	10%	100%	6%	112%	17%	0.5-100	0.981	-4%
22	Bendiocarb	0.003	0.009	44%	14%	50%	11%	49%	15%	0.5-100	0.993	3%
23	Bensulfuron-methyl	0.005	0.015	127%	5%	79%	15%	79%	15%	1-100	0.988	-8%
24	Benthiavalicarb Iso-propyl	0.003	0.009	115%	16%	108%	2%	114%	4%	0.5-100	0.996	-3%
25	Benzoximate	0.003	0.009	120%	15%	118%	12%	110%	9%	0.5-101	0.990	15%
26	Benzoylprop-ethyl	0.003	0.009	101%	1%	108%	13%	111%	11%	0.5-100	0.990	-3%
27	Bifenazate	0.003	0.009	49%	16%	42%	17%	47%	1%	0.5-100	0.990	11%
28	Bifenthrin	0.003	0.009	118%	18%	114%	5%	113%	13%	0.5-100	0.992	-8%
29	Bitertanol	0.003	0.009	110%	12%	110%	6%	102%	5%	0.5-101	0.990	-10%
30	Boscalid	0.003	0.009	96%	15%	91%	16%	96%	3%	0.5-100	0.986	11%
31	Bromacil	0.003	0.009	103%	5%	102%	9%	100%	1%	0.5-100	0.998	-15%
32	Bromophos-methyl	0.003	0.009	102%	5%	104%	1%	107%	17%	0.5-100	0.992	-10%
33	Bromoxynil	0.003	0.009	107%	7%	119%	2%	116%	12%	0.5-100	0.986	15%
34	Bromuconazole (sum)	0.003	0.009	98%	14%	107%	19%	107%	13%	0.5-100	0.990	6%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
35	Bupirimate	0.003	0.009	97%	7%	99%	12%	106%	7%	0.5-100	0.983	14%
36	Buprofezin	0.003	0.009	114%	11%	113%	19%	113%	10%	0.5-100	0.991	-15%
37	Cadusafos	0.003	0.009	71%	20%	72%	2%	70%	6%	0.5-100	0.993	-8%
38	Carbaryl	0.003	0.009	98%	4%	92%	8%	94%	19%	0.5-100	0.998	8%
39	Carbendazim	0.003	0.009	93%	7%	95%	19%	103%	5%	0.5-100	0.986	-13%
40	Carbofuran	0.003	0.009	94%	10%	87%	14%	92%	14%	0.5-100	0.991	12%
41	Carbosulfan	0.005	0.015	135%	19%	111%	19%	111%	17%	1-100	0.981	13%
42	Carfentrazone Ethyl	0.003	0.009	64%	20%	70%	14%	67%	19%	0.5-100	0.983	11%
43	Chlorantranilprole	0.005	0.015	119%	20%	88%	7%	98%	11%	1-100	0.986	15%
44	Chlorfenvinphos	0.003	0.009	111%	11%	114%	11%	112%	19%	0.5-100	0.997	7%
45	Chlorpyrifos	0.003	0.009	87%	13%	78%	10%	83%	11%	0.5-100	0.987	-15%
46	Chlozolinate	0.005	0.015	46%	29%	93%	8%	103%	6%	1-100	0.991	-15%
47	Chromafenozide	0.005	0.015	132%	2%	115%	10%	119%	11%	1-100	0.984	8%
48	Clofentezine	0.005	0.015	34%	26%	79%	13%	87%	15%	1-100	0.984	0%
49	Cloquintocet	0.005	0.015	80%	21%	85%	18%	86%	19%	1-101	0.899	10%
50	Cloquintocet-mexyl	0.003	0.009	97%	17%	94%	19%	98%	12%	0.5-100	0.997	13%
51	Clothianidin	0.003	0.009	97%	11%	96%	7%	92%	5%	0.5-100	0.995	7%
52	Coumaphos	0.003	0.009	103%	3%	107%	14%	110%	14%	0.5-100	0.992	-7%
53	Cyanazine	0.003	0.009	93%	5%	104%	10%	103%	15%	0.5-100	0.994	13%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
54	Cyantraniliprole	0.003	0.009	97%	19%	99%	5%	97%	9%	0.5-100	0.981	-1%
55	Cyazofamid	0.003	0.009	101%	16%	98%	5%	106%	8%	0.5-100	0.992	-4%
56	Cyflufenamid	0.003	0.009	102%	3%	105%	7%	101%	4%	0.5-100	0.991	3%
57	Cyflumetofen	0.003	0.009	36%	7%	33%	15%	35%	19%	0.5-100	0.984	3%
58	Cymoxanil	0.005	0.015	122%	4%	33%	16%	35%	4%	1-100	0.990	0%
59	Cyproconazole	0.003	0.009	82%	18%	78%	3%	87%	13%	0.5-100	0.996	2%
60	Cyprodinil	0.003	0.009	105%	20%	111%	2%	117%	15%	0.5-100	0.984	8%
61	Demeton-S- methylsulfone	0.003	0.009	54%	17%	55%	12%	55%	3%	0.5-100	0.984	-1%
62	Desethyl-Atrazine	0.003	0.009	101%	8%	111%	16%	107%	16%	0.5-100	0.994	-12%
63	Desisopropyl-Atrazine	0.003	0.009	97%	9%	103%	19%	104%	8%	0.5-100	0.995	-12%
64	Desmedipham	0.003	0.009	114%	7%	111%	9%	118%	9%	0.5-100	0.997	-1%
65	Desmethyl-pirimicarb	0.003	0.009	105%	8%	110%	11%	112%	2%	0.5-100	0.989	-8%
66	Diazinon	0.003	0.009	78%	19%	75%	1%	81%	1%	0.5-100	0.993	-13%
67	Dichlorvos	0.003	0.009	32%	13%	34%	5%	33%	9%	0.5-100	0.982	-10%
68	Dicrotophos	0.003	0.009	120%	8%	113%	1%	119%	1%	0.5-100	0.985	6%
69	Diethofencarb	0.003	0.009	104%	7%	100%	14%	109%	16%	0.5-100	0.993	13%
70	Difenoconazole	0.003	0.009	112%	10%	105%	7%	110%	18%	0.5-100	0.999	-8%
71	Diflubenzuron	0.015	0.045	31%	29%	103%	3%	111%	7%	2-100	0.994	-2%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
72	Dimethoate	0.003	0.009	108%	2%	107%	13%	107%	1%	0.5-100	0.990	10%
73	Dimethomorph	0.003	0.009	101%	10%	104%	10%	112%	18%	0.5-100	0.982	15%
74	Dimoxystrobin	0.003	0.009	98%	6%	96%	12%	107%	2%	0.5-100	0.988	-3%
75	Diniconazole	0.003	0.009	93%	3%	97%	6%	102%	11%	0.5-100	0.984	-8%
76	Diphenamid	0.003	0.009	98%	15%	101%	17%	107%	8%	0.5-100	0.981	8%
77	Diuron	0.003	0.009	114%	6%	108%	7%	110%	14%	0.5-100	0.994	14%
78	Dodemorph	0.003	0.009	66%	13%	64%	12%	68%	3%	0.5-100	0.994	7%
79	Enamectin Benzoate	0.003	0.009	106%	3%	103%	16%	114%	6%	0.5-100	0.992	5%
	B1a											
80	Epoxiconazole	0.003	0.009	107%	9%	102%	12%	102%	2%	0.5-100	0.992	4%
81	Etaconazole Isomer	0.003	0.009	94%	13%	108%	17%	104%	5%	0.5-100	0.997	3%
82	Ethirimol	0.003	0.009	97%	16%	87%	7%	95%	12%	0.5-100	0.988	10%
83	Ethofumesate	0.003	0.009	98%	15%	92%	9%	102%	3%	0.5-100	0.987	-13%
84	Ethoprophos	0.003	0.009	66%	20%	64%	5%	64%	19%	0.5-100	0.982	1%
85	Ethoxyquin	0.003	0.009	85%	15%	89%	14%	91%	12%	0.5-101	0.990	9%
86	Etofenprox	0.003	0.009	94%	19%	95%	12%	97%	13%	0.5-100	0.988	-11%
87	Etoxazole	0.003	0.009	123%	16%	119%	14%	117%	14%	0.5-100	0.996	1%
88	Etrifos	0.003	0.009	79%	3%	79%	2%	82%	3%	0.5-100	0.990	15%
89	Fenamidone	0.003	0.009	106%	16%	98%	2%	101%	8%	0.5-100	0.999	-6%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
90	Fenamiphos	0.003	0.009	108%	2%	103%	9%	104%	15%	0.5-100	0.993	-12%
91	Fenarimol	0.005	0.015	139%	3%	82%	18%	89%	17%	1-100	0.999	-2%
92	Fenazaquin	0.003	0.009	105%	16%	110%	6%	112%	6%	0.5-100	0.998	-10%
93	Fenbuconazole	0.003	0.009	113%	4%	105%	5%	112%	1%	0.5-100	0.982	-7%
94	Fenbutatin-oxide	0.003	0.009	67%	3%	74%	12%	74%	18%	0.5-100	0.999	2%
95	Fenhexamid	0.003	0.009	103%	17%	90%	17%	99%	10%	0.5-100	0.984	7%
96	Fenothiocarb	0.003	0.009	93%	14%	91%	5%	94%	8%	0.5-100	0.987	6%
97	Fenoxaprop	0.003	0.009	95%	16%	98%	10%	100%	8%	0.5-101	0.990	-5%
98	Fenoxycarb	0.003	0.009	99%	2%	100%	17%	106%	11%	0.5-100	0.985	-7%
99	Fenpropidin	0.003	0.009	60%	5%	67%	14%	66%	17%	0.5-100	0.987	4%
100	Fenpropimorph (sum of isomers)	0.003	0.009	78%	19%	73%	2%	81%	5%	0.5-100	0.997	-13%
101	Fenpyrazamine	0.003	0.009	112%	16%	106%	14%	114%	11%	0.5-100	0.998	-6%
102	Fenpyroximat	0.003	0.009	116%	20%	107%	11%	110%	12%	0.5-100	0.999	-11%
103	Fenpyroximate	0.003	0.009	116%	20%	107%	11%	110%	12%	0.5-100	0.999	-11%
104	Fenthion-sulfoxide	0.003	0.009	108%	1%	111%	9%	108%	5%	0.5-100	0.985	-13%
105	Fipronil	0.003	0.009	93%	1%	106%	12%	104%	17%	0.5-100	0.996	3%
106	Fipronil-sulfone	0.003	0.009	97%	6%	105%	7%	105%	9%	0.5-100	0.992	-13%
107	Flazasulfuron	0.005	0.015	125%	9%	65%	12%	65%	5%	1-100	0.998	7%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
108	Fonicamid	0.003	0.009	102%	16%	105%	18%	100%	10%	0.5-100	0.983	6%
109	Florasulam	0.003	0.009	92%	8%	92%	16%	98%	13%	0.5-100	0.988	8%
110	Fluazifop	0.005	0.015	59%	25%	33%	8%	34%	4%	1-100	0.980	-2%
111	Fluazifop-P-Butyl	0.003	0.009	101%	17%	111%	5%	107%	1%	0.5-100	0.985	6%
112	Fluazinam	0.003	0.009	117%	14%	111%	12%	116%	2%	0.5-100	0.987	-3%
113	Fludioxonil	0.005	0.015	33%	34%	103%	16%	106%	12%	1-100	0.984	-12%
114	Flufenacet	0.003	0.009	94%	10%	100%	15%	105%	18%	0.5-100	0.987	-4%
115	Flufenoxuron	0.003	0.009	112%	8%	116%	15%	120%	19%	0.5-100	0.993	-2%
116	Fluopicolide	0.003	0.009	90%	9%	85%	7%	93%	15%	0.5-100	0.985	0%
117	Fluopyram	0.003	0.009	81%	19%	82%	4%	85%	13%	0.5-100	0.984	-2%
118	Flupyradifurone	0.003	0.009	101%	18%	106%	10%	111%	16%	0.5-100	0.991	8%
119	Fluquinconazole	0.005	0.015	130%	10%	45%	3%	45%	17%	1-100	0.999	-2%
120	Fluroxypyr	0.005	0.015	139%	5%	117%	7%	116%	10%	1-100	0.989	-7%
121	Fluroxypyr-I- methylheptyl ester	0.003	0.009	113%	1%	108%	2%	116%	4%	0.5-100	0.994	-11%
122	Flusilazole	0.003	0.009	106%	9%	111%	15%	106%	1%	0.5-100	0.998	-6%
123	Flutriafol	0.005	0.015	57%	34%	99%	11%	107%	7%	1-100	0.999	-10%
124	Fluxapyroxad	0.003	0.009	96%	20%	89%	7%	93%	8%	0.5-100	0.990	-2%
125	Fonofos	0.003	0.009	69%	19%	69%	10%	67%	8%	0.5-100	0.992	12%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
126	Formetanate - hy- drochloride	0.003	0.009	36%	4%	36%	3%	35%	1%	0.5-100	0.984	-13%
127	Fosthiazate	0.003	0.009	94%	10%	102%	17%	100%	3%	0.5-100	0.982	-11%
128	Fuberidazole	0.003	0.009	112%	7%	102%	13%	108%	10%	0.5-100	0.984	4%
129	Furalaxyl	0.003	0.009	107%	20%	99%	11%	103%	9%	0.5-100	0.987	3%
130	Furathiocarb	0.003	0.009	111%	12%	120%	8%	118%	1%	0.5-100	0.992	-4%
131	Heptenophos	0.003	0.009	60%	17%	64%	8%	65%	16%	0.5-100	0.998	7%
132	Hexaconazole	0.003	0.009	99%	2%	103%	12%	107%	9%	0.5-100	0.981	11%
133	Hexythiazox	0.003	0.009	112%	17%	110%	4%	112%	2%	0.5-100	0.983	-4%
134	Imazalil	0.003	0.009	111%	12%	109%	16%	110%	18%	0.5-100	0.986	-2%
135	Imazaquin	0.005	0.015	127%	20%	44%	5%	43%	7%	1-100	0.997	-7%
136	Imazosulfuron	0.005	0.015	132%	4%	96%	7%	92%	6%	1-100	0.991	10%
137	Imidacloprid	0.003	0.009	93%	16%	95%	1%	99%	19%	0.5-100	0.981	-7%
138	Indoxacarb	0.003	0.009	122%	1%	118%	14%	120%	13%	0.5-100	0.989	-11%
139	Ipconazole Isomer	0.003	0.009	120%	11%	119%	17%	116%	14%	0.5-100	0.993	-9%
140	Iprovalicarb	0.003	0.009	106%	18%	105%	12%	103%	19%	0.5-100	0.980	-10%
141	Isofetamid	0.003	0.009	100%	11%	114%	6%	108%	8%	0.5-100	0.988	4%
142	Isopropalin	0.005	0.015	49%	25%	72%	16%	80%	18%	1-100	0.983	-3%
143	Isoproturon	0.003	0.009	106%	20%	104%	6%	104%	15%	0.5-100	0.994	-14%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
144	Isoprazam	0.003	0.009	114%	12%	100%	16%	111%	5%	0.5-100	0.998	3%
145	Lenacil	0.003	0.009	105%	12%	109%	10%	105%	13%	0.5-100	0.988	-9%
146	Linuron	0.003	0.009	92%	3%	85%	4%	94%	1%	0.5-100	0.983	-8%
147	Malaon	0.003	0.009	55%	14%	56%	9%	56%	17%	0.5-100	0.993	-9%
148	Mandipropamid	0.003	0.009	113%	18%	109%	7%	112%	5%	0.5-100	0.983	15%
149	Mecarbam	0.003	0.009	43%	5%	43%	2%	43%	2%	0.5-100	0.984	4%
150	Mefenitruconazole	0.003	0.009	90%	13%	95%	15%	95%	5%	0.5-101	0.990	-10%
151	Mepanipirim	0.005	0.015	131%	6%	99%	9%	101%	10%	1-100	0.988	3%
152	Mepronil	0.003	0.009	85%	5%	94%	4%	95%	19%	0.5-100	0.995	-3%
153	Mephtyldinocap	0.025	0.075	126%	18%	116%	19%	110%	6%	2-200	0.999	-11%
154	Metaxyl	0.003	0.009	117%	12%	110%	7%	116%	6%	0.5-100	0.998	5%
155	Metamitron	0.003	0.009	107%	7%	108%	19%	107%	12%	0.5-100	0.983	11%
156	Metazachlor	0.003	0.009	106%	19%	106%	8%	101%	18%	0.5-100	0.990	12%
157	Metconazole (sum of isomers)	0.003	0.009	107%	4%	101%	10%	102%	2%	0.5-100	0.995	15%
158	Methamidophos	0.003	0.009	34%	13%	36%	13%	36%	5%	0.5-100	0.986	-10%
159	Methidathion	0.003	0.009	98%	17%	109%	15%	104%	5%	0.5-100	0.984	1%
160	Methiocarb-sulfone	0.003	0.009	105%	15%	100%	6%	98%	6%	0.5-101	0.989	1%
161	Methiocarb-sulfoxyde	0.003	0.009	34%	1%	36%	16%	37%	3%	0.5-100	0.999	-7%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
162	Methomyl	0.003	0.009	112%	5%	106%	17%	118%	19%	0.5-100	0.982	-12%
163	Methoxyfenozide	0.005	0.015	59%	22%	107%	16%	114%	11%	1-100	0.988	-3%
164	Metolachlor	0.003	0.009	100%	14%	98%	8%	97%	5%	0.5-100	0.999	14%
165	Metrafenone	0.003	0.009	121%	5%	106%	19%	117%	3%	0.5-100	0.981	10%
166	Metribuzin	0.003	0.009	108%	9%	102%	18%	104%	5%	0.5-100	0.990	2%
167	Mevinphos	0.005	0.015	130%	7%	63%	7%	69%	2%	1-100	0.989	-4%
168	Monocrotophos	0.003	0.009	107%	18%	113%	15%	119%	13%	0.5-100	0.994	-3%
169	Monolinuron	0.003	0.009	91%	10%	104%	3%	99%	11%	0.5-100	0.990	0%
170	Monuron	0.003	0.009	116%	17%	118%	10%	113%	17%	0.5-100	0.980	8%
171	Myclobutanil	0.003	0.009	89%	5%	95%	13%	95%	17%	0.5-100	0.993	4%
172	Napropamide	0.003	0.009	96%	9%	108%	15%	107%	14%	0.5-100	0.985	-3%
173	Nicosulfuron	0.003	0.009	41%	8%	42%	16%	43%	18%	0.5-100	0.982	-9%
174	Nuarimol	0.003	0.009	95%	17%	107%	19%	103%	17%	0.5-100	0.999	4%
175	Omethoate	0.003	0.009	37%	7%	37%	14%	36%	19%	0.5-100	0.999	11%
176	Oxadiazon	0.003	0.009	103%	1%	116%	8%	112%	19%	0.5-100	0.989	-10%
177	Oxadixyl	0.003	0.009	100%	20%	113%	8%	107%	11%	0.5-100	0.983	5%
178	Oxamyl	0.003	0.009	92%	6%	95%	17%	91%	18%	0.5-100	0.980	9%
179	Oxathiapiprolin	0.015	0.045	134%	4%	91%	19%	91%	10%	2-100	0.995	0%
180	Oxycarboxin	0.003	0.009	63%	4%	58%	15%	62%	14%	0.5-100	0.982	1%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
181	Paclobutrazol	0.003	0.009	91%	16%	99%	10%	99%	10%	0.5-100	0.999	-6%
182	Paraoxon	0.003	0.009	106%	9%	97%	19%	104%	7%	0.5-100	0.991	-3%
183	Penconazole	0.003	0.009	118%	15%	116%	12%	116%	16%	0.5-100	0.999	-10%
184	Pencycuron	0.003	0.009	100%	11%	104%	7%	106%	9%	0.5-100	0.983	-10%
185	Pendimethalin	0.005	0.015	60%	21%	84%	16%	93%	14%	1-100	0.982	-14%
186	Penoxsulam	0.003	0.009	79%	25%	82%	19%	90%	10%	0.5-100	0.990	3%
187	Penthiopyrad	0.003	0.009	108%	3%	106%	5%	108%	17%	0.5-100	0.999	-9%
188	Permethrin (sum)	0.003	0.009	114%	9%	120%	2%	116%	3%	0.5-100	0.985	-2%
189	Pethoxamid	0.003	0.009	98%	13%	108%	1%	106%	8%	0.5-100	0.995	4%
190	Phoxim	0.005	0.015	40%	21%	92%	12%	95%	14%	1-100	0.985	7%
191	Picoxystrobin	0.003	0.009	110%	19%	104%	7%	111%	1%	0.5-100	0.988	11%
192	Piperonyl Butoxide	0.003	0.009	100%	19%	100%	14%	110%	2%	0.5-100	0.991	-15%
193	Pirimicarb	0.003	0.009	108%	18%	106%	19%	117%	14%	0.5-100	0.985	-12%
194	Pirimiphos-methyl	0.003	0.009	89%	18%	95%	2%	99%	18%	0.5-100	0.993	-11%
195	Prochloraz	0.003	0.009	109%	6%	109%	9%	117%	1%	0.5-100	0.992	7%
196	Profenofos	0.003	0.009	96%	12%	93%	11%	92%	15%	0.5-100	0.988	15%
197	Promecarb	0.003	0.009	100%	1%	99%	4%	96%	8%	0.5-100	0.998	-1%
198	Prometon	0.005	0.015	130%	20%	97%	10%	106%	8%	1-100	0.993	-12%
199	Prometryn	0.003	0.009	99%	7%	107%	16%	103%	9%	0.5-100	0.995	4%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
200	Propamocarb	0.003	0.009	35%	8%	32%	4%	34%	19%	0.5-100	0.989	7%
201	Propanil	0.003	0.009	102%	19%	102%	9%	101%	10%	0.5-100	0.993	2%
202	Propanquizafoxop	0.003	0.009	90%	23%	98%	15%	95%	15%	0.5-100	0.990	9%
203	Propargite	0.003	0.009	110%	3%	114%	6%	110%	17%	0.5-100	0.990	-7%
204	Propham	0.015	0.045	45%	22%	58%	4%	63%	9%	2-100	0.980	5%
205	Propiconazole	0.003	0.009	104%	20%	98%	19%	106%	16%	0.5-100	0.993	11%
206	Propoxur	0.003	0.009	99%	14%	90%	8%	100%	17%	0.5-100	0.985	-11%
207	Propyzamide	0.005	0.015	58%	22%	75%	8%	82%	14%	1-100	0.984	-14%
208	Proquinazid	0.003	0.009	104%	18%	101%	14%	101%	1%	0.5-100	0.998	9%
209	Prosulfocarb	0.003	0.009	93%	2%	96%	15%	93%	4%	0.5-100	0.982	-3%
210	Prosulfuron	0.005	0.015	125%	2%	104%	3%	100%	17%	1-100	0.992	1%
211	Prothioconazole- desthio	0.003	0.009	110%	21%	115%	15%	112%	8%	0.5-100	0.990	2%
212	Pyraclostrobin	0.003	0.009	112%	9%	117%	9%	114%	9%	0.5-100	0.985	1%
213	Pyraflufen Ethyl	0.003	0.009	71%	20%	67%	10%	69%	10%	0.5-100	0.995	12%
214	Pyrazophos	0.003	0.009	107%	18%	108%	16%	112%	15%	0.5-100	0.990	-9%
215	Pyrethrins	0.05	0.15	66%	23%	97%	2%	93%	12%	5-200	0.994	12%
216	Pyridaben	0.003	0.009	119%	11%	109%	12%	115%	17%	0.5-100	0.992	6%
217	Pyridaphenthion	0.005	0.015	55%	27%	81%	16%	88%	18%	1-100	0.994	8%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
218	PyrifenoX (sum)	0.003	0.009	96%	4%	99%	12%	103%	4%	0.5-100	0.985	6%
219	Pyrimethanil	0.003	0.009	100%	7%	110%	12%	105%	3%	0.5-100	0.999	13%
220	Pyriofenone	0.003	0.009	105%	18%	109%	2%	114%	14%	0.5-100	0.989	-3%
221	Pyriproxyfen	0.003	0.009	88%	12%	96%	14%	95%	12%	0.5-100	0.998	4%
222	Quinalphos	0.003	0.009	96%	5%	104%	14%	101%	5%	0.5-100	0.996	-5%
223	Quinoxifen	0.003	0.009	94%	14%	97%	11%	96%	16%	0.5-100	0.999	2%
224	Quisqualofop Ethyl	0.003	0.009	105%	6%	105%	9%	108%	18%	0.5-100	0.998	-2%
225	Simazine	0.015	0.045	62%	23%	102%	16%	102%	11%	2-100	0.996	7%
226	Spinetoram (sum)	0.003	0.009	121%	9%	117%	13%	119%	12%	0.5-100	0.981	-13%
227	Spinosad D	0.003	0.009	114%	17%	118%	8%	113%	8%	0.5-100	0.981	8%
228	Spirodiclofen	0.003	0.009	74%	15%	72%	7%	79%	17%	0.5-100	0.988	-6%
229	Spirotetramat	0.003	0.009	32%	9%	32%	9%	34%	2%	0.5-100	0.987	-9%
230	Spirotetramat-enol-glucoside	0.003	0.009	70%	21%	81%	19%	85%	15%	0.5-100	0.990	-7%
231	Spirotetramat-ketohydroxy	0.005	0.015	88%	20%	105%	2%	117%	2%	1-100	0.999	12%
232	Spiroxamine	0.003	0.009	86%	1%	75%	19%	82%	2%	0.5-100	0.981	2%
233	Sulfotep	0.003	0.009	61%	20%	54%	2%	60%	1%	0.5-100	0.984	-5%
234	Sulfoxaflor	0.005	0.015	120%	20%	116%	15%	115%	3%	1-100	0.999	-3%
235	Tebuconazole	0.003	0.009	101%	6%	103%	6%	108%	6%	0.5-100	0.997	-11%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
236	Tebufenozide	0.003	0.009	109%	18%	110%	13%	112%	19%	0.5-100	0.988	-1%
237	Tebufenpyrad	0.003	0.009	100%	17%	92%	7%	102%	17%	0.5-100	0.982	1%
238	Tebupirimifos	0.003	0.009	61%	12%	58%	7%	63%	2%	0.5-100	0.981	-6%
239	Terbumeton	0.003	0.009	97%	15%	106%	12%	107%	15%	0.5-100	0.998	-14%
240	Terbuthylazine	0.003	0.009	95%	15%	96%	9%	99%	3%	0.5-100	0.992	10%
241	Terbutryn	0.003	0.009	104%	3%	108%	16%	103%	3%	0.5-100	0.998	7%
242	Tetrachlorvinphos	0.003	0.009	112%	11%	103%	16%	108%	1%	0.5-100	0.989	2%
243	Tetraconazole	0.003	0.009	106%	12%	105%	16%	107%	14%	0.5-100	0.996	14%
244	Tetramethrin (sum)	0.003	0.009	39%	11%	36%	9%	38%	7%	0.5-100	0.990	7%
245	Thiabendazole	0.003	0.009	42%	20%	41%	2%	43%	10%	0.5-100	0.995	2%
246	Thiacloprid	0.003	0.009	113%	4%	116%	16%	111%	7%	0.5-100	0.984	1%
247	Thiamethoxam	0.003	0.009	116%	3%	118%	16%	117%	9%	0.5-100	0.983	7%
248	Thifensulfuron-methyl	0.005	0.015	56%	29%	90%	17%	88%	14%	1-100	0.996	10%
249	Thiobencarb	0.003	0.009	105%	4%	100%	13%	101%	15%	0.5-100	0.998	13%
250	Thiodicarb	0.003	0.009	85%	12%	87%	14%	90%	18%	0.5-100	0.983	-3%
251	Tolcofos methyl	0.005	0.015	67%	34%	45%	18%	44%	7%	1-100	0.989	3%
252	Triadimefon	0.005	0.015	61%	24%	52%	18%	55%	12%	1-100	0.991	-15%
253	Tri-allate	0.003	0.009	99%	3%	106%	15%	103%	4%	0.5-100	0.993	2%
254	Triasulfuron	0.005	0.015	136%	9%	84%	19%	85%	7%	1-100	0.991	-1%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
255	Triazamate	0.003	0.009	86%	20%	89%	19%	94%	15%	0.5-100	0.995	-10%
256	Triazophos	0.003	0.009	50%	10%	46%	7%	48%	8%	0.5-100	0.996	-14%
257	Trichlorfon	0.003	0.009	88%	17%	87%	1%	92%	14%	0.5-100	0.999	7%
258	Triclopyr	0.015	0.045	54%	23%	45%	3%	49%	6%	2-100	0.981	11%
259	Tricyclazole	0.003	0.009	105%	5%	107%	2%	113%	17%	0.5-100	0.991	-3%
260	Trifloxystrobin	0.003	0.009	123%	2%	110%	16%	117%	12%	0.5-100	0.990	-8%
261	Triflumizole	0.003	0.009	86%	5%	85%	19%	86%	1%	0.5-100	0.999	-6%
262	Triflumuron	0.003	0.009	114%	16%	114%	12%	111%	17%	0.5-100	0.997	-10%
263	Triticonazole	0.003	0.009	108%	20%	96%	13%	103%	3%	0.5-100	0.982	12%
264	Tritosulfuron	0.003	0.009	111%	14%	104%	9%	107%	18%	0.5-100	0.991	-8%
265	Valifenalate	0.003	0.009	82%	13%	96%	15%	91%	6%	0.5-100	0.985	-12%
266	Vamidothion	0.003	0.009	113%	13%	105%	19%	111%	5%	0.5-100	0.992	-8%
267	Zoxamide	0.003	0.009	107%	12%	103%	2%	107%	1%	0.5-100	0.982	11%
268	Acetochlor	0.005	0.015	69%	30%	113%	17%	118%	17%	1-100	0.998	14%
269	Acrinathrin	0.005	0.015	41%	26%	33%	1%	33%	13%	1-100	0.985	-2%
270	Alachlor	0.015	0.045	132%	7%	113%	19%	113%	14%	2-100	0.984	7%
271	Aldrin	0.005	0.015	31%	25%	70%	14%	70%	15%	1-100	0.980	3%
272	Benfluralin	0.005	0.015	57%	32%	65%	5%	63%	9%	1-100	0.986	5%
273	Bromophos-ethyl	0.005	0.015	131%	5%	112%	1%	118%	1%	1-100	0.990	14%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
274	Bromopropylate	0.005	0.015	133%	20%	116%	12%	118%	7%	1-100	0.990	0%
275	Captan (THPI)	0.015	0.045	138%	7%	112%	6%	114%	10%	2-100	0.992	13%
276	Chinomethionat	0.005	0.015	64%	33%	42%	1%	45%	4%	1-100	0.999	6%
277	Chlorfenapyr	0.015	0.045	68%	35%	113%	15%	120%	1%	2-100	0.999	12%
278	Chlorfenson	0.005	0.015	62%	33%	118%	18%	120%	1%	1-100	0.983	-4%
279	Chlormephos	0.015	0.045	34%	29%	47%	13%	45%	11%	2-100	0.987	5%
280	Chlorpropham	0.015	0.045	135%	3%	110%	3%	116%	9%	2-100	0.987	-6%
281	Chlorpyrifos-methyl	0.005	0.015	135%	12%	110%	1%	115%	17%	1-100	0.994	-1%
282	Cyfluthrin (sum of isomers)	0.015	0.045	64%	26%	51%	9%	52%	10%	2-100	0.994	8%
283	Cyhalofop-butyl	0.005	0.015	43%	20%	56%	15%	56%	7%	1-100	0.986	-5%
284	Cyhalothrin (Lambda)	0.015	0.045	57%	34%	67%	16%	73%	3%	2-100	0.991	-15%
285	Cypermethrin (sum of isomers)	0.015	0.045	46%	28%	39%	1%	43%	3%	2-100	0.984	3%
286	DDT (sum of DDT-o,p'; DDT-p,p'; DDE-o,p'; DDE-p,p'; DDD-o,p'; DDD-p,p')	0.05	0.15	120%	6%	106%	7%	107%	3%	5-200	0.980	-10%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
287	Deltamethrin	0.005	0.015	139%	4%	46%	1%	49%	10%	1-100	0.989	13%
288	Dichlobenil	0.005	0.015	33%	31%	35%	15%	39%	10%	1-100	0.991	4%
289	Dichlofenthion	0.005	0.015	126%	4%	77%	7%	82%	15%	1-100	0.985	-11%
290	Dichloran	0.015	0.045	59%	21%	104%	19%	107%	7%	2-100	0.999	2%
291	Dichloroaniline, 3,5-	0.015	0.045	135%	3%	39%	5%	41%	18%	2-100	0.996	6%
292	Dicofol (sum of isomers)	0.015	0.045	40%	23%	112%	13%	113%	7%	2-100	0.992	-9%
293	Dieldrin	0.015	0.045	137%	13%	102%	17%	110%	1%	2-100	0.988	7%
294	Diphenylamine	0.015	0.045	45%	25%	89%	4%	91%	18%	2-100	0.989	3%
295	Endosulfan I (alpha isomer)	0.005	0.015	33%	26%	105%	18%	101%	6%	1-100	0.998	-14%
296	Endosulfan II (beta isomer)	0.015	0.045	134%	15%	106%	8%	114%	19%	2-100	0.996	-14%
297	Endosulfan sulfate	0.015	0.045	122%	1%	109%	3%	115%	19%	2-100	0.983	-8%
298	EPN	0.015	0.045	61%	28%	110%	7%	115%	9%	2-100	0.986	5%
299	Ethalfuralin	0.005	0.015	54%	21%	78%	3%	82%	1%	1-100	0.984	15%
300	Etridiazole	0.005	0.015	130%	6%	53%	5%	50%	10%	1-100	0.988	-7%
301	Famoxadone	0.005	0.015	122%	20%	114%	13%	116%	2%	1-100	0.998	0%
302	Fenclorim	0.015	0.045	42%	20%	67%	2%	65%	10%	2-100	0.991	13%
303	Fenitrothion	0.005	0.015	136%	16%	107%	1%	119%	5%	1-100	0.980	2%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
304	Fenpropathrin	0.005	0.015	128%	3%	115%	1%	109%	1%	1-100	0.988	7%
305	Fenson	0.005	0.015	140%	4%	117%	2%	117%	17%	1-100	0.984	-6%
306	Fenvalerate (sum of isomers)	0.005	0.015	68%	25%	90%	14%	85%	18%	1-100	0.986	-4%
307	Flucythrinate (sum of isomers)	0.005	0.015	128%	9%	93%	1%	88%	6%	1-100	0.992	14%
308	Heptachlor	0.005	0.015	56%	22%	83%	14%	90%	17%	1-100	0.997	11%
309	Hexachlorobenzene	0.015	0.045	140%	5%	49%	10%	49%	4%	2-100	0.999	-15%
310	Hexaflumuron	0.015	0.045	44%	28%	104%	5%	111%	8%	2-100	0.996	2%
311	Iprodione	0.015	0.045	140%	6%	30%	13%	32%	14%	2-100	0.985	-12%
312	Kresoxim-methyl	0.005	0.015	68%	26%	106%	4%	117%	16%	1-100	0.999	4%
313	Malathion	0.005	0.015	59%	34%	109%	8%	108%	14%	1-100	0.981	-2%
314	Methoxychlor	0.005	0.015	127%	10%	94%	2%	102%	10%	1-100	0.984	-4%
315	Orthophenilphenol	0.015	0.045	41%	22%	120%	17%	118%	2%	2-100	0.989	-5%
316	Paraoxon-methyl	0.005	0.015	134%	1%	65%	12%	67%	2%	1-100	0.999	10%
317	Parathion-ethyl	0.015	0.045	132%	1%	102%	9%	100%	10%	2-100	0.993	14%
318	Parathion-methyl	0.005	0.015	138%	10%	110%	8%	115%	5%	1-100	0.983	-5%
319	Permethrin (sum of isomers)	0.005	0.015	38%	20%	88%	4%	84%	2%	1-100	0.999	4%

