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The Use of Passive Samplers to Reveal Industrial and Agricultural Pollution Trends in Swiss Rivers

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Abstract: This study shows the efficiency of passive sampling to reveal industrial and agricultural pollution trends. Two practical applications for nonpolar and polar contaminants are presented. Low-density polyethylene (LDPE) samplers were deployed for one year in the Venoge River (VD) to monitor indicator PCBs (iPCBs, IUPAC nos. 28, 52, 101, 138, 153 and 180). The results showed that the impact of PCB emissions into the river is higher in summer than in other seasons due to the low flow rate of the river during this period. Polar organic chemical integrative samplers (POCIS) were deployed for 4 months in the Sion-Riddes canal (VS) to investigate herbicides (terbuthylazine, diuron and linuron). Desisopropylatrazine-d5 (DIA-d5) was tested as a performance reference compound (PRC) to estimate aqueous concentration. The results showed an increase of water contamination due to the studied agricultural area. The maximal contamination was observed in April and corresponds to the period of herbicide application on the crops.

Keywords: Herbicides · LDPE · Passive sampling · PCB · POCIS

Introduction

General

The Water Framework Directive (WFD) requires EU Members States to achieve 'good chemical status' for surface water by 2015.[1] Although Switzerland does not belong to EU, it strives to follow the same objectives as its neighbours. Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) are a critical issue for the environment because of their toxicity and their persistence. By ratifying the Stockholm Convention on POPs, countries have committed to reduce or cease emissions of such pollutants into the environment. Regarding herbicides, Pimentel[2] found that more than 99.9% of pesticides applied on crops move in the environment and could impact human health. However, only a small percentage of such contaminants seems to be found in the aquatic environment.[3] In Switzerland, the Waters Protection Ordinance (WPO, SR 814.201) sets the maximal limit of organic herbicides in water at 0.1 µg L^{-1}. In order to achieve these requirements, tools are needed to investigate pollutants in an inexpensive and effective way. In this paper, two different cases involving passive sampling are presented. PCBs were monitored for one year (January 2012 to January 2013) in the Venoge River and herbicides for 4 months (March 2013 to June 2013) in the Sion-Riddes canal.

Passive Sampling

Passive sampling has been used many times to monitor the aquatic environment.[4–7] It is inexpensive, very sensitive and can provide time weighted average (TWA) concentrations of the free dissolved fraction of monitored pollutants.[8] It has many advantages compared to traditional water sampling. Indeed, results obtained by spot sampling are not always representative of the level of contamination because episodic pollution could be missed. An automatic sampling system is more representative than spot sampling but it is expensive and needs power. In addition, for nonpolar contaminants (such as PCBs), which are at low concentration in water, high quantities of water have to be collected. The transport of these water samples to the laboratory incurs the risk of losses of contaminants through wall adsorption.[9] By measuring free dissolved concentrations, passive sampling provides valuable data about pollutant bioavailability (concentrations to which organisms are exposed).[8] However, one must bear in mind that limits set by the WFD and most other legislation are expressed (even if questionable) as total concentrations in the whole water sample.[10] There are many manufactured passive sampling media referenced in the literature with their uptake capacity and affinity for contaminants.[11] These media have the advantage of being more homogenous than sediment or biota. Therefore, the required number of samples and the matrix effect are lower than for these two natural media.[8] In this study, low-density polyethylene (LDPE) strips were selected to monitor PCBs and polar organic chemical integrative samplers (POCIS) to monitor herbicides. LDPE strips are popular for the sampling of nonpolar contaminants due to the fact that they are single-phase samplers with an inexpensive and simple construction.[12] POCIS are widely used for polar compounds.[13] The uptake of pollutants by passive samplers is given by Eqn. (1)

$$C_s = \frac{N_s}{m_s} = C_w K_{sw} \left[1 - \exp\left(-\frac{R_s}{K_{sw} m_s} t\right)\right] \quad (1)$$

where C_s (ng kg^{-1}) and C_w (ng L^{-1}) are the concentrations of pollutants, respectively, in the sampler and in water. N_s (ng) is the amount of pollutants in the sampler, m_s (kg) is the mass of the sampler, K_{sw} (L kg^{-1}) is the partition coefficient of the pollutant between water and the sampler, t (d) is the sampling time and Rs (L d^{-1}) the sampling rate.