	Compound	LOD _W ($\mu\text{g L}^{-1}$)	LOQ _W ($\mu\text{g L}^{-1}$)	0.005 ($\mu\text{g L}^{-1}$)		0.05 ($\mu\text{g L}^{-1}$)		0.5 ($\mu\text{g L}^{-1}$)		Calibration range ($\mu\text{g L}^{-1}$)	R ²	Matrix effect (%)
				Rec%	RSD%	Rec%	RSD%	Rec%	RSD%			
320	Phosalone	0.005	0.015	135%	2%	65%	5%	70%	15%	1-100	0.996	-2%
321	Phosmet	0.005	0.015	139%	20%	107%	6%	116%	12%	1-100	0.997	12%
322	Phthalimide	0.015	0.045	63%	26%	110%	8%	109%	15%	2-100	0.981	15%
323	Procymidone	0.005	0.015	138%	3%	109%	8%	119%	14%	1-100	0.991	-8%
324	Profluralin	0.005	0.015	124%	9%	94%	18%	97%	17%	1-100	0.994	-10%
325	Prothiofos	0.005	0.015	46%	24%	83%	11%	92%	7%	1-100	0.982	9%
326	Tecnazene	0.005	0.015	131%	6%	31%	12%	32%	16%	1-100	0.999	10%
327	Tefluthrin	0.015	0.045	65%	24%	120%	14%	118%	12%	2-100	0.996	-11%
328	Thiometon	0.015	0.045	59%	32%	73%	15%	71%	2%	2-100	0.994	3%
329	Triadimenol	0.015	0.045	33%	31%	109%	12%	119%	7%	2-100	0.995	-7%
330	Trifluralin	0.015	0.045	33%	23%	110%	4%	113%	14%	2-100	0.981	-15%
331	Vinclozolin	0.005	0.015	46%	27%	115%	18%	112%	6%	1-100	0.994	15%

Table 10 – Limit of detection¹ (LOD_{POCIS}, µg) and limits of quantification² (LOQ_{POCIS}, µg) for the analytes extracted from POCIS, recoveries and their relative standard deviation at different level of concentration and matrix effect (%). ¹: limit of detection (LOD) was estimated as one third quantification limit; ²: limit of quantification (LOQ) was assessed in accordance with the SANTE/11312/2021 guideline; *: sum of isomers

	Compound	LOD _{POCIS} (µg)	LOQ _{POCIS} (µg)	0.001 (µg)		0.05 (µg)		0.5 (µg)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
1	3-Hydroxycarbofuran	0.001	0.003	72%	6%	83%	9%	79%	15%	14%
2	3-Ketocarbofuran	0.001	0.003	114%	14%	114%	8%	111%	9%	13%
3	6-Benzyladenine	0.001	0.003	98%	1%	107%	9%	105%	15%	-15%
4	Abamectin (B1a)	0.002	0.005	63%	29%	76%	6%	80%	7%	-15%
5	Acephate	0.001	0.003	115%	15%	119%	14%	116%	5%	-10%
6	Acetamiprid	0.001	0.003	112%	8%	114%	7%	119%	11%	7%
7	Acibenzolar-S-methyl	0.001	0.003	122%	6%	111%	11%	116%	13%	-13%
8	Aldicarb	0.005	0.015	46%	35%	80%	7%	78%	9%	5%
9	Aldicarb sulfone	0.001	0.003	67%	12%	69%	1%	70%	1%	8%
10	Aldicarb sulfoxide	0.001	0.003	108%	15%	115%	6%	114%	2%	-10%
11	Allethrin	0.002	0.005	130%	13%	95%	12%	99%	10%	-4%
12	Ametocradin	0.001	0.003	97%	14%	92%	3%	92%	1%	-8%
13	Ametryn	0.001	0.003	97%	12%	105%	13%	102%	13%	7%
14	Amidosulfuron	0.001	0.003	93%	3%	93%	15%	93%	12%	-14%
15	Amisulbron	0.005	0.015	52%	27%	112%	12%	115%	10%	-9%
16	Atrazine	0.001	0.003	106%	20%	103%	1%	108%	3%	6%
17	Azaconazole	0.001	0.003	86%	17%	94%	13%	92%	10%	2%

	Compound	LOD _{POCIS} (μg)	LOQ _{POCIS} (μg)	0.001 (μg)		0.05 (μg)		0.5 (μg)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
18	Azinphos-methyl	0.002	0.005	137%	4%	119%	2%	119%	11%	-14%
19	Azoxystrobin	0.001	0.003	99%	2%	106%	6%	101%	11%	15%
20	Beflubutamid	0.001	0.003	87%	9%	92%	13%	90%	4%	-7%
21	Benalaxyl	0.001	0.003	113%	12%	116%	7%	117%	3%	-5%
22	Bendiocarb	0.001	0.003	65%	16%	69%	8%	72%	2%	-3%
23	Bensulfuron-methyl	0.002	0.005	120%	20%	112%	8%	109%	4%	9%
24	Benthiavalcarb Isopropyl	0.001	0.003	107%	20%	110%	4%	106%	11%	-11%
25	Benzoximate	0.001	0.003	113%	9%	114%	5%	103%	6%	15%
26	Benzoylprop-ethyl	0.001	0.003	119%	11%	117%	2%	116%	7%	4%
27	Bifenazate	0.001	0.003	87%	18%	93%	8%	94%	6%	9%
28	Bifenthrin	0.001	0.003	100%	9%	100%	2%	102%	8%	-4%
29	Bitertanol	0.001	0.003	77%	20%	82%	19%	90%	6%	4%
30	Boscalid	0.001	0.003	95%	9%	102%	8%	98%	10%	14%
31	Bromacil	0.001	0.003	122%	10%	115%	13%	116%	9%	-11%
32	Bromophos-methyl	0.001	0.003	95%	7%	96%	1%	100%	4%	-9%
33	Bromoxynil	0.001	0.003	118%	19%	118%	1%	118%	14%	-3%
34	Bromuconazole *	0.001	0.003	108%	11%	117%	6%	111%	4%	-11%
35	Bupirimate	0.001	0.003	108%	20%	110%	14%	115%	9%	11%
36	Buprofezin	0.001	0.003	72%	6%	73%	4%	72%	9%	-9%

	Compound	LOD _{POCIS} (μg)	LOQ _{POCIS} (μg)	0.001 (μg)		0.05 (μg)		0.5 (μg)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
37	Cadusafos	0.001	0.003	101%	13%	108%	14%	111%	14%	-13%
38	Carbaryl	0.001	0.003	90%	8%	97%	3%	100%	1%	-15%
39	Carbendazim	0.001	0.003	106%	3%	113%	4%	109%	4%	0%
40	Carbofuran	0.001	0.003	113%	6%	120%	3%	120%	13%	14%
41	Carbosulfan	0.002	0.005	56%	29%	97%	13%	94%	10%	4%
42	Carfentrazone Ethyl	0.001	0.003	74%	18%	71%	11%	74%	7%	6%
43	Chlorantranilprole	0.002	0.005	62%	24%	93%	6%	91%	2%	-6%
44	Chlorfenvinphos	0.001	0.003	102%	2%	113%	10%	110%	15%	2%
45	Chlorpyrifos	0.001	0.003	80%	3%	85%	2%	89%	8%	0%
46	Chlozolinate	0.002	0.005	135%	1%	103%	6%	108%	3%	4%
47	Chromafenozide	0.002	0.005	61%	27%	74%	13%	75%	1%	-2%
48	Clofentezine	0.002	0.005	39%	30%	82%	11%	83%	15%	-14%
49	Cloquintocet	0.002	0.006	127%	25%	125%	20%	117%	16%	-11%
50	Cloquintocet-mexyl	0.001	0.003	67%	7%	69%	6%	70%	7%	-2%
51	Clothianidin	0.001	0.003	72%	20%	73%	4%	77%	6%	7%
52	Coumaphos	0.001	0.003	87%	7%	85%	12%	84%	12%	-4%
53	Cyanazine	0.001	0.003	91%	12%	91%	11%	87%	2%	13%
54	Cyantranilprole	0.001	0.003	81%	6%	89%	6%	88%	13%	-11%
55	Cyazofamid	0.001	0.003	73%	12%	70%	12%	73%	1%	13%

	Compound	LOD _{POCIS} (μg)	LOQ _{POCIS} (μg)	0.001 (μg)		0.05 (μg)		0.5 (μg)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
56	Cyflufenamid	0.001	0.003	87%	17%	86%	5%	83%	10%	-13%
57	Cyflumetofen	0.001	0.003	71%	4%	78%	13%	76%	15%	-9%
58	Cymoxanil	0.002	0.005	55%	29%	101%	10%	104%	15%	0%
59	Cyproconazole	0.001	0.003	105%	13%	104%	4%	106%	10%	-2%
60	Cyprodinil	0.001	0.003	105%	15%	112%	12%	115%	9%	-2%
61	Demeton-S-methylsulfone	0.001	0.003	97%	20%	95%	5%	94%	13%	2%
62	Desethyl-Atrazine	0.001	0.003	121%	3%	114%	3%	119%	5%	-5%
63	Desisopropyl-Atrazine	0.001	0.003	119%	6%	119%	1%	117%	12%	4%
64	Desmedipham	0.001	0.003	86%	15%	84%	4%	82%	1%	-6%
65	Desmethyl-pirimicarb	0.001	0.003	85%	9%	96%	13%	94%	11%	2%
66	Diazinon	0.001	0.003	75%	3%	74%	6%	77%	15%	-13%
67	Dichlorvos	0.001	0.003	89%	9%	91%	12%	92%	9%	3%
68	Dicrotophos	0.001	0.003	106%	9%	119%	6%	113%	1%	-6%
69	Diethofencarb	0.001	0.003	74%	2%	67%	14%	70%	12%	4%
70	Difenoconazole	0.001	0.003	85%	15%	88%	12%	89%	2%	-12%
71	Diflubenzuron	0.005	0.015	138%	2%	75%	3%	75%	14%	12%
72	Dimethoate	0.001	0.003	113%	18%	114%	14%	112%	3%	-1%
73	Dimethomorph	0.001	0.003	82%	8%	88%	10%	88%	6%	7%
74	Dimoxystrobin	0.001	0.003	101%	4%	104%	14%	104%	9%	-15%

	Compound	LOD _{POCIS} (μg)	LOQ _{POCIS} (μg)	0.001 (μg)		0.05 (μg)		0.5 (μg)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
75	Diniconazole	0.001	0.003	88%	7%	87%	7%	91%	5%	-6%
76	Diphenamid	0.001	0.003	79%	1%	79%	12%	77%	9%	-15%
77	Diuron	0.001	0.003	89%	4%	93%	4%	90%	5%	10%
78	Dodemorph	0.001	0.003	71%	13%	73%	2%	74%	14%	-13%
79	Emamectin Benzoate B1a	0.001	0.003	115%	1%	111%	14%	117%	2%	-13%
80	Epoxiconazole	0.001	0.003	83%	8%	88%	14%	88%	14%	-13%
81	Etaconazole Isomer	0.001	0.003	86%	16%	87%	5%	86%	11%	-9%
82	Ethirimol	0.001	0.003	75%	12%	81%	14%	83%	6%	-8%
83	Ethofumesate	0.001	0.003	105%	2%	110%	3%	115%	10%	-5%
84	Ethoprophos	0.001	0.003	86%	3%	81%	7%	82%	1%	12%
85	Ethoxyquin	0.001	0.003	105%	20%	103%	14%	93%	4%	-2%
86	Etofenprox	0.001	0.003	124%	15%	120%	3%	120%	6%	5%
87	Etoxazole	0.001	0.003	64%	14%	69%	12%	70%	2%	3%
88	Etrinfos	0.001	0.003	83%	5%	88%	2%	88%	4%	9%
89	Fenamidone	0.001	0.003	117%	2%	116%	11%	114%	14%	-12%
90	Fenamiphos	0.001	0.003	110%	12%	108%	2%	112%	5%	11%
91	Fenarimol	0.002	0.005	135%	7%	99%	14%	96%	12%	11%
92	Fenazaquin	0.001	0.003	102%	5%	112%	15%	112%	1%	9%
93	Fenbuconazole	0.001	0.003	113%	9%	117%	1%	116%	15%	-9%

	Compound	LOD _{POCIS} (μ g)	LOQ _{POCIS} (μ g)	0.001 (μ g)		0.05 (μ g)		0.5 (μ g)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
94	Fenbutatin-oxide	0.001	0.003	100%	9%	101%	15%	100%	9%	-6%
95	Fenhexamid	0.001	0.003	74%	17%	76%	9%	80%	1%	-12%
96	Fenothiocarb	0.001	0.003	76%	14%	76%	14%	79%	6%	5%
97	Fenoxaprop	0.001	0.003	121%	12%	114%	20%	112%	13%	5%
98	Fenoxycarb	0.001	0.003	100%	18%	105%	11%	100%	15%	-5%
99	Fenpropidin	0.001	0.003	82%	12%	81%	12%	83%	8%	2%
100	Fenpropimorph *	0.001	0.003	100%	13%	113%	9%	110%	2%	3%
101	Fenpyrazamine	0.001	0.003	76%	15%	80%	8%	82%	2%	-5%
102	Fenpyroximat	0.003	0.009	106%	7%	102%	1%	112%	7%	0%
103	Fenpyroximate	0.001	0.003	98%	3%	100%	7%	96%	3%	10%
104	Fenthion-sulfoxide	0.001	0.003	76%	5%	79%	14%	83%	12%	12%
105	Fipronil	0.001	0.003	99%	12%	105%	12%	108%	3%	10%
106	Fipronil-sulfone	0.001	0.003	111%	16%	113%	11%	113%	1%	-9%
107	Flazasulfuron	0.002	0.005	121%	19%	78%	15%	81%	7%	-11%
108	Flonicamid	0.001	0.003	98%	2%	101%	10%	102%	4%	1%
109	Florasulam	0.001	0.003	110%	9%	117%	5%	111%	6%	8%
110	Fluazifop	0.002	0.005	67%	22%	94%	2%	90%	9%	-7%
111	Fluazifop-P-Butyl	0.001	0.003	82%	7%	79%	13%	79%	11%	-2%
112	Fluazinam	0.001	0.003	108%	6%	104%	5%	109%	6%	13%

	Compound	LOD _{POCIS} (μ g)	LOQ _{POCIS} (μ g)	0.001 (μ g)		0.05 (μ g)		0.5 (μ g)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
113	Fludioxonil	0.002	0.005	58%	28%	104%	6%	103%	7%	-12%
114	Flufenacet	0.001	0.003	73%	14%	82%	4%	80%	2%	-5%
115	Flufenoxuron	0.001	0.003	82%	5%	81%	12%	83%	10%	5%
116	Fluopicolide	0.001	0.003	74%	12%	80%	9%	78%	14%	-2%
117	Fluopyram	0.001	0.003	81%	15%	84%	7%	80%	15%	4%
118	Flupyradifurone	0.001	0.003	116%	17%	118%	8%	113%	11%	14%
119	Fluquinconazole	0.002	0.005	49%	24%	107%	14%	111%	4%	-5%
120	Fluroxypyr	0.002	0.005	31%	28%	99%	5%	95%	12%	-15%
121	Fluroxypyr-1-methylheptyl ester	0.001	0.003	106%	2%	105%	13%	110%	13%	13%
122	Flusilazole	0.001	0.003	86%	5%	95%	10%	90%	12%	12%
123	Flutriafol	0.002	0.005	42%	27%	93%	6%	96%	13%	3%
124	Fluxapyroxad	0.001	0.003	98%	15%	94%	8%	97%	6%	-5%
125	Fonofos	0.001	0.003	101%	10%	95%	7%	99%	13%	-12%
126	Formetanate - hydrochloride	0.001	0.003	87%	12%	97%	8%	96%	7%	-14%
127	Fosthiazate	0.001	0.003	111%	7%	114%	13%	112%	9%	-5%
128	Fuberidazole	0.001	0.003	102%	5%	114%	6%	109%	9%	12%
129	Furalaxyl	0.001	0.003	80%	9%	81%	3%	77%	14%	12%
130	Furathiocarb	0.001	0.003	76%	19%	80%	7%	84%	3%	7%

	Compound	LOD _{POCIS} (μg)	LOQ _{POCIS} (μg)	0.001 (μg)		0.05 (μg)		0.5 (μg)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
131	Heptenophos	0.001	0.003	85%	4%	95%	5%	94%	13%	-10%
132	Hexaconazole	0.001	0.003	97%	1%	102%	9%	104%	4%	-12%
133	Hexythiazox	0.001	0.003	73%	19%	69%	7%	72%	15%	-5%
134	Imazalil	0.001	0.003	111%	8%	111%	1%	106%	3%	13%
135	Imazaquin	0.002	0.005	137%	17%	79%	8%	81%	5%	-6%
136	Imazosulfuron	0.002	0.005	32%	32%	67%	11%	70%	12%	-6%
137	Imidacloprid	0.001	0.003	119%	5%	117%	1%	118%	6%	5%
138	Indoxacarb	0.001	0.003	89%	6%	82%	13%	86%	3%	-11%
139	Ipconazole Isomer	0.001	0.003	98%	1%	105%	3%	104%	12%	-9%
140	Iprovalicarb	0.001	0.003	71%	13%	77%	7%	76%	1%	-5%
141	Isofetamid	0.001	0.003	100%	19%	98%	12%	100%	2%	-6%
142	Isopropalin	0.002	0.005	51%	31%	86%	2%	88%	6%	2%
143	Isoproturon	0.001	0.003	85%	6%	82%	3%	85%	2%	-13%
144	Isopyrazam	0.001	0.003	82%	13%	76%	3%	79%	5%	-13%
145	Lenacil	0.001	0.003	106%	2%	112%	6%	114%	2%	13%
146	Linuron	0.001	0.003	112%	11%	110%	1%	109%	10%	-14%
147	Malaoxon	0.001	0.003	70%	1%	69%	10%	72%	5%	-7%
148	Mandipropamid	0.001	0.003	114%	8%	105%	1%	110%	7%	-14%
149	Mecarbam	0.001	0.003	80%	4%	82%	11%	82%	10%	15%

	Compound	LOD _{POCIS} (μ g)	LOQ _{POCIS} (μ g)	0.001 (μ g)		0.05 (μ g)		0.5 (μ g)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
150	Mefentrifluconazole	0.001	0.003	86%	24%	93%	12%	91%	7%	-11%
151	Mepanipyrim	0.002	0.005	130%	17%	93%	5%	94%	3%	-12%
152	Mepronil	0.001	0.003	103%	3%	113%	2%	108%	5%	-1%
153	Mepthylidinocap	0.008	0.025	57%	28%	106%	11%	101%	3%	0%
154	Metalaxyl	0.001	0.003	67%	2%	74%	1%	73%	6%	1%
155	Metamitron	0.001	0.003	119%	4%	120%	5%	119%	10%	-10%
156	Metazachlor	0.001	0.003	67%	17%	73%	9%	74%	3%	-6%
157	Metconazole *	0.001	0.003	115%	2%	116%	6%	113%	5%	2%
158	Methamidophos	0.001	0.003	77%	14%	85%	13%	83%	2%	3%
159	Methidathion	0.001	0.003	96%	13%	88%	9%	93%	8%	-9%
160	Methiocarb-sulfone	0.001	0.003	108%	12%	109%	10%	120%	6%	3%
161	Methiocarb-sulfoxyde	0.001	0.003	81%	2%	80%	4%	81%	12%	12%
162	Methomyl	0.001	0.003	77%	5%	83%	2%	85%	8%	-2%
163	Methoxyfenozide	0.002	0.005	134%	18%	99%	11%	100%	3%	13%
164	Metolachlor	0.001	0.003	102%	8%	108%	1%	103%	6%	-4%
165	Metrafenone	0.001	0.003	84%	18%	92%	9%	90%	2%	-12%
166	Metribuzin	0.001	0.003	64%	9%	71%	4%	70%	2%	10%
167	Mevinphos	0.002	0.005	136%	12%	118%	4%	120%	1%	4%
168	Monocrotophos	0.001	0.003	73%	13%	72%	7%	71%	13%	0%