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The key issue of passive sampling is the fact that Rs depends on exposure conditions such as velocity, biofouling and temperature. Investigating LDPE, Booij *et al.*[14] showed that an increase of temperature from 2 to 13 °C does not impact Rs whereas an increase from 2 to 30 °C leads to a doubling of Rs. Estoppey *et al.*[15] showed that velocity variations in the range from 1.6–100 cm s^{-1} do not impact Rs by more than a factor 2 for PCB 28 and 52. For the other indicator PCBs (iPCBs), the factor 2 is only exceeded when a large difference of velocity occurs. Regarding biofouling, only studies using similar samplers (semipermeable membrane devices) are available. Richardson *et al.*[16] reported a decrease of Rs by a factor 2 in fouling condition whereas Harman *et al.*[17] reported an insignificant effect.

Concerning POCIS, Li *et al.*[18] showed that water velocity has a low impact on the uptake of contaminants. Indeed, velocity variations between 2.6 and 37 cm s^{-1} do not impact Rs by more than a factor 2. According to Li *et al.*,[19] temperature has only a small impact on the uptake and it may not be necessary to adjust Rs under a narrow range of temperature. Contrary to PCBs, the uptake of polar contaminants can be influenced by pH variations. Using an HLB phase, the neutral form of compounds is better adsorbed by POCIS than the ions. Therefore the uptake of acidic compounds is maximized at low pH whereas basic compounds have a maximal uptake at high pH. Between pH 3 and 9, the uptake is influenced at most by a factor 3.[20]

Monitoring carried out over months and/or at different sites implies variations of exposure conditions. These variations have to be taken into account to compare the resulting data. This can be done either using the factors by which exposure conditions influenced the uptake (*e.g.* factors described in the two previous paragraphs) or by using performance reference compounds (PRCs). PRCs are spiked on the sampler before immersion and their dissipation rate is used to estimate Rs. The PRC method assumes that PRCs follow similar kinetics to the studied contaminants (isotropic exchanges) and thus that Rs based on PRCs take into account variations of exposure conditions.[21,22] This assumption was shown to be valid for nonpolar samplers such as LDPE strips whereas contradictory evidence exists for polar samplers such as POCIS.[21] Indeed, for these latter samplers, Rs estimation is complicated by strong sorption of most compounds to the adsorbents and intensive research is being conducted to validate the use of PRCs for these samplers.[23] In this study, in addition to revealing pollution trends by comparing C_S (in space and time), the use of PRCs in estimating C_w with the POCIS was assessed.

The use of PRCs requires calibration. During this step, a calibrated Rs (Rs_{cal}) is calculated for each compound by immersing the POCIS and retrieving them after different times (*e.g.* 1 week, 2 weeks and 3 weeks). Simultaneously to the exposition of POCIS, the concentration in water (C_w) is determined using an automatic sampler. Then, the amount of contaminants in POCIS (N_S) is plotted versus time (t). Knowing the average C_w, Rs_{cal} can be calculated using the slope of the trendline (Eqn. (2)).

$$R_s = \frac{N_s}{\overline{C_w} t} \qquad (2)$$

The calibration step also enables the determination of a calibrated desorption constant rate (ke_{cal}) from PRC dissipation data. When the natural logarithmic of the PRC retained fraction ($C_{PRC(t0)}/C_{PRC(t)}$) is plotted versus time (t), the slope of the trendline corresponds to ke_{cal} (Eqn. (3)).

$$k_e = \frac{ln\left(C_{PRC(t0)}/C_{PRC(t)}\right)}{t} \qquad (3)$$

PRC dissipation data obtained *in situ* are used to determine *in situ* ke (ke_{insitu}) according to Eqn. (3). Then, *in situ* Rs (Rs_{insitu}) is calculated from Eqn. (4) and C_w can be determined using a rearrangement of Eqn. (2).

$$R_{Sinsitu} = R_{Scal}\left(\frac{k_{einsitu}}{k_{ecal}}\right) \qquad (4)$$

Description of the Venoge River and the Sion-Riddes Canal

The first site monitored was the Venoge River because the level of dioxin-like PCBs detected in fish was higher than the maximal level permitted by the EU.[24] This river is located at an average altitude of 685 m. It flows 36 km from the foot of Jura Mountains to the Lake of Geneva. It had an average flow of 4.21 m^3 s^{-1} in 2012 and a watershed of 228 km^2 with 10% of urban area, 60% of agricultural area and 30% of wooded area.[25]

The second site, the Sion-Riddes canal, was investigated following an interest of the state of Valais to assess agricultural pollution in this area. The canal measures 8 km, takes its source in Sion and flows into the Rhône River at Riddes. The canal has a watershed composed of agricultural area and vineyard.

Method

LDPE

LDPE strips were cut (size 30 × 3 cm) and cleaned with dichloromethane (24 h) and methanol (24 h) in a 1 L Soxhlet. The cleaned strips were then transferred to a 1 L sealed amber glass and conserved in a fridge until deployment.

In the field, each sampler was constructed from six LDPE strips attached to an iron bar. Simultaneously, one sampler was exposed to air (method blank). Deployed samplers were immersed for 6 weeks in the river whereas the method blank was stored in the freezer (–20 °C). The velocity and the temperature were measured weekly. At the end of the sampling period, the strips were cut off the bars and collected in sealed aluminum containers. During the recovery of the deployed samplers, method blanks were also exposed to air. In the lab, the strips were quickly rinsed with Milli-Q® water and dried alongside the method blank on aluminium sheets. Then, strips were placed in the freezer (–20 °C) until extraction.

Before extraction, LDPE strips were cut to 20 cm length and weighed. They were cut in 1–3 cm pieces and placed in a 100 mL Soxhlet with a canister in which the sinter is protected with 0.5 cm of sodium sulphate (Na_2SO_4). The surrogate (PCB 189 and labeled iPCBs) was added to the strips and the extraction was carried out for 16 h with dichloromethane at a temperature of 70 °C.

After the extraction, hexane (1 mL) was added to the extract and reduced to 1 mL with a Rotavapor®. It was purified on a column of Florisil 60–80 mesh (5 g previously deactivated with 4% water and protected with 4 g of sodium sulphate). After the elution with 50 mL hexane, the sample was again concentrated to 1 mL and transferred to a centrifuge tube. Sulphuric acid (H_2SO_4) was added to purify the extract. After centrifugation (3000 rpm for 10 min), the supernatant was transferred to a 2 mL vial and reduced to 0.5 mL under a nitrogen flux. It was solvent exchanged to isooctane and reduced to 0.3 mL. Finally, the extract was transferred to a vial with a 300 µL insert which was kept in the freezer (–20 °C) until analysis.

Extracts from LDPE were quantified by GC-MS/MS (Thermo Scientific: Trace 1310 coupled with TSQ Quantum XLS Ultra). 2 µL of the extracts were injected at 280 °C in splitless mode on a ZB-5MS column (60 m × 0.25 mm, id 0.25 µm) with a constant flow rate of 1.5 mL min^{-1}. The temperature program started at 80 °C (0.5 min), increased to 160 °C (20 °C min^{-1}), and then to 300 °C (4 °C min^{-1}) with a hold time of 10 min. Helium was used as carrier gas and argon as collision gas.

The mass spectrometer was operated in electron impact at –70 eV in the selected reactive monitoring mode (SRM). For each PCB congener, two transitions were used for quantification and confirmation. The transfer line was set at 290 °C and ion source at 250 °C. The separation of PCB 28 and PCB 31 is not possible on the ZB-5MS column. Therefore, they were quantified together.

POCIS

POCIS were prepared by adding 200 mg of HLB adsorbent between two polyethersulfone membranes. They were packed in aluminum sheets and conserved in a freezer (–20 °C) until deployment. The HLB phase was previously spiked with the PRC DIA-5 (2 µg/g of HLB). The methanolic solution was placed in an ultrasonic bath for 5 min. Then, the powder was dried by Rotavapor® under nitrogen flux.

In the field, three POCIS were placed in a cage fastened to an iron bar. A method blank was exposed to air. The samplers were immersed for 21 days whereas the method blank was stored in the freezer (–20 °C). Velocity, temperature and pH were measured weekly.

At the end of the sampling period, the POCIS were collected in sealed aluminum containers. During recovery, method blanks were also exposed to air. In the lab, polyethersulfone membranes were cut and the HLB phase was put in SPE cartridges. The cartridges were packed in aluminum sheets and stored in freezer until extraction.

Surrogates (linuron-d6, terbuthylazine-d5 and diuron-d6) were added in the SPE cartridges before extraction. As soon as the HLB phase was dried, the cartridges were eluted using a Gilson SPE GX-274 ASPEC with 6 ml of methanol at 6 mL min^{-1}. 1 mL was taken from the eluate for analysis.