	Compound	LOD _{POCIS} (μg)	LOQ _{POCIS} (μg)	0.001 (μg)		0.05 (μg)		0.5 (μg)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
169	Monolinuron	0.001	0.003	106%	18%	120%	13%	115%	8%	1%
170	Monuron	0.001	0.003	98%	17%	96%	2%	94%	11%	-4%
171	Myclobutanil	0.001	0.003	92%	17%	87%	11%	89%	2%	-12%
172	Napropamide	0.001	0.003	92%	8%	97%	6%	102%	4%	15%
173	Nicosulfuron	0.001	0.003	104%	16%	102%	15%	102%	14%	-7%
174	Nuarimol	0.001	0.003	93%	5%	98%	2%	98%	4%	8%
175	Omethoate	0.001	0.003	103%	4%	118%	9%	112%	10%	6%
176	Oxadiazon	0.001	0.003	69%	7%	72%	15%	76%	3%	8%
177	Oxadixyl	0.001	0.003	90%	6%	100%	11%	98%	3%	12%
178	Oxamyl	0.001	0.003	105%	14%	104%	10%	103%	2%	-6%
179	Oxathiapiprolin	0.005	0.015	62%	34%	97%	4%	100%	11%	6%
180	Oxycarboxin	0.001	0.003	101%	3%	105%	13%	104%	5%	4%
181	Paclobutrazol	0.001	0.003	98%	10%	98%	6%	103%	7%	-13%
182	Paraoxon	0.001	0.003	90%	14%	91%	6%	93%	14%	-1%
183	Penconazole	0.001	0.003	105%	6%	105%	7%	103%	8%	5%
184	Pencycuron	0.001	0.003	93%	3%	98%	5%	96%	12%	14%
185	Pendimethalin	0.002	0.005	65%	21%	82%	2%	85%	13%	13%
186	Penoxsulam	0.001	0.003	109%	19%	106%	5%	104%	9%	-30%
187	Penthiopyrad	0.001	0.003	106%	12%	107%	1%	107%	5%	-2%

	Compound	LOD _{POCIS} (μ g)	LOQ _{POCIS} (μ g)	0.001 (μ g)		0.05 (μ g)		0.5 (μ g)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
188	Permethrin *	0.001	0.003	87%	5%	99%	8%	97%	4%	-4%
189	Pethoxamid	0.001	0.003	112%	7%	115%	2%	111%	12%	10%
190	Phoxim	0.002	0.005	30%	27%	88%	2%	89%	6%	-13%
191	Picoxystrobin	0.001	0.003	108%	16%	108%	1%	110%	8%	-4%
192	Piperonyl Butoxide	0.001	0.003	111%	17%	116%	11%	112%	2%	4%
193	Pirimicarb	0.001	0.003	79%	11%	81%	6%	85%	14%	5%
194	Pirimiphos-methyl	0.001	0.003	76%	3%	87%	11%	84%	11%	-2%
195	Prochloraz	0.001	0.003	98%	7%	108%	12%	104%	15%	-14%
196	Profenofos	0.001	0.003	110%	20%	113%	13%	117%	15%	4%
197	Promecarb	0.001	0.003	121%	13%	120%	1%	120%	1%	5%
198	Prometon	0.002	0.005	133%	17%	72%	5%	70%	6%	-10%
199	Prometryn	0.001	0.003	120%	7%	114%	6%	114%	2%	8%
200	Propamocarb	0.001	0.003	89%	11%	90%	10%	92%	14%	-8%
201	Propanil	0.001	0.003	100%	1%	100%	8%	98%	5%	-14%
202	Propaquizafop	0.001	0.003	98%	21%	91%	12%	94%	10%	-2%
203	Propargite	0.001	0.003	91%	8%	99%	4%	97%	15%	4%
204	Propham	0.005	0.015	128%	19%	83%	7%	85%	11%	-6%
205	Propiconazole	0.001	0.003	85%	20%	89%	11%	89%	14%	-7%
206	Propoxur	0.001	0.003	105%	1%	100%	14%	102%	14%	2%

	Compound	LOD _{POCIS} (μg)	LOQ _{POCIS} (μg)	0.001 (μg)		0.05 (μg)		0.5 (μg)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
207	Propyzamide	0.002	0.005	40%	24%	80%	7%	78%	11%	-10%
208	Proquinazid	0.001	0.003	112%	9%	116%	6%	117%	11%	8%
209	Prosulfocarb	0.001	0.003	106%	17%	113%	10%	114%	10%	12%
210	Prosulfuron	0.002	0.005	40%	25%	97%	8%	98%	9%	11%
211	Prothioconazole-desethio	0.001	0.003	126%	15%	109%	19%	105%	9%	3%
212	Pyraclostrobin	0.001	0.003	85%	7%	95%	1%	94%	8%	2%
213	Pyraflufen Ethyl	0.001	0.003	76%	16%	70%	7%	73%	6%	8%
214	Pyrazophos	0.001	0.003	92%	20%	97%	8%	99%	9%	9%
215	Pyrethrins	0.017	0.050	132%	3%	118%	11%	119%	4%	-6%
216	Pyridaben	0.001	0.003	104%	18%	101%	6%	100%	6%	-2%
217	Pyridaphenthion	0.002	0.005	40%	22%	105%	9%	109%	1%	9%
218	Pyrifeno [*]	0.001	0.003	119%	14%	119%	5%	114%	15%	-11%
219	Pyrimethanil	0.001	0.003	110%	13%	105%	15%	106%	4%	3%
220	Pyriofenone	0.001	0.003	77%	1%	83%	9%	86%	4%	-6%
221	Pyriproxyfen	0.001	0.003	89%	17%	91%	13%	90%	5%	1%
222	Quinalphos	0.001	0.003	74%	18%	75%	6%	75%	7%	-11%
223	Quinoxifen	0.001	0.003	114%	7%	118%	5%	120%	13%	-1%
224	Quizalofop Ethyl	0.001	0.003	88%	20%	83%	6%	85%	15%	12%
225	Simazine	0.005	0.015	35%	25%	81%	14%	82%	10%	14%

	Compound	LOD _{POCIS} (μg)	LOQ _{POCIS} (μg)	0.001 (μg)		0.05 (μg)		0.5 (μg)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
226	Spinetoram *	0.001	0.003	92%	14%	88%	12%	92%	8%	12%
227	Spinosad D	0.001	0.003	87%	13%	86%	10%	88%	8%	12%
228	Spirodiclofen	0.001	0.003	102%	3%	101%	15%	97%	4%	13%
229	Spirotetramat	0.001	0.003	91%	7%	86%	11%	88%	3%	-5%
230	Spirotetramat-enol-glucoside	0.001	0.003	113%	15%	105%	12%	108%	3%	3%
231	Spirotetramat-ketohydroxy	0.002	0.005	129%	20%	114%	15%	119%	13%	1%
232	Spiroxamine	0.001	0.003	102%	3%	112%	10%	107%	2%	15%
233	Sulfotep	0.001	0.003	105%	5%	98%	3%	103%	2%	3%
234	Sulfoxaflor	0.002	0.005	133%	20%	99%	15%	102%	15%	9%
235	Tebuconazole	0.001	0.003	115%	9%	118%	1%	112%	2%	-5%
236	Tebufenozide	0.001	0.003	100%	1%	106%	1%	105%	14%	-4%
237	Tebufenpyrad	0.001	0.003	92%	8%	93%	6%	91%	1%	1%
238	Tebupirimifos	0.001	0.003	65%	13%	69%	14%	71%	1%	-9%
239	Terbumeton	0.001	0.003	103%	2%	103%	2%	99%	2%	5%
240	Terbuthylazine	0.001	0.003	81%	7%	80%	5%	81%	6%	11%
241	Terbutryn	0.001	0.003	106%	8%	120%	2%	117%	15%	4%
242	Tetrachlorvinphos	0.001	0.003	82%	1%	84%	8%	80%	15%	-1%
243	Tetraconazole	0.001	0.003	78%	4%	83%	7%	84%	4%	-8%

	Compound	LOD _{POCIS} (μ g)	LOQ _{POCIS} (μ g)	0.001 (μ g)		0.05 (μ g)		0.5 (μ g)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
244	Tetramethrin *	0.001	0.003	80%	6%	86%	12%	87%	5%	2%
245	Thiabendazole	0.001	0.003	86%	16%	88%	8%	93%	11%	-7%
246	Thiacloprid	0.001	0.003	106%	16%	119%	13%	113%	8%	-1%
247	Thiamethoxam	0.001	0.003	73%	13%	80%	10%	78%	6%	13%
248	Thifensulfuron-methyl	0.002	0.005	49%	20%	96%	3%	97%	5%	-2%
249	Thiobencarb	0.001	0.003	97%	18%	97%	13%	98%	2%	8%
250	Thiodicarb	0.001	0.003	89%	1%	84%	1%	85%	3%	-15%
251	Tolcofos methyl	0.002	0.005	121%	4%	102%	8%	98%	7%	-11%
252	Triadimefon	0.002	0.005	59%	30%	82%	6%	84%	8%	12%
253	Tri-allate	0.001	0.003	97%	3%	101%	14%	103%	6%	14%
254	Triasulfuron	0.002	0.005	36%	28%	111%	13%	114%	1%	-8%
255	Triazamate	0.001	0.003	84%	7%	82%	6%	86%	11%	14%
256	Triazophos	0.001	0.003	90%	5%	97%	1%	95%	10%	-6%
257	Trichlorfon	0.001	0.003	102%	13%	105%	8%	105%	14%	-13%
258	Triclopyr	0.005	0.015	140%	20%	91%	9%	90%	4%	-7%
259	Tricyclazole	0.001	0.003	106%	11%	112%	10%	107%	6%	-10%
260	Trifloxystrobin	0.001	0.003	89%	3%	93%	1%	94%	11%	-10%
261	Triflumizole	0.001	0.003	99%	10%	93%	4%	95%	13%	-11%
262	Triflumuron	0.001	0.003	93%	7%	91%	13%	90%	7%	10%

	Compound	LOD _{POCIS} (μg)	LOQ _{POCIS} (μg)	0.001 (μg)		0.05 (μg)		0.5 (μg)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
263	Triticonazole	0.001	0.003	96%	16%	104%	14%	99%	10%	-13%
264	Tritosulfuron	0.001	0.003	88%	18%	92%	8%	90%	15%	11%
265	Valifenalate	0.001	0.003	81%	20%	85%	4%	84%	5%	10%
266	Vamidothion	0.001	0.003	101%	15%	113%	15%	112%	4%	-2%
267	Zoxamide	0.001	0.003	126%	11%	120%	9%	120%	10%	-1%
268	Acetochlor	0.002	0.005	52%	21%	120%	9%	114%	7%	-5%
269	Acrinathrin	0.002	0.005	54%	21%	81%	11%	79%	12%	4%
270	Alachlor	0.005	0.015	125%	12%	104%	6%	108%	1%	-14%
271	Aldrin	0.002	0.005	42%	35%	75%	8%	76%	10%	0%
272	Benfluralin	0.002	0.005	60%	26%	77%	13%	79%	15%	12%
273	Bromophos-ethyl	0.002	0.005	130%	12%	73%	7%	74%	4%	1%
274	Bromopropylate	0.002	0.005	129%	1%	116%	8%	114%	15%	7%
275	Captan (THPI)	0.005	0.015	125%	4%	98%	2%	103%	1%	-5%
276	Chinomethionat	0.002	0.005	132%	6%	120%	15%	119%	10%	0%
277	Chlorfenapyr	0.005	0.015	137%	8%	90%	4%	88%	12%	14%
278	Chlorfenson	0.002	0.005	42%	29%	80%	7%	78%	11%	-9%
279	Chlormephos	0.005	0.015	122%	5%	87%	2%	84%	5%	11%
280	Chlorpropham	0.005	0.015	33%	23%	92%	5%	95%	9%	-10%
281	Chlorpyrifos-methyl	0.002	0.005	38%	31%	119%	15%	118%	15%	4%

	Compound	LOD _{POCIS} (μ g)	LOQ _{POCIS} (μ g)	0.001 (μ g)		0.05 (μ g)		0.5 (μ g)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
282	Cyfluthrin *	0.005	0.015	61%	31%	85%	15%	83%	7%	-2%
283	Cyhalofop-butyl	0.002	0.005	122%	19%	84%	10%	82%	9%	10%
284	Cyhalothrin (Lambda)	0.005	0.015	42%	23%	120%	4%	118%	11%	-12%
285	Cypermethrin *	0.005	0.015	140%	15%	70%	1%	72%	12%	5%
286	DDT (sum of DDT-o,p'; DDT-p,p'; DDE-o,p'; DDE-p,p'; DDD-o,p'; DDD-p,p')	0.017	0.050	57%	21%	87%	6%	85%	14%	-15%
287	Deltamethrin	0.002	0.005	54%	24%	109%	10%	112%	3%	10%
288	Dichlobenil	0.002	0.005	130%	3%	82%	12%	79%	6%	3%
289	Dichlofenthion	0.002	0.005	130%	6%	86%	9%	90%	6%	14%
290	Dichloran	0.005	0.015	56%	30%	114%	13%	120%	11%	3%
291	Dichloroaniline, 3,5-	0.005	0.015	123%	13%	100%	12%	99%	13%	-7%
292	Dicofol *	0.005	0.015	70%	33%	86%	13%	90%	6%	-5%
293	Dieldrin	0.005	0.015	123%	6%	112%	3%	108%	9%	8%
294	Diphenylamine	0.005	0.015	68%	22%	95%	1%	100%	1%	-3%
295	Endosulfan I (alpha isomer)	0.002	0.005	132%	1%	108%	2%	106%	2%	-3%
296	Endosulfan II (beta isomer)	0.005	0.015	52%	33%	118%	4%	119%	14%	-8%
297	Endosulfan sulfate	0.005	0.015	120%	14%	93%	11%	93%	15%	-8%

	Compound	LOD _{POCIS} (μ g)	LOQ _{POCIS} (μ g)	0.001 (μ g)		0.05 (μ g)		0.5 (μ g)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
298	EPN	0.005	0.015	122%	5%	90%	13%	87%	9%	0%
299	Ethalfuralin	0.002	0.005	132%	11%	73%	6%	76%	5%	7%
300	Etridiazole	0.002	0.005	136%	7%	114%	12%	111%	13%	-11%
301	Famoxadone	0.002	0.005	131%	12%	91%	3%	96%	12%	2%
302	Fenclorim	0.005	0.015	140%	4%	86%	2%	83%	15%	6%
303	Fenitrothion	0.002	0.005	41%	35%	104%	4%	107%	11%	13%
304	Fenpropathrin	0.002	0.005	131%	7%	81%	7%	85%	3%	0%
305	Fenson	0.002	0.005	53%	31%	92%	4%	88%	2%	-9%
306	Fenvalerate *	0.002	0.005	120%	8%	109%	10%	105%	2%	1%
307	Flucythrinate *	0.002	0.005	126%	14%	98%	7%	93%	3%	-14%
308	Heptachlor	0.002	0.005	54%	24%	111%	10%	108%	6%	-5%
309	Hexachlorobenzene	0.005	0.015	125%	13%	101%	7%	103%	4%	7%
310	Hexaflumuron	0.005	0.015	42%	35%	95%	11%	96%	1%	1%
311	Iprodione	0.005	0.015	69%	20%	105%	14%	110%	11%	3%
312	Kresoxim-methyl	0.002	0.005	134%	6%	111%	9%	107%	14%	-2%
313	Malathion	0.002	0.005	57%	24%	83%	11%	83%	8%	4%
314	Methoxychlor	0.002	0.005	139%	8%	84%	4%	88%	5%	4%
315	Orthophenilphenol	0.005	0.015	34%	28%	118%	12%	118%	13%	-2%
316	Paraoxon-methyl	0.002	0.005	35%	35%	110%	4%	109%	4%	10%

	Compound	LOD _{POCIS} (μg)	LOQ _{POCIS} (μg)	0.001 (μg)		0.05 (μg)		0.5 (μg)		Matrix effect
				Rec	RSD	Rec	RSD	Rec	RSD	
317	Parathion-ethyl	0.005	0.015	59%	31%	77%	3%	74%	2%	0%
318	Parathion-methyl	0.002	0.005	42%	28%	101%	9%	101%	4%	-5%
319	Permethrin *	0.002	0.005	67%	29%	95%	15%	99%	11%	-4%
320	Phosalone	0.002	0.005	59%	30%	86%	13%	85%	5%	14%
321	Phosmet	0.002	0.005	126%	11%	107%	4%	111%	11%	5%
322	Phthalimide	0.005	0.015	131%	15%	104%	11%	107%	8%	-4%
323	Procymidone	0.002	0.005	58%	27%	76%	11%	75%	3%	-12%
324	Profluralin	0.002	0.005	138%	12%	89%	7%	90%	12%	11%
325	Prothiofos	0.002	0.005	138%	7%	94%	3%	90%	2%	7%
326	Tecnazene	0.002	0.005	47%	21%	86%	12%	86%	14%	-4%
327	Tefluthrin	0.005	0.015	36%	23%	88%	6%	90%	14%	-5%
328	Thiometon	0.005	0.015	63%	20%	101%	13%	98%	12%	6%
329	Triadimenol	0.005	0.015	58%	33%	99%	15%	95%	2%	1%
330	Trifluralin	0.005	0.015	133%	5%	99%	9%	95%	3%	0%
331	Vinclozolin	0.002	0.005	70%	30%	106%	10%	110%	9%	1%

APPENDIX D. DATA AND RESULTS OF LABORATORY TESTS

Table 11 – Initial mean pesticide concentration in beakers evaluated by triplicate analysis after addition of pesticides to water at a theoretical concentration of approximately $0.1 \mu\text{g L}^{-1}$.