Extracts from POCIS were quantified by UPLC-MS/MS (Waters AQUITY™ UPLC coupled with Xevo TQ MS). 30 µL were injected on a Acquity UPLC HSS T3 (C_{18}, 21 × 100 mm, 1.8 µm) column with a mobile phase constituted by two eluents A (95% H_2O, 5% MeOH, 1% formic acid, 2.5% 200 mM ammonium formate) and B (5% H_2O, 95% MeOH, 1% formic acid, 2.5% 200 mM ammonium formate). The gradient was set as follow: 0 min, 95% A; 2 min 50% A; 9 min 5% A; 11 min 95% A; 14 min 95% A. The column temperature was set at 30 °C. The flow rate of the eluent was set at 0.4 mL min^{-1}. The mass spectrometer was operated in ESI positive mode for all compounds. The detection was done in MRM mode. Therefore, two transitions were used for quantification and confirmation.

Sampling Campaign

The one-year monitoring in the Venoge River was carried out downstream of a PCB source detected in 2010.[15] This source is a wastewater treatment plant (WWTP) which has an average outflow of 0.03 m^3 s^{-1} and treats wastewater from urban and industrial areas. Each week, a new sampler was deployed for 6 weeks. In the first three months (January to March), one new sampler was deployed each week. From April to December, two samplers were deployed each week to estimate the variability. In overall, 91 samplers were deployed in one year and 13 method blanks were done. The six indicators PCBs (iPCBs, IUPAC nos. 28, 52, 101, 138, 153 and 180) were selected because they are present in high quantity in commercial mixtures.

The Sion-Riddes canal was monitored both upstream and downstream of the town of Sion to determine the impact of the agricultural pollution. Each week, three samplers were deployed for 21 days. The campaign was conducted from 25 March to 10 June 2013 because herbicides are mostly used during this period of the year. During the campaign, a calibration of the POCIS was done according to Mazzella *et al.*[22] using an automatic sampler (ISCO). 40 mL of water per hour were sampled during the experiment. A 500 mL composite sample was created to reflect the average concentration during the sampling time of 21 days. The analysis of the water sample was conducted using the method applied to the HLB phase of POCIS (extraction of contaminants by SPE and quantification by UPLC-MS/MS).

Results and Discussion

PCB Pollution in the Venoge River

The variation of the sum of the six iPCB concentrations in samplers (C_S) obtained during the one-year monitoring in the Venoge River is presented in Fig. 1. Maximal C_S were measured during summer (from mid-July to the beginning of September). C_S was relatively stable during the other seasons with a slight decrease in winter.

According to Fig. 1, it could suggest that the WWTP released more PCBs in summer than the rest of the year. However, the flow contribution of the WWTP to the overall flow of the Venoge River must be studied. The WWTP outflow was constant over the sampling period whereas the flow of the Venoge River decreased in summer. Thus, as shown in Fig. 1, the contribution of the WWTP to the overall flow of the river was higher in summer. Plotting C_S on the same graph reveals that the increase of C_S in summer is most likely explained by the high contribution of the WWTP during this season due to the low flow rate of the Venoge River (Pearson correlation of 0.89).

As mentioned in the section 'Passive Sampling', potential variation of exposure conditions (temperature, velocity and biofouling) need to be taken into account to confirm the pollution trend in the Venoge River. As shown in Fig. 2A, the temperature increased by 16 °C between December and August. As mentioned by Booij *et al.*,[14] such an increase of temperature leads only to a very small increase of Rs (much less than a factor 2). As the increase of C_S between summer and the rest of the year was often much more than a factor 2, it cannot be explained by this increase of temperature. Regarding water velocity, Fig. 2B shows that this was lower in summer than in the rest of the year. According to Estoppey *et al.*,[15] an increase of velocity leads to an increase of Rs. The uptake of LDPE strips was thus lower in summer than in the rest of the year. Therefore, the increase of C_S between these seasons cannot be explained by the velocity variations and was probably even slightly underestimated. Similarly, biofouling cannot explain this increase of C_S. Indeed, the mass of biofouling recovered on the samplers was much higher in summer than in the rest of the year. As the presence of biofouling tends to decrease Rs, the increase of C_S between these seasons was probably even slightly underestimated.