Compound	Average initial concentration ($\mu\text{g L}^{-1}$)	RSD (%)
3-Hydroxycarbofuran	0.090	1%
3-Ketocarbofuran	0.035	10%
6-Benzyladenine	0.064	8%
Acetamiprid	0.119	7%
Acibenzolar-S-methyl	0.104	9%
Aldicarb sulfone	0.107	1%
Aldicarb sulfoxide	0.144	1%
Ametocradin	0.035	8%
Amidosulfuron	0.098	1%
Amisulbron	0.812	1%
Atrazine	0.178	7%
Azaconazole	0.105	6%
Azoxystrobin	0.086	10%
Beflubutamid	0.097	11%
Benalaxyl	0.120	13%
Bendiocarb	0.064	7%
Benthiavalicarb Isopropyl	0.115	10%
Benzoximate	0.093	7%
Benzoylprop-ethyl	0.101	12%
Bifenazate	0.055	11%
Bifenthrin	0.060	8%
Bitertanol	0.122	9%
Boscalid	0.100	11%
Bromoxynil	0.101	16%

Compound	Average initial concentration ($\mu\text{g L}^{-1}$)	RSD (%)
Bromuconazole (sum)	0.106	14%
Buprofezin	0.060	2%
Cadusafos	0.107	12%
Carbaryl	0.095	8%
Carbendazim	0.082	1%
Carbofuran	0.113	13%
Carfentrazone Ethyl	0.041	1%
Chlorantranilprole	0.031	2%
Chlorfenvinphos	0.117	14%
Chlozolate	0.051	9%
Chromafenozide	0.050	1%
Clofentezine	0.045	9%
Cloquintocet	0.134	1%
Cloquintocet-mexyl	0.077	2%
Clothianidin	0.111	4%
Cyanazine	0.112	5%
Cyantraniliprole	0.069	11%
Cyazofamid	0.080	7%
Cyflufenamid	0.071	12%
Cyflumetofen	0.039	15%
Cymoxanil	0.018	2%
Cyproconazole	0.126	11%
Cyprodinil	0.024	11%
Demeton-S-methylsulfone	0.147	3%
Desethyl-Atrazine	0.094	5%
Desisopropyl-Atrazine	0.103	2%
Desmedipham	0.045	8%
Desmethyl-pirimicarb	0.111	4%
Dichlorvos	0.352	3%
Dicrotophos	0.136	2%

Compound	Average initial concentration ($\mu\text{g L}^{-1}$)	RSD (%)
Dimethomorph	0.092	14%
Dimoxystrobin	0.085	7%
Diniconazole	0.129	13%
Diphenamid	0.109	13%
Diuron	0.101	13%
Emamectin Benzoate B1a	0.033	1%
Epoxiconazole	0.104	12%
Etaconazole Isomer	0.106	6%
Ethirimol	0.006	12%
Ethofumesate	0.115	6%
Ethoprophos	0.134	14%
Ethoxyquin	0.108	6%
Etofenprox	0.058	8%
Etoxazole	0.070	7%
Fenamidone	0.046	3%
Fenarimol	0.135	11%
Fenazaquin	0.086	5%
Fenbuconazole	0.109	15%
Fenbutatin-oxide	0.092	9%
Fenoxaprop	0.110	19%
Fenoxycarb	0.122	10%
Fenpropidin	0.042	3%
Fenpyroximat	0.068	8%
Flazasulfuron	0.083	1%
Flonicamid	0.042	1%
Florasulam	0.109	16%
Fluazifop	0.110	16%
Fluazifop-P-Butyl	0.080	7%
Fluazinam	0.032	13%
Fludioxonil	0.068	10%

Compound	Average initial concentration ($\mu\text{g L}^{-1}$)	RSD (%)
Flufenacet	0.104	8%
Fluopicolide	0.115	13%
Fluopyram	0.147	13%
Fluquinconazole	0.086	7%
Fluroxypyr	0.108	6%
Fluroxypyr-1-methylheptyl ester	0.052	3%
Flusilazole	0.122	11%
Flutriafol	0.098	4%
Fluxapyroxad	0.107	6%
Formetanate - hydrochloride	0.037	3%
Fosthiazate	0.107	6%
Fuberidazole	0.080	15%
Furalaxyl	0.110	9%
Furathiocarb	0.082	7%
Heptenophos	0.112	16%
Hexaconazole	0.119	14%
Hexythiazox	0.075	13%
Imazalil	0.126	1%
Imazaquin	0.103	14%
Imidacloprid	0.117	6%
Indoxacarb	0.066	10%
Ipconazole Isomer	0.115	1%
Iprovalicarb	0.114	8%
Isofetamid	0.093	10%
Isoproturon	0.090	12%
Isopyrazam	0.079	4%
Linuron	0.105	10%
Malaoxon	0.165	5%
Mandipropamid	0.106	5%
Mefentrifluconazole	0.128	9%

Compound	Average initial concentration ($\mu\text{g L}^{-1}$)	RSD (%)
Mepanipyrim	0.081	3%
Metalaxyl	0.102	6%
Metamitron	0.073	6%
Metazachlor	0.125	7%
Metconazole (sum of isomers)	0.110	11%
Methiocarb-sulfone	0.011	9%
Methiocarb-sulfoxyde	0.150	4%
Methomyl	0.090	8%
Metolachlor	0.102	8%
Metrafenone	0.129	4%
Metribuzin	0.095	5%
Mevinphos	0.133	18%
Monocrotophos	0.120	3%
Monolinuron	0.115	12%
Monuron	0.100	13%
Myclobutanil	0.108	10%
Napropamide	0.079	9%
Nicosulfuron	0.073	1%
Nuarimol	0.102	7%
Omethoate	0.146	1%
Oxadiazon	0.101	11%
Oxadixyl	0.106	7%
Oxamyl	0.076	1%
Oxathiopiprolin	1.063	4%
Oxycarboxin	0.082	1%
Paraoxon	0.202	11%
Penconazole	0.152	14%
Pencycuron	0.097	1%
Pendimethalin	0.082	7%
Penoxsulam	0.097	6%

Compound	Average initial concentration ($\mu\text{g L}^{-1}$)	RSD (%)
Pethoxamid	0.106	8%
Picoxystrobin	0.100	6%
Piperonyl Butoxide	0.075	5%
Pirimicarb	0.050	1%
Prochloraz	0.117	8%
Profenofos	0.133	1%
Promecarb	0.120	13%
Prometon	0.110	8%
Propanil	0.101	13%
Propaquizafop	0.078	8%
Propargite	0.108	8%
Propoxur	0.118	7%
Propyzamide	0.062	13%
Proquinazid	0.105	2%
Prosulfuron	0.090	6%
Prothioconazole-desthio	0.103	8%
Pyraflufen Ethyl	0.075	1%
Pyridaben	0.038	1%
Pyrifenoxy (sum)	0.118	12%
Pirimethanil	0.054	4%
Pyriofenone	0.095	9%
Pyriproxyfen	0.093	9%
Quinoxifen	0.100	1%
Quizalofop Ethyl	0.107	6%
Simazine	0.942	16%
Spirodiclofen	0.059	8%
Spirotetramat	0.075	7%
Spirotetramat-enol-glucoside	0.122	1%
Sulfoxaflor	0.134	8%
Tebuconazole	0.110	14%

Compound	Average initial concentration ($\mu\text{g L}^{-1}$)	RSD (%)
Tebufofenpyrad	0.085	6%
Terbumeton	0.109	8%
Terbuthylazine	0.104	8%
Tetrachlorvinphos	0.142	11%
Tetraconazole	0.095	10%
Thiabendazole	0.083	10%
Thiacloprid	0.105	13%
Thiamethoxam	0.101	3%
Thifensulfuron-methyl	0.118	2%
Thiodicarb	0.050	1%
Triadimefon	0.110	13%
Triasulfuron	0.098	9%
Triazamate	0.057	10%
Trichlorfon	0.062	11%
Tricyclazole	0.105	12%
Trifloxystrobin	0.068	7%
Triflumizole	0.081	13%
Triticonazole	0.118	5%
Tritosulfuron	0.034	4%
Valifenalate	0.088	12%
Zoxamide	0.085	10%
Aldrin	0.196	3%
Bromopropylate	0.065	1%
Chinomethionate (Oxythioquinox)	0.044	15%
Chlorfenapyr	0.109	1%
Chlorfenson	0.085	1%
Chlorpropham	0.101	1%
Chlorpyrifos-methyl	0.069	1%
Cyhalothrin (Lambda)	0.091	4%
Dichlofenthion	0.040	8%

Compound	Average initial concentration ($\mu\text{g L}^{-1}$)	RSD (%)
Dichloran	0.077	10%
Dicofol (sum of isomers)	0.080	1%
Dieldrin	0.229	8%
Diphenylamine	0.068	9%
Endosulfan-alfa	0.090	3%
Endosulfan II (beta isomer)	0.089	4%
Endosulfan sulfate	0.085	4%
Famoxadone	0.020	10%
Fenpropathrin	0.089	4%
Fenson	0.088	1%
Fenvalerate (sum con isomers)	0.078	6%
Flucythrinate (sum con isomers)	0.088	2%
Heptachlor	0.186	12%
Hexaflumuron	0.065	1%
Kresoxim-methyl	0.075	3%
Malathion	0.080	2%
Parathion-methyl	0.048	15%
Permethrin, (1R)-cis-	0.092	5%
Procymidone	0.113	4%
Prothiofos	0.025	7%
Tefluthrine	0.069	3%
Trifluralin	0.139	4%

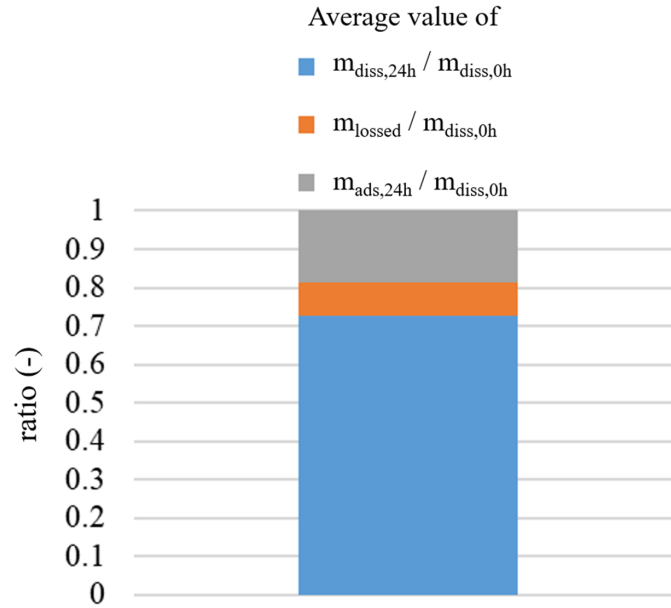


Figure 30 – Breakdown between average amount of phytopharmaceuticals present in water after 24 hours, amount lost and amount adsorbed by passive samplers, expressed in relation to the amount initially present in water. Where: $m_{diss,0h}$ is the amount of pesticide dissolved in water at the beginning of the experiment ($t=0$); $m_{ads,24h}$ is the amount of pesticide adsorbed by the samplers (POCIS and membrane) after 24 hours of their exposure; $m_{diss,24h}$ is the amount of pesticide dissolved in water after 24 hours of samplers exposure; m_{losses} is the difference between the previous amounts.

Table 12 – Accumulated mass fraction of analyte in the PES membrane to that in the total POCIS (f_{PES}). N.F. = compound not found in passive sampler

Compound	f_{PES}			
	4 days	7 days	14 days	mean value
3-Hydroxycarbofuran	0%	0%	2%	1%
3-Ketocarbofuran	6%	0%	5%	4%
6-Benzyladenine	28%	23%	24%	25%
Acetamiprid	22%	15%	20%	19%
Acibenzolar-S-methyl	97%	96%	97%	97%
Aldicarb sulfone	0%	0%	3%	1%
Aldicarb sulfoxide	0%	0%	0%	1%
Ametocradin	87%	77%	78%	80%
Amidosulfuron	30%	20%	24%	24%
Amisulbron	100%	100%	100%	100%
Atrazine	26%	18%	25%	23%
Azaconazole	27%	17%	22%	22%
Azoxystrobin	90%	82%	80%	84%
Beflubutamid	92%	81%	83%	85%
Benalaxyl	57%	42%	46%	48%
Bendiocarb	20%	11%	17%	16%
Benthiavalicarb Isopropyl	35%	22%	27%	28%
Benzoximate	100%	98%	93%	97%
Benzoylprop-ethyl	85%	74%	70%	77%
Bifenazate	100%	100%	100%	100%
Bifenthrin	100%	100%	100%	100%
Bitertanol	93%	89%	87%	90%
Boscalid	79%	72%	72%	74%
Bromoxynil	90%	82%	88%	87%
Bromuconazole (sum)	58%	45%	47%	50%
Buprofezin	55%	35%	25%	38%
Cadusafos	53%	30%	41%	41%
Carbaryl	62%	54%	62%	59%

Compound	f_{PES}			mean value
	4 days	7 days	14 days	
Carbendazim	26%	18%	24%	23%
Carbofuran	57%	43%	48%	49%
Carfentrazone Ethyl	89%	76%	76%	81%
Chlorantranilprole	56%	42%	52%	50%
Chlorfenvinphos	72%	58%	58%	63%
Chlozolate	51%	43%	49%	48%
Chromafenozide	66%	58%	63%	62%
Clofentezine	100%	100%	100%	100%
Cloquintocet	N.F.	N.F.	N.F.	N.F.
Cloquintocet-mexyl	100%	100%	98%	99%
Clothianidin	24%	20%	26%	23%
Cyanazine	16%	11%	14%	14%
Cyantranilprole	51%	45%	47%	48%
Cyazofamid	79%	64%	62%	68%
Cyflufenamid	89%	78%	66%	78%
Cyflumetofen	100%	100%	100%	100%
Cymoxanil	29%	24%	29%	27%
Cyproconazole	21%	15%	20%	19%
Cyprodinil	84%	69%	70%	74%
Demeton-S-methylsulfone	2%	1%	2%	2%
Desethyl-Atrazine	16%	15%	22%	18%
Desisopropyl-Atrazine	18%	23%	29%	23%
Desmedipham	100%	98%	97%	98%
Desmethyl-pirimicarb	3%	2%	3%	2%
Dichlorvos	100%	78%	96%	91%
Dicrotophos	0%	0%	1%	0%
Dimethomorph	61%	47%	50%	53%
Dimoxystrobin	76%	63%	64%	68%
Diniconazole	61%	54%	55%	56%
Diphenamid	27%	17%	21%	22%

Compound	f_{PES}			mean value
	4 days	7 days	14 days	
Diuron	71%	65%	73%	70%
Emamectin Benzoate B1a	100%	100%	91%	97%
Epoxiconazole	55%	42%	49%	49%
Etaconazole Isomer	23%	18%	26%	22%
Ethirimol	N.F.	N.F.	N.F.	N.F.
Ethofumesate	65%	49%	55%	56%
Ethoprophos	30%	15%	25%	23%
Ethoxyquin	27%	19%	25%	23%
Etofenprox	100%	100%	100%	100%
Etoxazole	100%	98%	88%	95%
Fenamidone	64%	55%	56%	59%
Fenarimol	47%	44%	48%	46%
Fenazaquin	100%	100%	100%	100%
Fenbuconazole	90%	81%	79%	83%
Fenbutatin-oxide	100%	100%	100%	100%
Fenoxaprop	N.F.	50%	62%	56%
Fenoxycarb	100%	100%	100%	100%
Fenpropidin	0%	0%	0%	1%
Fenpyroximat	100%	100%	100%	100%
Flazasulfuron	14%	7%	10%	10%
Flonicamid	0%	0%	0%	1%
Florasulam	49%	41%	34%	41%
Fluazifop	0%	13%	15%	9%
Fluazifop-P-Butyl	100%	100%	98%	99%
Fluazinam	100%	100%	100%	100%
Fludioxonil	95%	92%	90%	92%
Flufenacet	25%	16%	19%	20%
Fluopicolide	66%	50%	56%	57%
Fluopyram	56%	39%	44%	46%
Fluquinconazole	69%	59%	59%	62%

Compound	f_{PES}			mean value
	4 days	7 days	14 days	
Fluroxypyr	100%	100%	99%	100%
Fluroxypyr-1-methylheptyl ester	100%	100%	100%	100%
Flusilazole	74%	62%	64%	67%
Flutriafol	22%	16%	23%	20%
Fluxapyroxad	78%	71%	71%	73%
Formetanate - hydrochloride	0%	0%	0%	1%
Fosthiazate	7%	3%	6%	5%
Fuberidazole	47%	43%	52%	47%
Furalaxyl	30%	18%	23%	24%
Furathiocarb	97%	90%	84%	90%
Heptenophos	42%	22%	36%	34%
Hexaconazole	67%	58%	57%	60%
Hexythiazox	100%	99%	94%	98%
Imazalil	0%	0%	0%	0%
Imazaquin	0%	0%	0%	1%
Imidacloprid	26%	18%	23%	23%
Indoxacarb	100%	100%	98%	99%
Ipconazole Isomer	90%	83%	80%	84%
Iprovalicarb	20%	10%	14%	15%
Isofetamid	79%	68%	66%	71%
Isoproturon	36%	27%	35%	33%
Isopyrazam	93%	87%	82%	87%
Linuron	85%	78%	83%	82%
Malaoxon	9%	5%	7%	7%
Mandipropamid	100%	98%	96%	98%
Mefentrifluconazole	95%	92%	88%	92%
Mepanipyrim	83%	77%	76%	79%
Metalaxyl	5%	3%	4%	4%
Metamitron	30%	25%	33%	29%
Metazachlor	15%	9%	12%	12%

Compound	f_{PES}			mean value
	4 days	7 days	14 days	
Metconazole (sum of isomers)	76%	68%	66%	70%
Methiocarb-sulfone	20%	16%	17%	18%
Methiocarb-sulfoxyde	3%	2%	3%	3%
Methomyl	44%	44%	57%	48%
Metolachlor	23%	13%	17%	18%
Metrafenone	97%	91%	83%	90%
Metribuzin	17%	10%	15%	14%
Mevinphos	28%	12%	28%	23%
Monocrotophos	0%	0%	2%	1%
Monolinuron	68%	59%	70%	66%
Monuron	44%	42%	52%	46%
Myclobutanil	42%	30%	37%	36%
Napropamide	55%	39%	44%	46%
Nicosulfuron	0%	0%	0%	1%
Nuarimol	31%	22%	29%	27%
Omethoate	0%	0%	0%	1%
Oxadiazon	86%	72%	60%	73%
Oxadixyl	0%	0%	2%	1%
Oxamyl	0%	0%	2%	1%
Oxathiopiprolin	100%	99%	97%	99%
Oxycarboxin	14%	8%	10%	11%
Paraoxon	45%	32%	40%	39%
Penconazole	70%	56%	62%	63%
Pencycuron	96%	90%	85%	90%
Pendimethalin	100%	97%	88%	95%
Penoxsulam	19%	11%	17%	16%
Pethoxamid	23%	13%	16%	17%
Picoxystrobin	88%	77%	71%	78%
Piperonyl Butoxide	100%	98%	96%	98%
Pirimicarb	8%	3%	6%	6%

Compound	f_{PES}			
	4 days	7 days	14 days	mean value
Prochloraz	94%	77%	78%	83%
Profenofos	97%	91%	88%	92%
Promecarb	61%	47%	55%	54%
Prometon	9%	5%	8%	7%
Propanil	87%	82%	84%	84%
Propaquizafop	100%	100%	100%	100%
Propargite	100%	100%	100%	100%
Propoxur	12%	7%	11%	10%
Propyzamide	58%	39%	46%	48%
Proquinazid	99%	97%	92%	96%
Prosulfuron	42%	28%	38%	36%
Prothioconazole-desthio	34%	24%	32%	30%
Pyraflufen Ethyl	100%	100%	99%	100%
Pyridaben	100%	100%	100%	100%
PyrifenoX (sum)	68%	38%	48%	51%
Pyrimethanil	66%	57%	64%	62%
Pyriofenone	85%	75%	72%	77%
Pyriproxyfen	100%	100%	100%	100%
Quinoxifen	100%	100%	98%	99%
Quizalofop Ethyl	100%	100%	99%	100%
Simazine	25%	20%	27%	24%
Spirodiclofen	100%	100%	92%	97%
Spirotetramat	33%	22%	28%	28%
Spirotetramat-enol-glucoside	0%	0%	0%	1%
Sulfoxaflor	0%	0%	6%	2%
Tebuconazole	68%	56%	62%	62%
Tebufenpyrad	99%	97%	92%	96%
Terbumeton	16%	6%	10%	11%
Terbuthylazine	30%	20%	26%	26%
Tetrachlorvinphos	74%	61%	64%	66%

Compound	f_{PES}			mean value
	4 days	7 days	14 days	
Tetraconazole	58%	47%	52%	53%
Thiabendazole	57%	51%	42%	50%
Thiacloprid	44%	32%	39%	38%
Thiamethoxam	5%	3%	5%	4%
Thifensulfuron-methyl	12%	6%	9%	9%
Thiodicarb	71%	36%	40%	49%
Triadimefon	41%	28%	35%	35%
Triasulfuron	10%	5%	8%	7%
Triazamate	31%	11%	16%	19%
Trichlorfon	0%	0%	0%	1%
Tricyclazole	29%	25%	34%	29%
Trifloxystrobin	100%	97%	89%	96%
Triflumizole	74%	34%	41%	50%
Triticonazole	20%	12%	18%	17%
Tritosulfuron	74%	55%	74%	68%
Valifenalate	32%	21%	26%	26%
Zoxamide	84%	76%	71%	77%
Aldrin	100%	98%	94%	97%
Bromopropylate	100%	99%	96%	98%
Chinomethionate (Oxythioquinox)	97%	98%	97%	97%
Chlorfenapyr	96%	94%	97%	96%
Chlorfenson	98%	97%	97%	97%
Chlorpropham	88%	81%	81%	83%
Chlorpyrifos-methyl	88%	80%	75%	81%
Cyhalothrin (Lambda)	100%	100%	100%	100%
Dichlofenthion	100%	100%	100%	100%
Dichloran	95%	93%	93%	94%
Dicofol (sum of isomers)	100%	99%	100%	100%
Dieldrin	89%	80%	69%	79%
Diphenylamine	100%	93%	93%	95%

Compound	f_{PES}			mean value
	4 days	7 days	14 days	
Endosulfan I (alfa isomer)	85%	73%	64%	74%
Endosulfan II (beta isomer)	89%	78%	70%	79%
Endosulfan sulfate	100%	100%	100%	100%
Famoxadone	96%	97%	98%	97%
Fenpropathrin	100%	100%	100%	100%
Fenson	100%	98%	97%	98%
Fenvalerate (sum con isomers)	100%	100%	100%	100%
Flucythrinate (sum con isomers)	100%	100%	100%	100%
Heptachlor	97%	93%	86%	92%
Hexaflumuron	35%	83%	20%	46%
Kresoxim-methyl	85%	74%	65%	75%
Malathion	67%	50%	47%	55%
Parathion-methyl	96%	92%	90%	93%
Permethrin, (1R)-cis-	100%	100%	100%	100%
Procymidone	60%	43%	39%	47%
Prothiofos	100%	100%	100%	100%
Tefluthrine	100%	100%	100%	100%
Trifluralin	100%	92%	86%	93%

Table 13 – Sampling rate estimated from laboratory data for Oasis HLB phase $R_{S,HLB}$, PES membrane $R_{S,PES}$, POCIS R_S and PES membrane in PES-single sampler configuration $R_{S,PES-alone}$ with respective R^2 values.

Compound	$R_{S,HLB}$	R^2	$R_{S,PES}$	R^2	R_S	R^2	$R_{S,PES-alone}$	R^2
3-Hydroxycarbofuran	0.110	0.968	-	-	0.111	0.971	-	-
3-Ketocarbofuran	-	-	-	-	-	-	-	-
6-Benzyladenine	0.143	0.995	0.045	0.998	0.189	0.997	0.073	0.988
Acetamiprid	0.156	0.979	0.036	0.989	0.193	0.984	0.054	0.984
Acibenzolar-S-methyl	0.046	0.997	1.342	0.998	1.388	0.998	1.544	0.998
Aldicarb sulfone	0.062	0.949	-	-	0.063	0.955	-	-
Aldicarb sulfoxide	-	0.775	-	-	-	0.775	-	-
Ametocradin	0.229	0.962	0.819	0.977	1.047	0.977	1.110	0.959
Amidosulfuron	0.032	0.937	0.010	0.968	0.042	0.948	0.013	0.921
Amisulbron	-	-	-	0.795	-	0.795	-	0.753
Atrazine	0.138	0.976	0.043	0.994	0.181	0.985	0.068	0.984
Azaconazole	0.141	0.979	0.037	0.980	0.179	0.983	0.062	0.961
Azoxystrobin	0.124	0.994	0.542	0.986	0.666	0.992	0.699	0.983
Beflubutamid	0.086	0.962	0.424	0.988	0.510	0.989	0.628	0.997
Benalaxyl	0.185	0.984	0.157	0.974	0.342	0.985	0.229	0.948
Bendiocarb	0.150	0.957	0.028	0.950	0.177	0.963	0.041	0.939
Benthiavdicarb propyl	0.178	0.980	0.064	0.977	0.242	0.986	0.104	0.935

Compound	$R_{S,HLB}$	R^2	$R_{S,PES}$	R^2	R_S	R^2	$R_{S,PES-alone}$	R^2
Benzoximate	-	-	0.444	0.992	0.471	0.996	0.436	0.984
Benzoylprop-ethyl	0.129	0.996	0.334	0.962	0.463	0.984	0.483	0.957
Bifenazate	-	-	-	-	-	-	-	-
Bifenthrin	-	-	0.189	0.990	0.189	0.990	0.189	0.999
Bitertanol	0.106	0.998	0.755	0.961	0.861	0.971	0.930	0.957
Boscalid	0.089	0.987	0.238	0.966	0.328	0.974	0.332	0.953
Bromoxynil	-	0.860	-	0.922	-	0.921	-	0.844
Bromuconazole *	0.157	0.990	0.144	0.966	0.301	0.984	0.218	0.940
Buprofezin	0.251	0.987	-	0.921	0.353	0.992	0.118	0.904
Cadusafos	0.129	0.911	0.081	0.966	0.210	0.950	0.133	0.925
Carbaryl	0.182	0.979	0.278	0.997	0.460	0.994	0.393	0.993
Carbendazim	-	0.754	-	0.887	-	0.784	-	0.807
Carbofuran	0.167	0.979	0.153	0.980	0.321	0.985	0.205	0.975
Carfentrazone Ethyl	0.114	0.994	0.394	0.975	0.509	0.989	0.506	0.971
Chlorantranilprole	-	0.836	-	0.932	-	0.892	-	0.860
Chlorfenvinphos	0.173	0.993	0.253	0.964	0.426	0.984	0.405	0.947
Chlozolinate	0.094	0.971	0.086	0.984	0.180	0.979	0.128	0.978
Chromafenozide	0.177	0.929	0.284	0.965	0.461	0.953	0.368	0.975
Clofentezine	-	-	0.237	0.949	0.237	0.949	0.240	0.938

Compound	$R_{S,HLB}$	R^2	$R_{S,PES}$	R^2	R_S	R^2	$R_{S,PES-alone}$	R^2
Cloquintocet	-	-	-	-	-	-	-	-
Cloquintocet-mexyl	-	-	0.571	0.974	0.581	0.975	0.677	0.994
Clothianidin	0.077	0.970	0.025	0.994	0.101	0.980	0.036	0.983
Cyanazine	0.115	0.980	0.018	0.986	0.133	0.983	0.037	0.973
Cyantraniliprole	0.096	0.958	0.086	0.959	0.183	0.960	0.130	0.918
Cyazofamid	0.082	0.991	0.142	0.980	0.224	0.994	0.195	0.984
Cyflufenamid	0.083	0.972	0.196	0.954	0.278	0.989	0.233	0.980
Cyflumetofen	-	-	-	-	-	-	-	-
Cymoxanil	-	0.870	-	0.931	-	0.890	0.063	0.933
Cyproconazole	0.144	0.978	0.033	0.985	0.177	0.983	0.046	0.971
Cyprodinil	0.254	0.970	0.605	0.966	0.859	0.976	0.893	0.902
Demeton-S-methylsulfone	0.103	0.988	0.002	0.990	0.106	0.988	0.003	0.993
Desethyl-Atrazine	0.085	0.971	0.021	0.998	0.106	0.982	0.031	0.998
Desisopropyl-Atrazine	0.044	0.974	0.017	0.998	0.061	0.988	0.021	0.998
Desmedipham	-	-	-	-	-	-	-	-
Desmethyl-pirimicarb	0.188	0.977	0.005	0.995	0.193	0.978	0.008	0.991
Dichlorvos	-	-	-	-	-	-	-	-
Dicrotophos	0.091	0.972	-	-	0.092	0.974	-	-

Compound	$R_{S,HLB}$	R^2	$R_{S,PES}$	R^2	R_S	R^2	$R_{S,PES-alone}$	R^2
Dimethomorph	0.144	0.984	0.145	0.962	0.289	0.980	0.206	0.938
Dimoxystrobin	0.214	0.989	0.397	0.982	0.611	0.990	0.544	0.954
Diniconazole	0.149	0.984	0.184	0.976	0.334	0.982	0.274	0.931
Diphenamid	0.187	0.980	0.048	0.986	0.235	0.985	0.076	0.944
Diuron	0.149	0.980	0.364	0.998	0.513	0.998	0.525	0.996
Emamectin Benzoate	-	-	0.050	0.949	0.054	0.964	-	0.842
B1a								
Epoxiconazole	0.121	0.980	0.111	0.985	0.232	0.989	0.147	0.973
Etaconazole Isomer	0.119	0.970	0.037	0.998	0.157	0.982	0.055	0.976
Ethirimol	-	-	-	-	-	-	-	-
Ethofumesate	0.130	0.984	0.154	0.980	0.284	0.990	0.234	0.955
Ethoprophos	-	0.843	0.021	0.970	-	0.887	0.034	0.951
Ethoxyquin	0.113	0.981	0.035	0.989	0.148	0.988	0.056	0.969
Etofenprox	-	-	0.524	0.996	0.524	0.996	0.459	0.994
Etoxazole	-	-	0.292	0.965	0.321	0.981	0.295	0.981
Fenamidone	0.175	0.957	0.230	0.949	0.405	0.956	-	0.893
Fenarimol	0.091	0.974	0.080	0.988	0.171	0.982	0.113	0.977
Fenazaquin	-	-	0.674	0.989	0.675	0.989	0.699	0.995
Fenbuconazole	0.085	0.988	0.342	0.987	0.427	0.995	0.428	0.986

Compound	$R_{S,HLB}$	R^2	$R_{S,PES}$	R^2	R_S	R^2	$R_{S,PES-alone}$	R^2
Fenbutatin-oxide	-	-	0.184	0.972	0.184	0.972	0.198	0.996
Fenoxaprop	-	-	-	-	-	-	-	-
Fenoxycarb	-	-	0.881	0.993	0.882	0.993	0.873	0.996
Fenpropidin	-	0.618	-	-	-	0.618	-	-
Fenpyroximat	-	-	0.439	0.991	0.439	0.991	0.439	0.989
Flazasulfuron	0.066	0.979	0.007	0.990	0.073	0.984	0.012	0.959
Flonicamid	-	0.829	-	-	-	0.829	-	-
Florasulam	0.018	0.996	0.010	0.963	0.028	0.994	0.013	0.943
Fluazifop	0.021	0.973	-	-	0.024	0.977	-	-
Fluazifop-P-Butyl	-	-	0.322	0.975	0.325	0.977	0.322	0.997
Fluazinam	-	-	1.221	0.979	1.225	0.980	1.058	0.914
Fludioxonil	0.238	0.980	2.329	0.990	2.566	0.991	2.745	0.993
Flufenacet	0.170	0.981	0.039	0.972	0.209	0.983	0.060	0.967
Flupicolide	0.199	0.982	0.250	0.957	0.450	0.976	0.354	0.927
Fluopyram	0.154	0.989	0.118	0.967	0.272	0.988	0.174	0.950
Fluquinconazole	0.175	0.983	-	0.938	0.434	0.961	0.371	0.918
Fluroxypyr	-	-	-	-	-	-	-	-
Fluroxypyr-l-methylheptyl ester	-	-	0.403	0.990	0.403	0.990	0.453	0.991

Compound	$R_{S,HLB}$	R^2	$R_{S,PES}$	R^2	R_S	R^2	$R_{S,PES-alone}$	R^2
Flusilazole	0.138	0.996	0.251	0.983	0.389	0.993	0.338	0.965
Flutriafof	0.102	0.972	0.027	0.991	0.129	0.980	0.045	0.966
Fluxapyroxad	0.130	0.988	0.330	0.966	0.460	0.975	0.433	0.953
Formetanate - hy- drochloride	0.154	0.932	-	-	-	0.932	-	-
Fosthiazate	0.174	0.970	0.010	0.986	0.184	0.974	0.019	0.962
Fuberidazole	0.187	0.965	0.186	0.999	0.373	0.989	0.279	0.994
Furalaxyl	0.181	0.976	0.052	0.980	0.233	0.983	0.084	0.942
Furathiocarb	0.090	0.943	0.554	0.992	0.643	0.998	0.656	0.991
Heptenophos	-	0.846	0.040	0.973	-	0.908	0.062	0.950
Hexaconazole	0.131	0.997	0.182	0.969	0.313	0.985	-	0.889
Hexythiazox	-	-	0.273	0.982	0.286	0.986	0.305	0.996
Imazalil	0.189	0.958	-	-	0.189	0.957	-	-
Imazaquin	0.011	0.999	-	-	0.011	0.999	-	-
Imidacloprid	0.105	0.979	0.030	0.986	0.136	0.984	0.046	0.969
Indoxacarb	-	-	0.180	0.965	0.183	0.968	0.184	0.971
Ipconazole Isomer	0.096	0.997	0.429	0.961	0.525	0.974	0.751	0.956
Iprovalicarb	0.164	0.981	0.026	0.971	0.190	0.986	0.043	0.937
Isofetamid	0.121	0.996	0.253	0.990	0.374	0.997	0.335	0.989

Compound	$R_{S,HLB}$	R^2	$R_{S,PES}$	R^2	R_S	R^2	$R_{S,PES-alone}$	R^2
Isoproturon	0.182	0.971	0.090	0.992	0.271	0.983	0.138	0.977
Isoprazam	0.122	0.981	0.629	0.987	0.751	0.994	0.751	0.989
Linuron	0.128	0.990	0.583	0.996	0.711	0.997	0.772	0.995
Malaonoxon	0.191	0.985	0.014	0.976	0.205	0.987	0.023	0.966
Mandipropamid	0.037	0.902	0.968	0.996	1.005	0.997	1.057	0.995
Mefentrifluconazole	0.069	0.981	0.592	0.961	0.661	0.971	0.967	0.946
Mepanipyrin	0.180	0.988	0.604	0.984	0.784	0.987	0.787	0.979
Metalaxyl	0.173	0.979	0.007	0.993	0.180	0.981	0.012	0.969
Metamitron	0.101	0.927	0.045	0.992	0.146	0.954	0.065	0.982
Metazachlor	0.173	0.977	0.023	0.985	0.196	0.981	0.036	0.953
Metconazole *	0.140	0.997	0.285	0.957	0.425	0.976	0.448	0.914
Methiocarb-sulfone	-	-	-	-	-	-	-	-
Methiocarb-sulfoxide	0.122	0.960	-	0.911	0.126	0.959	-	0.891
Methomyl	0.069	0.925	0.077	0.999	0.147	0.978	0.086	0.995
Metolachlor	0.157	0.976	0.031	0.977	0.188	0.982	0.051	0.949
Metrafenone	0.082	0.932	0.476	0.989	0.558	0.997	0.550	0.992
Metribuzin	0.137	0.938	0.022	0.980	0.160	0.950	0.036	0.950
Mevinphos	-	0.752	0.016	0.994	-	0.828	0.024	0.987
Monocrotophos	0.064	0.961	-	-	0.065	0.964	-	-

Compound	$R_{S,HLB}$	R^2	$R_{S,PES}$	R^2	R_S	R^2	$R_{S,PES-alone}$	R^2
Monolinuron	0.147	0.975	0.307	0.998	0.455	0.998	0.435	0.998
Monuron	0.161	0.974	0.155	1.000	0.315	0.994	0.226	1.000
Myclobutanil	0.150	0.973	0.083	0.976	0.233	0.981	0.118	0.949
Napropamide	0.208	0.976	0.161	0.984	0.369	0.986	0.228	0.943
Nicosulfuron	0.053	0.977	-	-	0.053	0.977	-	-
Nuarimol	0.102	0.977	0.039	0.986	0.141	0.985	0.063	0.951
Omethoate	-	0.785	-	-	-	0.785	-	-
Oxadiazon	0.107	0.980	0.195	0.949	0.302	0.990	0.267	0.980
Oxadixyl	0.175	0.979	-	-	0.177	0.981	-	-
Oxamyl	0.094	0.956	-	-	0.095	0.961	-	-
Oxathiopiprolin	-	-	0.086	0.998	0.088	0.998	0.089	0.997
Oxycarboxin	0.147	0.972	0.017	0.965	0.164	0.974	0.027	0.953
Paraoxon	0.157	0.983	0.098	0.982	0.255	0.989	0.145	0.966
Penconazole	0.163	0.985	0.257	0.980	0.420	0.988	0.372	0.959
Pencycuron	0.071	0.947	0.453	0.993	0.524	0.998	0.478	0.991
Pendimethalin	-	-	0.240	0.956	0.264	0.974	0.257	0.996
Penoxsulam	0.103	0.975	0.020	0.988	0.123	0.982	0.032	0.945
Pethoxamid	0.170	0.981	0.032	0.977	0.202	0.985	0.051	0.963
Picoxystrobin	0.126	0.985	0.345	0.980	0.472	0.995	0.462	0.975

Compound	$R_{S,HLB}$	R^2	$R_{S,PES}$	R^2	R_S	R^2	$R_{S,PES-alone}$	R^2
Piperonyl Butoxide	0.036	0.911	1.145	0.995	1.181	0.996	1.202	0.992
Pirimicarb	0.334	0.914	0.018	0.971	-	0.921	-	0.893
Prochloraz	0.096	0.986	-	0.913	0.468	0.953	0.590	0.954
Profenofos	0.088	0.960	0.699	0.993	0.787	0.997	0.832	0.993
Promecarb	0.144	0.971	0.167	0.982	0.311	0.984	0.255	0.965
Prometon	0.198	0.980	0.016	0.987	0.214	0.984	0.030	0.962
Propanil	0.101	0.988	0.531	0.998	0.631	0.998	0.757	0.995
Propaquizafop	-	-	0.763	0.994	0.763	0.994	0.754	0.996
Propargite	-	-	0.320	0.985	0.320	0.985	0.312	0.988
Propoxur	0.125	0.952	0.014	0.991	0.139	0.960	0.023	0.977
Propyzamide	0.160	0.974	0.135	0.959	0.294	0.978	0.226	0.922
Proquinazid	-	0.861	0.443	0.994	0.476	0.994	0.482	0.996
Prosulfuron	0.069	0.944	0.038	0.976	0.107	0.966	0.056	0.948
Prothioconazole-desthio	0.128	0.969	0.055	0.986	0.183	0.981	0.084	0.960
Pyraflufen Ethyl	-	-	0.559	0.987	0.564	0.988	0.721	0.994
Pyridaben	-	-	0.477	0.976	0.477	0.976	0.472	0.941
Pyrifenoxy *	0.162	0.991	-	0.901	0.313	0.977	-	0.868
Pyrimethanil	0.279	0.922	0.454	0.977	0.733	0.960	0.700	0.966

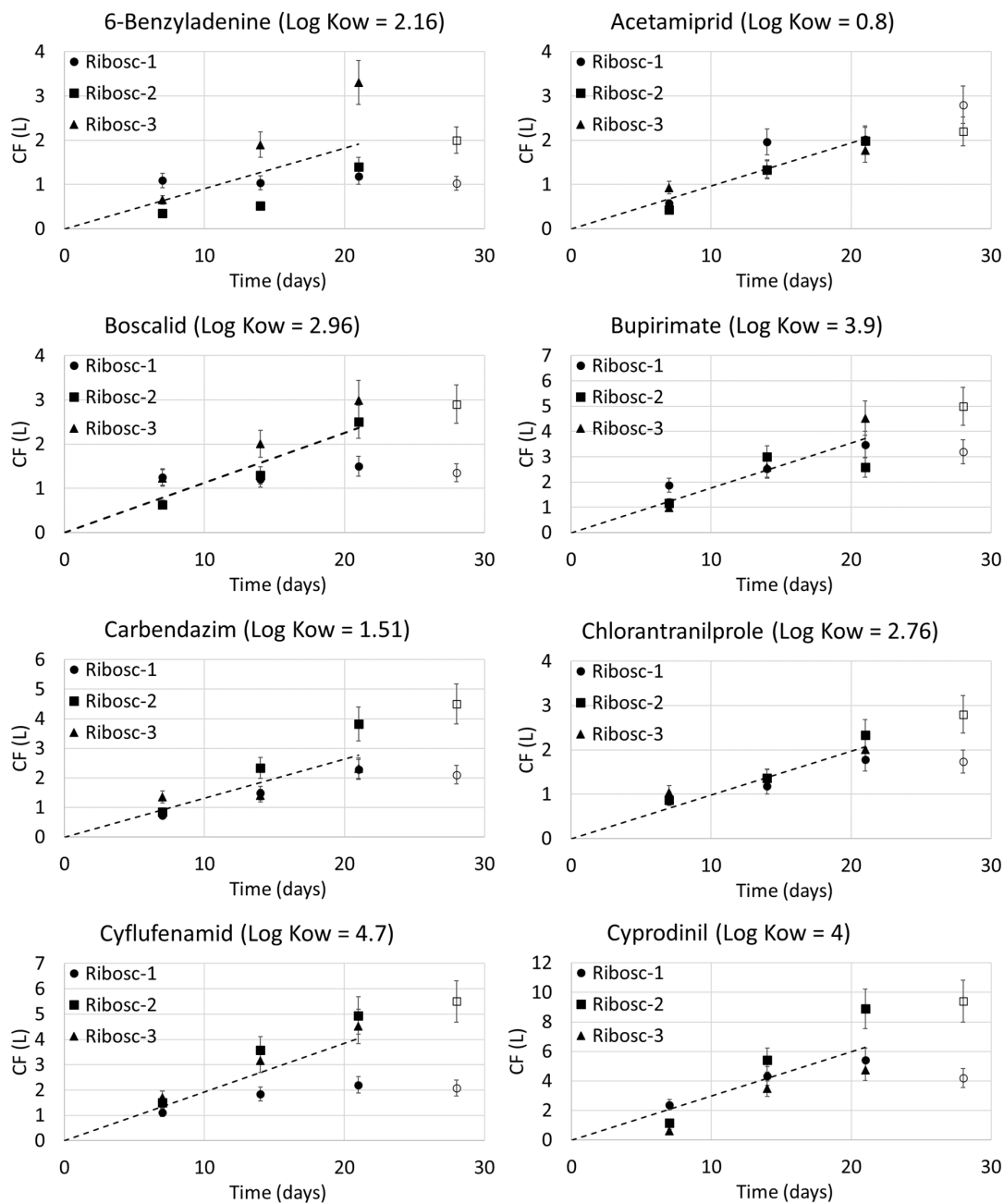
Compound	$R_{S,HLB}$	R^2	$R_{S,PES}$	R^2	R_S	R^2	$R_{S,PES-alone}$	R^2
Pyriofenone	0.154	0.995	0.431	0.973	0.584	0.987	0.557	0.970
Pyriproxyfen	-	-	0.620	0.987	0.620	0.987	0.623	0.993
Quinoxifen	-	-	0.596	0.971	0.605	0.973	0.694	0.993
Quizalofop Ethyl	-	-	0.531	0.995	0.534	0.995	0.533	0.993
Simazine	0.022	0.975	0.007	0.997	0.029	0.986	0.012	0.992
Spirodiclofen	-	-	0.214	0.987	0.227	0.992	0.209	0.978
Spirotetramat	0.223	0.965	0.082	0.991	0.305	0.978	-	0.896
Spirotetramat-enol-glucoside	0.057	0.979	-	-	0.057	0.979	-	-
Sulfoxaflor	0.197	0.976	-	-	0.206	0.984	-	-
Tebuconazole	0.145	0.981	0.227	0.979	0.372	0.985	0.333	0.935
Tebuufenpyrad	-	0.887	0.766	0.995	0.819	0.997	0.856	0.995
Terbumeton	0.209	0.984	-	0.937	0.231	0.987	-	0.873
Terbutylazine	0.149	0.978	0.050	0.986	0.199	0.985	0.079	0.964
Tetrachlorvinphos	0.151	0.991	0.267	0.981	0.418	0.990	0.366	0.968
Tetraconazole	0.115	0.987	0.123	0.988	0.239	0.991	0.168	0.981
Thiabendazole	0.165	0.954	0.131	0.994	0.296	0.976	0.200	0.998
Thiacloprid	0.189	0.983	0.115	0.989	0.303	0.990	0.163	0.974
Thiamethoxam	0.109	0.978	0.005	0.986	0.114	0.979	0.008	0.974

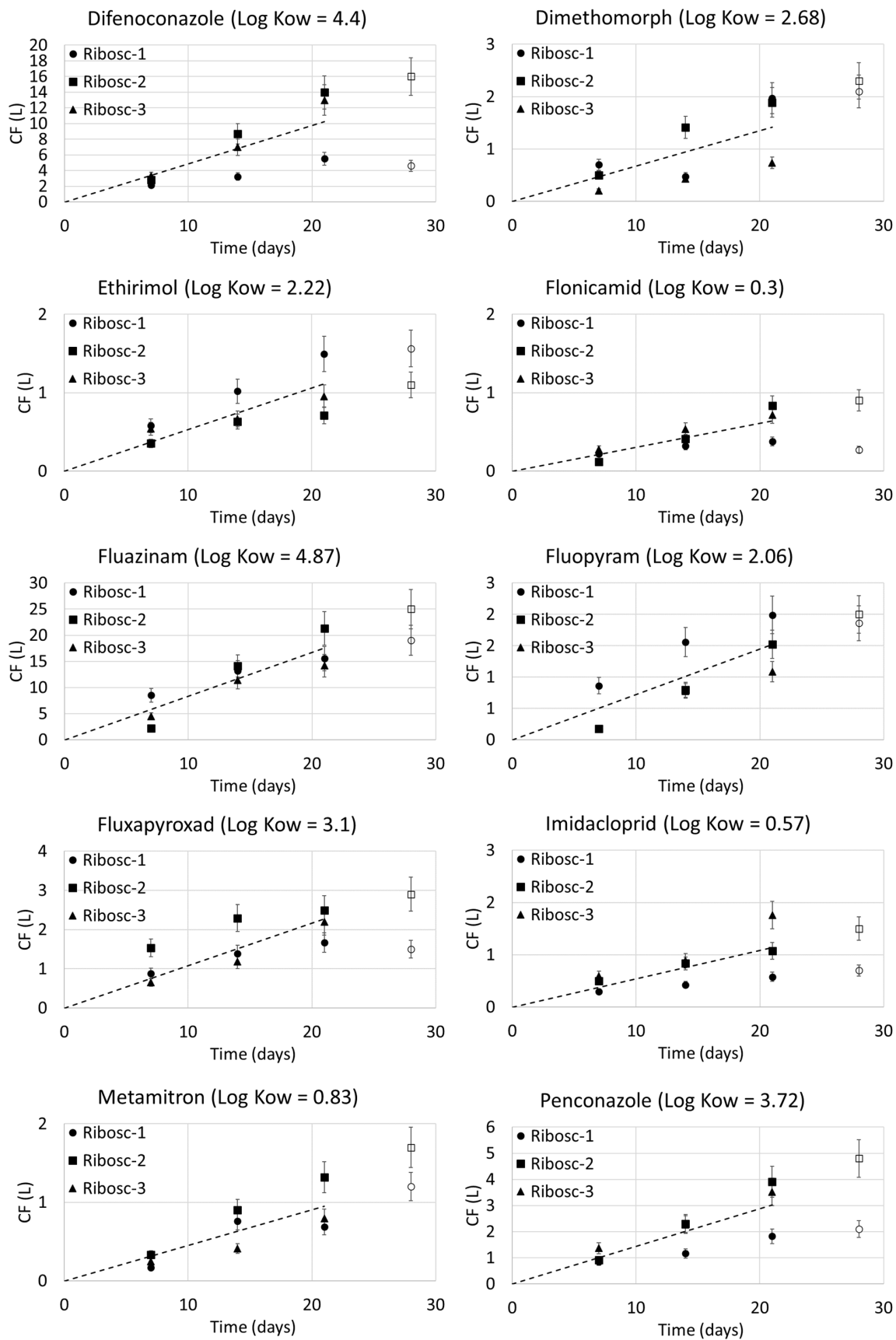
Compound	$R_{S,HLB}$	R^2	$R_{S,PES}$	R^2	R_S	R^2	$R_{S,PES-alone}$	R^2
Thifensulfuron-methyl	0.052	0.968	0.005	0.971	0.057	0.972	0.008	0.959
Thiodicarb	0.471	0.925	0.325	0.967	0.796	0.960	0.510	0.918
Triadimefon	0.139	0.966	0.071	0.975	0.210	0.975	0.090	0.957
Triasulfuron	0.111	0.956	0.009	0.969	0.120	0.961	0.015	0.922
Triazamate	0.212	0.978	-	0.796	0.252	0.970	-	0.736
Trichlorfon	-	-	-	-	-	-	-	-
Tricyclazole	0.184	0.977	0.085	0.999	0.269	0.990	0.112	0.998
Trifloxystrobin	-	-	0.295	0.981	0.322	0.990	0.319	0.992
Triflumizole	0.190	0.996	-	0.808	0.336	0.969	0.284	0.900
Triticonazole	0.099	0.976	0.020	0.977	0.119	0.983	0.030	0.942
Triosulfuron	-	0.805	0.190	0.971	-	0.945	-	0.897
Valifenalate	0.179	0.973	0.061	0.988	0.241	0.982	0.094	0.955
Zoxamide	0.116	0.998	0.318	0.969	0.433	0.985	0.442	0.968
Aldrin	-	-	-	-	-	-	-	-
Bromopropylate	-	-	1.168	0.996	1.206	0.997	1.209	0.993
Chinomethionate	0.030	0.939	-	0.920	-	0.920	-	0.896
(Oxythioquinox)								
Chlorfenapyr	-	0.806	1.183	0.994	1.224	0.991	1.206	0.994
Chlorfenson	0.042	0.991	1.329	0.999	1.371	0.999	1.370	0.996

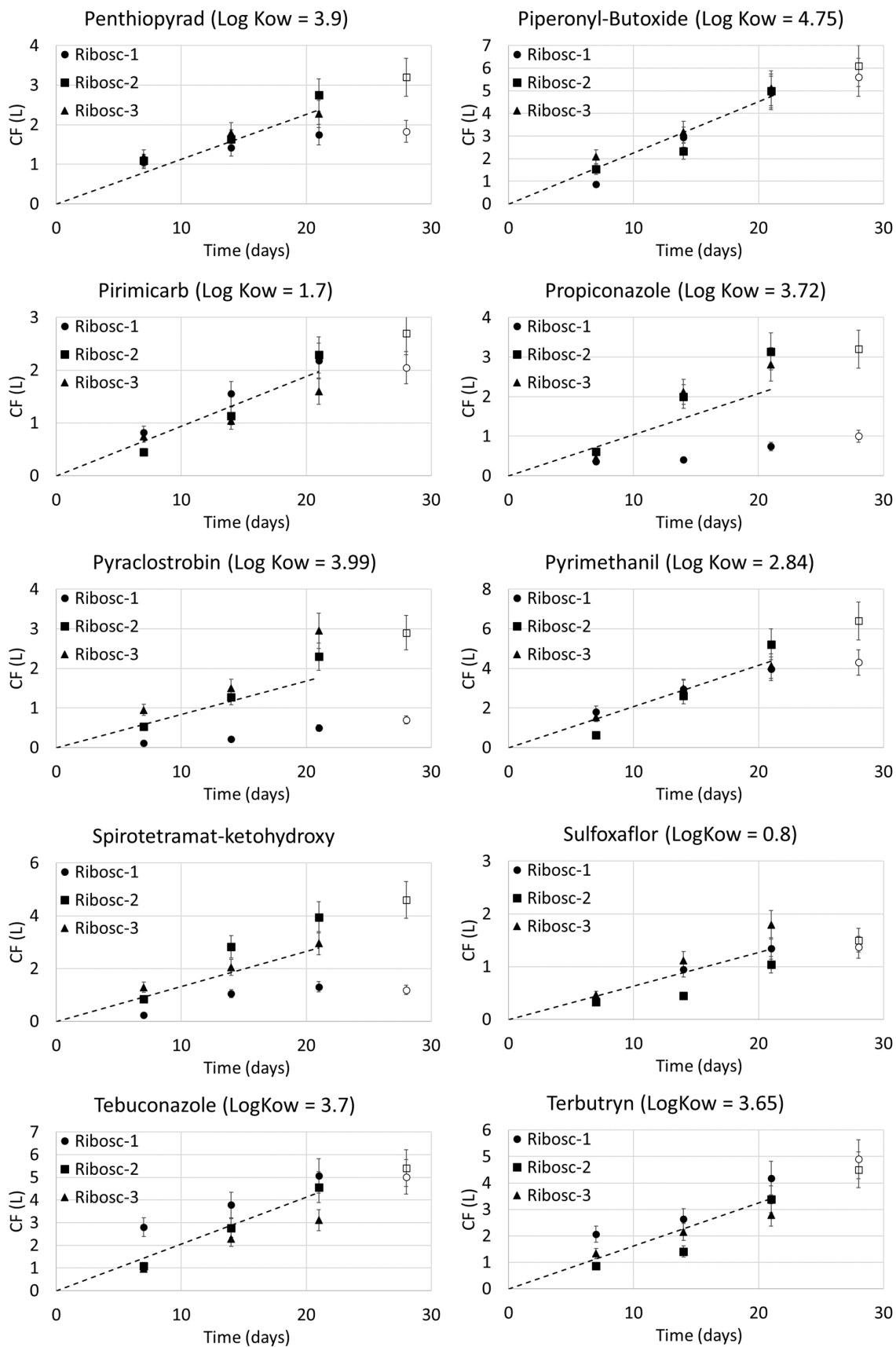
Compound	$R_{S,HLB}$	R^2	$R_{S,PES}$	R^2	R_S	R^2	$R_{S,PES-alone}$	R^2
Chlorpropham	0.117	0.984	0.505	0.989	0.622	0.990	0.640	0.989
Chlorpyrifos-methyl	0.110	0.986	0.374	0.956	0.484	0.970	0.394	0.959
Cyhalothrin (Lambda)	-	-	0.665	0.999	0.665	0.999	0.642	0.999
Dichlofenthion	-	-	-	0.865	-	0.865	-	0.843
Dichloran	0.106	0.990	1.454	0.998	1.560	0.997	1.660	0.992
Dicofol *	-	-	1.629	1.000	1.632	1.000	1.657	0.997
Dieldrin	0.154	0.983	0.422	0.951	0.577	0.983	0.530	0.961
Diphenylamine	-	-	0.346	0.946	-	0.945	0.401	0.961
Endosulfan I (alfa isomer)	0.158	0.994	-	0.931	0.489	0.975	0.432	0.936
Endosulfan II (beta isomer)	0.164	0.988	0.445	0.951	0.608	0.982	0.539	0.945
Endosulfan sulfate	-	-	2.216	0.999	2.216	0.999	2.194	0.996
Famoxadone	-	-	-	-	-	-	-	-
Fenpropathrin	-	-	0.675	0.999	0.675	0.999	0.663	1.000
Fenson	-	-	1.116	0.998	1.148	0.999	1.170	0.996
Fenvalerate *	-	-	0.907	0.991	0.907	0.991	0.938	0.996
Flucythrinate *	-	-	1.121	0.995	1.121	0.995	1.140	0.996
Heptachlor	0.038	0.953	0.293	0.956	0.330	0.974	0.325	0.976
Hexaflumuron	-	0.842	-	0.944	-	0.933	-	0.881

Compound	$R_{S,HLLB}$	R^2	$R_{S,PES}$	R^2	R_S	R^2	$R_{S,PES-alone}$	R^2
Kresoxim-methyl	0.184	0.990	0.403	0.946	0.587	0.980	0.518	0.943
Malathion	-	0.810	-	0.775	-	0.799	-	0.706
Parathion-methyl	0.076	0.974	0.734	0.955	0.810	0.961	0.800	0.956
Permethrin, (1R)-cis-	-	-	1.444	0.994	1.444	0.994	1.464	0.995
Procymidone	0.216	0.990	-	0.920	0.371	0.975	-	0.876
Prothiofos	-	-	-	0.831	-	0.831	-	0.812
Tefluthrine	-	-	0.546	0.996	0.546	0.996	0.546	0.996
Trifluralin	-	-	-	-	-	-	-	-

APPENDIX E. ACCUMULATION TREND FOR 31 COMPOUNDS AFTER 7, 14 AND 21 EXPOSURE DAYS ON THE RIBOSC STREAM.







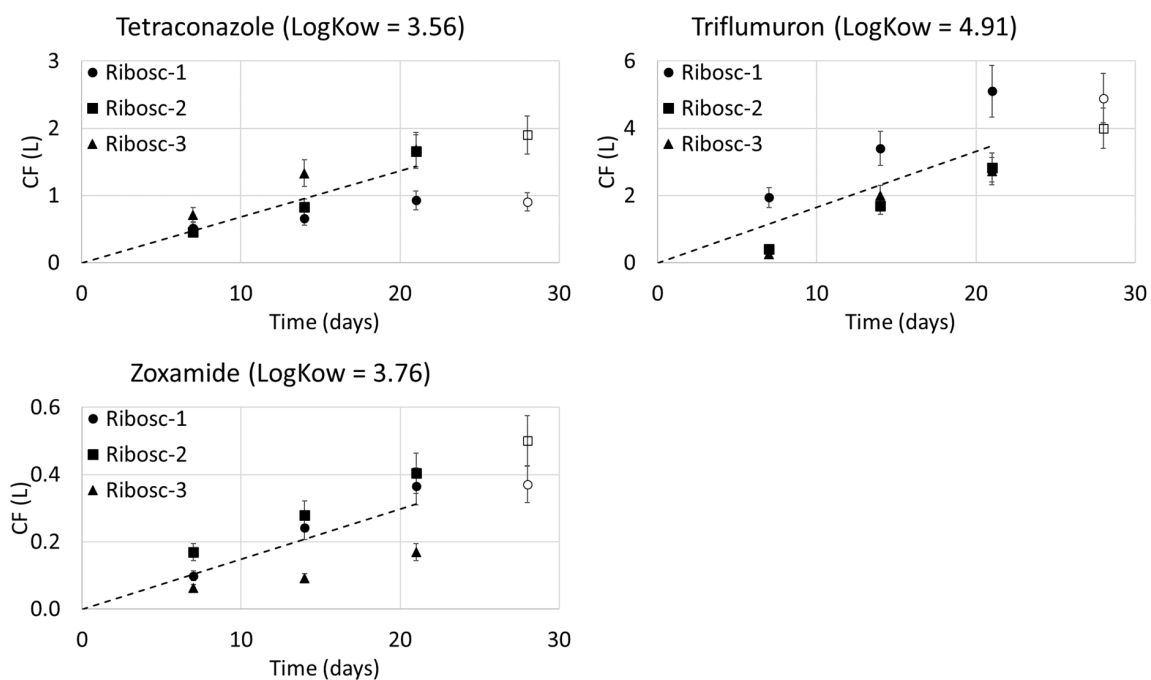


Figure 31 – Concentration Factor (CF, litre) for 31 compounds after 7, 14 and 21 exposure days. The CF values after 28 exposure days, data not used for the calibration, are reported as open symbols. The dashed line represents the calibration model obtained through a linear interpolation, which was performed using the three sampling campaigns together. The error bars represent the standard deviation of the data.

APPENDIX F. SPATIAL DISTRIBUTION OF PESTICIDES - PCA BILOT



Figure 32 – PCA biplot

**APPENDIX G. AMOUNT OF PESTICIDE ADSORBED BY POCIS DURING
THE SAMPLING PERIOD ON THE TRIBUTARY AND EMISSARY STREAM OF
THE WETLAND.**

Table 14 – Amount of pesticide adsorbed by POCIS during the sampling period on the tributary and emissary stream of the wetland.

		Sampling period																	
		2021												2022					
Compound		Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept
		Amount adsorbed by POCIS (ng)																	
6-Benzyladenine	tributary	5	116	20	-	-	-	-	-	-	-	-	-	3	49	14	2	-	-
6-Benzyladenine	emissary	-	22	1	-	-	-	-	-	-	-	-	-	-	2	1	-	-	-
Acetamidiprid	tributary	14	12	23	63	43	2	2	2	-	2	4	20	7	6	22	47	32	73
Acetamidiprid	emissary	2	5	3	6	5	4	1	2	1	8	1	1	-	2	1	2	8	6
Ametocradin	tributary	-	-	8	39	31	-	2	2	2	-	2	-	1	4	2	3	-	-
Ametocradin	emissary	6	-	7	47	2	-	16	1	-	2	43	2	3	2	2	3	1	-
Bitertanol	tributary	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	39
Bitertanol	emissary	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Boscalid	tributary	20	33	27	16	25	6	10	5	6	7	8	14	24	24	33	28	25	24
Boscalid	emissary	4	15	7	11	19	21	7	7	6	10	11	8	9	9	6	6	12	9
Bupirimate	tributary	312	73	164	20	22	12	12	2	5	7	58	352	119	216	216	62	46	53
Bupirimate	emissary	34	17	24	4	3	4	1	-	-	1	2	16	17	17	29	11	9	3
Buprofezin	tributary	-	-	-	-	-	-	-	-	-	-	-	-	-	4	5	2	1	-
Buprofezin	emissary	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Captan	tributary	910	-	-	-	-	-	194	-	1087	193	554	162	626	90	303	676	2833	
Captan	emissary	-	-	-	-	-	-	46	-	44	51	36	34	64	-	-	52	173	386
Carbaryl	tributary	-	-	-	-	-	-	-	-	7	1976	107	22	9	7	14	193	183	16
Carbaryl	emissary	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

		Sampling period																	
		2021												2022					
Compound		Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept
		Amount adsorbed by POCIS (ng)																	
Carbendazim	tributary	357	135	276	29	65	40	21	6	14	9	16	17	95	50	28	23	120	
Carbendazim	emissary	11	30	17	10	14	20	11	10	9	6	7	5	9	28	10	15	9	
Chlorantranilprole	tributary	76	174	1273	390	447	161	193	109	236	186	113	66	59	406	196	176	107	
Chlorantranilprole	emissary	68	219	199	288	413	407	90	71	65	61	56	51	53	87	75	96	55	
Chlorpyrifos	tributary	4	4	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Chlorpyrifos	emissary	1	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Cyflufenamid	tributary	2	27	49	20	11	2	3	2	5	6	10	31	79	77	41	28	17	
Cyflufenamid	emissary	3	21	6	4	6	5	3	2	2	2	2	14	36	12	8	10	5	
Cyprodinil	tributary	9	54	17	3	6	-	1	1	1	2	5	6	56	13	15	12	6	
Cyprodinil	emissary	5	23	10	3	3	1	2	2	1	2	2	3	7	2	6	6	5	
Desmethyl-pirimicarb	tributary	-	-	6	4	4	-	-	-	-	-	-	-	1	17	26	13	4	
Desmethyl-pirimicarb	emissary	-	-	1	2	1	1	-	-	-	-	-	-	-	2	9	9	1	
Difenoconazole	tributary	8	37	101	38	45	7	9	4	6	7	20	13	153	196	116	72	54	
Difenoconazole	emissary	3	19	8	6	6	-	2	3	3	3	4	3	25	14	9	9	6	
Dimethomorph	tributary	-	2	23	2	12	-	-	3	-	-	-	4	2	3	2	1	-	
Dimethomorph	emissary	-	2	10	18	4	-	12	-	-	4	-	2	6	2	3	1	-	
Diphenylamine	tributary	-	-	-	-	-	-	19	-	19	19	19	18	24	14	21	18	21	
Diphenylamine	emissary	-	-	-	-	-	-	21	26	16	19	23	21	20	17	19	18	25	
Ethirimol	tributary	13	15	41	4	2	-	1	-	6	2	4	46	29	40	6	13	10	

		Sampling period																	
		2021												2022					
Compound		Apr	May	Jun	Jul	Ago	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Ago	Sept
		Amount adsorbed by POCIS (ng)																	
Ethirimol	emissary	22	32	17	3	3	3	2	1	1	1	1	2	14	29	19	7	11	5
Etofenprox	tributary	72	26	10	-	15	-	-	-	-	-	-	9	13	29	10	8	-	-
Etofenprox	emissary	4	13	4	-	11	-	-	-	-	-	-	-	-	7	-	3	-	-
Fenbuconazole	tributary	-	2	3	-	1	-	-	-	-	-	-	-	-	16	3	2	6	1
Fenbuconazole	emissary	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Flonicamid	tributary	24	3	-	-	-	-	-	-	-	-	-	-	64	3	-	-	-	-
Flonicamid	emissary	22	5	-	-	-	-	-	-	-	-	-	-	9	4	-	-	-	-
Fluazinam	tributary	468	466	684	31	15	7	9	4	4	24	23	49	22	406	1400	109	120	39
Fluazinam	emissary	182	635	96	2	2	24	4	100	-	5	3	3	2	62	40	4	8	2
Fludioxonil	tributary	14	6	10	45	183	40	18	4	9	6	6	10	8	18	15	32	37	606
Fludioxonil	emissary	3	5	4	43	52	53	11	6	6	6	6	5	5	4	7	21	25	213
Fluopyram	tributary	1	27	66	12	14	5	9	4	3	10	4	4	3	12	73	28	18	11
Fluopyram	emissary	2	29	13	6	10	12	5	5	5	3	5	5	3	5	11	11	15	8
Fluxapyroxad	tributary	109	816	242	166	207	88	144	63	86	118	98	98	350	973	363	353	430	250
Fluxapyroxad	emissary	99	536	139	137	179	165	75	62	70	97	89	89	185	406	136	132	226	140
Hexaconazole	tributary	-	-	-	5	-	-	-	-	-	-	-	-	-	-	-	1	4	1
Hexaconazole	emissary	-	1	1	-	-	-	-	-	-	-	-	-	-	-	-	-	1	-
Imidacloprid	tributary	2	5	25	5	9	1	4	1	1	1	2	3	2	5	10	8	4	3
Imidacloprid	emissary	1	4	3	3	3	3	1	2	2	2	-	2	2	2	2	-	4	2

		Sampling period																
		2021												2022				
Compound		Apr	May	Jun	Jul-Ago	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Ago	Sept
		Amount adsorbed by POCIS (ng)																
Metalaxyl	tributary	-	-	4	-	-	-	-	-	-	-	-	-	5	2	1	-	-
Metalaxyl	emissary	-	1	2	-	-	-	-	-	-	-	-	-	1	-	-	-	-
Metamitron	tributary	-	7	8	-	-	-	-	-	-	-	-	-	9	8	-	-	-
Metamitron	emissary	-	5	-	-	-	-	-	-	-	-	-	-	22	-	-	-	-
Metrafenone	tributary	-	-	1	-	9	-	-	-	-	-	-	-	-	-	2	-	3
Metrafenone	emissary	7	-	1	2	3	-	-	-	-	-	-	-	-	-	3	-	-
Myclobutanil	tributary	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Myclobutanil	emissary	-	2	2	-	2	-	-	-	-	-	-	-	-	-	-	3	3
Penconazole	tributary	18	40	201	62	59	12	12	5	10	14	27	48	153	320	113	92	59
Penconazole	emissary	5	24	18	14	19	17	6	6	7	6	27	11	40	28	17	22	13
Pendimethalin	tributary	-	-	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pendimethalin	emissary	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Penthiopyrad	tributary	6	25	5	3	4	-	2	1	5	4	5	2	10	9	3	2	2
Penthiopyrad	emissary	5	29	7	4	4	3	3	3	3	4	3	2	6	2	2	5	3
Phosmet	tributary	-	-	-	-	-	-	-	-	-	-	2064	172	236	126	13	-	-
Phosmet	emissary	47	-	-	-	-	-	-	-	-	-	-	-	57	14	-	-	-
Phthalimide	tributary	-	-	-	-	-	-	45	29	42	67	2046	210	286	243	50	36	50
Phthalimide	emissary	-	-	-	-	-	-	37	41	47	38	124	89	116	123	30	27	38
Piperonyl Butoxide	tributary	-	-	-	1	1	-	-	1	-	-	2	3	14	4	1	2	2

		Sampling period																	
		2021												2022					
Compound		Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept
		Amount adsorbed by POCIS (ng)																	
Piperonyl Butoxide	emissary	-	-	3	5	3	3	2	3	3	4	2	5	7	4	5	14	14	28
Pirimicarb	tributary	40	8	62	16	20	3	2	3	1	2	3	8	9	9	316	166	77	37
Pirimicarb	emissary	9	5	7	5	4	1	2	1	1	1	1	1	1	10	12	59	27	5
Propiconazole	tributary	-	3	-	5	9	-	2	-	-	-	-	-	-	-	3	3	4	2
Propiconazole	emissary	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4
Pyraclostrobin	tributary	10	8	6	-	2	-	-	-	-	-	-	-	2	4	4	2	1	3
Pyraclostrobin	emissary	-	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pyrimethanil	tributary	114	572	101	27	35	7	10	3	3	9	8	29	129	493	95	63	40	24
Pyrimethanil	emissary	81	370	67	31	25	13	4	4	5	4	5	8	45	81	16	17	22	14
Simazine	tributary	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	19
Simazine	emissary	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Spinosad	tributary	-	-	10	-	-	-	-	-	-	-	-	-	-	-	13	4	-	5
Spinosad	emissary	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Spirotetramat	tributary	-	200	12	-	-	-	-	-	-	3	1	-	-	120	15	1	-	-
Spirotetramat	emissary	-	51	6	-	-	-	-	-	-	-	-	-	-	77	2	1	-	-
Spirotetramat-enolglucoside	tributary	-	29	6	10	6	-	-	-	-	4	-	3	-	246	8	-	-	-
Spirotetramat-enolglucoside	emissary	-	54	13	4	2	2	-	-	-	-	-	-	-	44	14	-	-	-

		Sampling period																	
		2021									2022								
Compound		Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept
		Amount adsorbed by POCIS (ng)																	
Spirotetramat-ketohydroxy	tributary	-	55	33	-	-	-	-	-	-	9	6	4	-	56	27	7	6	5
Spirotetramat-ketohydroxy	emissary	-	54	17	-	-	-	-	-	-	-	-	-	-	34	13	4	5	-
Spiroxamine	tributary	-	-	17	-	-	-	-	-	-	-	-	-	-	1	1	1	-	-
Spiroxamine	emissary	-	-	11	-	-	-	-	-	-	-	-	-	-	5	2	2	-	-
Sulfoxaflor	tributary	-	24	-	-	-	-	-	-	-	-	-	-	-	20	-	-	-	-
Sulfoxaflor	emissary	-	16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tebuconazole	tributary	17	86	147	33	43	8	-	-	-	-	-	-	-	-	-	49	35	28
Tebuconazole	emissary	6	46	15	7	12	12	-	-	-	-	-	-	-	-	-	9	13	6
Terbumeton	tributary	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Terbumeton	emissary	-	1	2	2	2	-	1	2	2	2	1	2	-	-	1	1	2	2
Terbutryn	tributary	1	3	4	3	4	1	6	2	2	2	3	2	2	2	11	8	8	6
Terbutryn	emissary	3	8	13	11	10	8	15	18	16	9	11	6	6	5	8	16	23	25
Tetraconazole	tributary	6	19	115	15	15	4	6	3	3	5	7	8	6	37	48	29	22	17
Tetraconazole	emissary	3	18	10	8	11	8	4	4	3	3	3	4	4	19	20	13	23	12
Trifloxystrobin	tributary	-	7	4	-	-	-	-	-	-	-	-	-	1	2	2	2	-	1
Trifloxystrobin	emissary	-	1	-	-	-	-	-	-	-	14	3	-	-	-	-	-	-	-
Triflumuron	tributary	15	5	4	-	-	-	-	-	-	-	-	-	-	-	-	-	1	-
Triflumuron	emissary	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

		Sampling period																	
		2021									2022								
Compound		Apr	May	Jun	Jul	Ago	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Ago	Sept
		Amount adsorbed by POCIS (ng)																	
Zoxamide	tributary	-	-	2	-	2	-	-	-	-	-	-	-	-	-	3	1	2	-
Zoxamide	emissary	0	0	2	0	0	0	0	0	0	0	0	0	0	3	1	0	0	0

**APPENDIX H. AMOUNT OF PESTICIDE ADSORBED BY POCIS AT THE
MEZZOCORONA MANHOLE.**

Table 15 – Amount of pesticide adsorbed by POCIS at the Mezzocorona manhole.

Period of sampling	May-20	June-20	July-20	May-21	June-21	July-21	May-23	June-23	July-23	May-24	June-24	July-24
Exposure days	25	31	27	28	28	26	21	22	26	23	27	34
Compound	pesticide adsorbed amount normalize at an exposure time of 21 days m_{21d} (ng)											
Acetamiprid	8551	1856	1529	35	1567	7879	500	105	278	5	9	120
Ametoctradin	33	407	6395	152	114	2847	20	18	169	6	8	38
Boscalid	6	6	16	2	4	4	3	2	4	4	3	2
Bupirimate	63	25	147	72	38	14	14	3	37	8	10	7
Buprofezin	9	18	32	20	19	19	4	4	7	1	1	2
Carbendazim	70	32	37	30	77	15	75	23	12	74	14	6
Chlorantraniliprole	21	236	94	9	1190	105	7	9	49	3	10	5
Chlorpyrifos	28	23	34	11	25	8	1	1	2	< LOD	1	< LOD
Cyflufenamid	59	642	2813	71	1919	3598	26	83	205	15	97	51
Cyprodinil	321	88	173	124	83	131	10	7	15	19	26	17
Difenoconazole	1307	248	279	48	63	37	40	21	31	16	26	16
Dimethomorph	202	1998	25588	12075	1247	8198	155	52	141	21	52	36
Diuron	11	3	3	5	2	4	3	12	12	< LOD	2	2
Ethirimol	1	3	6	3	2	2	3	1	6	< LOD	1	< LOD
Fluazinam	16100	3084	751	9850	1190	2390	1450	128	230	356	933	318
Fludioxonil	51	119	478	23	30	110	59	84	278	45	36	69
Fluopicolide	4	6	10	5	5	4	7	5	4	2	3	4
Fluxapyroxad	1918	545	292	1945	137	52	99	37	39	60	35	10

Period of sampling	May-20	June-20	July-20	May-21	June-21	July-21	May-23	June-23	July-23	May-24	June-24	July-24
Exposure days	25	31	27	28	28	26	21	22	26	23	27	34
Compound	pesticide adsorbed amount normalize at an exposure time of 21 days m_{21d} (ng)											
Imidacloprid	26	86	665	32	12	46	6	16	3	21	3	1
Metalaxyl	18	205	7	70	28	72	7	8	4	2	9	3
Metrafenone	123	13141	14103	308	3640	15588	105	214	565	46	36	210
Myclobutanil	5	8	10	7	7	8	5	2	3	2	< LOD	1
Penconazole	1806	1682	1218	3865	2227	3275	685	653	428	894	525	216
Piperonyl Butoxide	12	7	36	67	26	54	33	32	49	31	24	46
Pirimicarb	6	4	3	6	1132	105	40	4	3	3	4	8
Propiconazole	8	5	8	503	3	2	6	4	7	2	< LOD	< LOD
Pyrimethanil	55	45	45	116	101	57	12	4	4	37	128	12
Quinoxifen	42	59	122	19	23	27	4	4	9	2	2	5
Spiroxamine	32	4529	27014	1205	1245	8238	280	424	630	88	633	203
Tebuconazole	12	11	15	206	148	32	230	44	27	91	16	14
Terbutryn	2	3	2	3	11	37	69	33	73	9	8	5
Tetraconazole	169	66	391	16	47	18	115	124	137	31	34	31
Trifloxystrobin	< LOD	3	11	3	1	2	9	2	3	5	4	8
Zoxamide	1540	6762	13740	2922	3100	22171	475	539	407	346	392	117

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