Thus, based on the increase of C_S in summer and having verified that this increase was not due to exposure conditions, the data obtained by LDPE samplers revealed the high contribution of the WWTP during summer due to the low flow rate of the Venoge River. Passive sampling proved to be an easy-to-handle method to carry out this one-year monitoring, involving fewer practical constraints than the use of an autosampler.

Agricultural Pollution in the Sion-Riddes Canal

In the Sion-Riddes canal, the concentration of herbicides in the POCIS (C_S) immersed downstream of the agricultural area was higher than the one upstream (Fig. 3), revealing the release of these herbicides between the two sampling sites. An increase of C_S occurred in April and corresponded to the period of herbicide application on the crops.

Exposure conditions were stable over time and between the sites during the sampling period. Indeed, the temperature varied between 10.4 and 13.6 °C, the velocity between 23 and 42 cm s^{-1} and the pH between 7.4 and 7.9. Therefore, it can be assumed that the variations of C_S in time and between sites were not due to variations of exposure conditions.

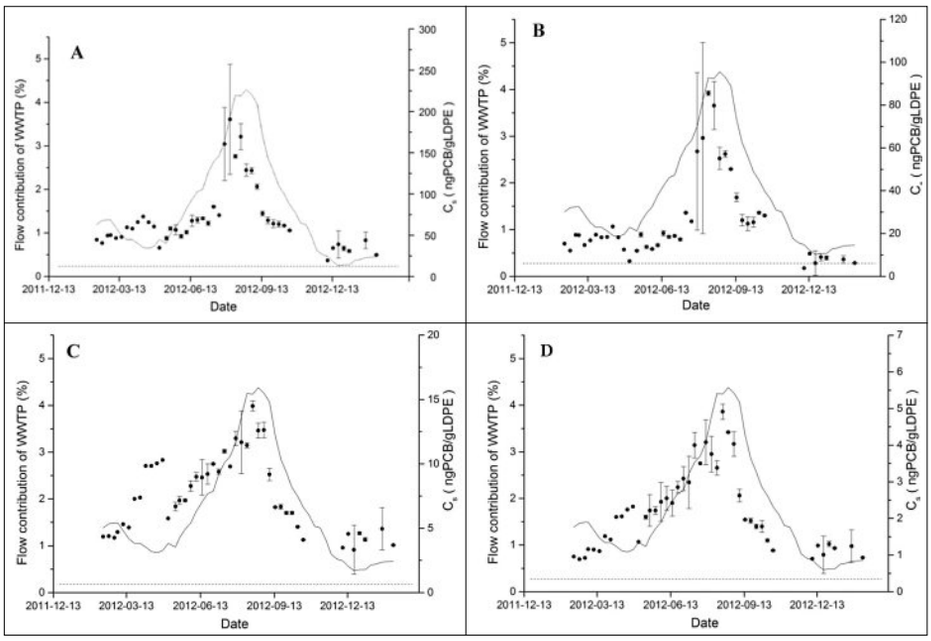

Fig. 1. Variation of the concentration of all iPCBs (A), PCB 28/31 (B), PCB 138 (C), PCB 180 (D) (circles) in samplers and flow contribution of the WWTP to the flow of the Venoge River (line). The dash line represents the limit of quantification.

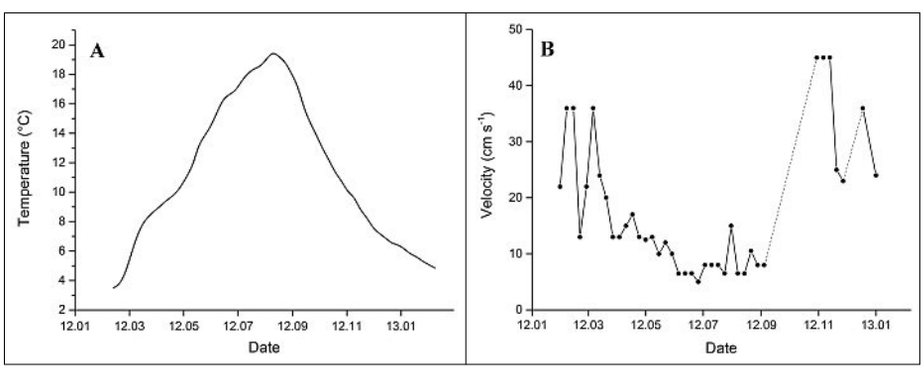

Fig. 2. Temperature (A) and velocity (B) during the one-year monitoring in the Venoge River.

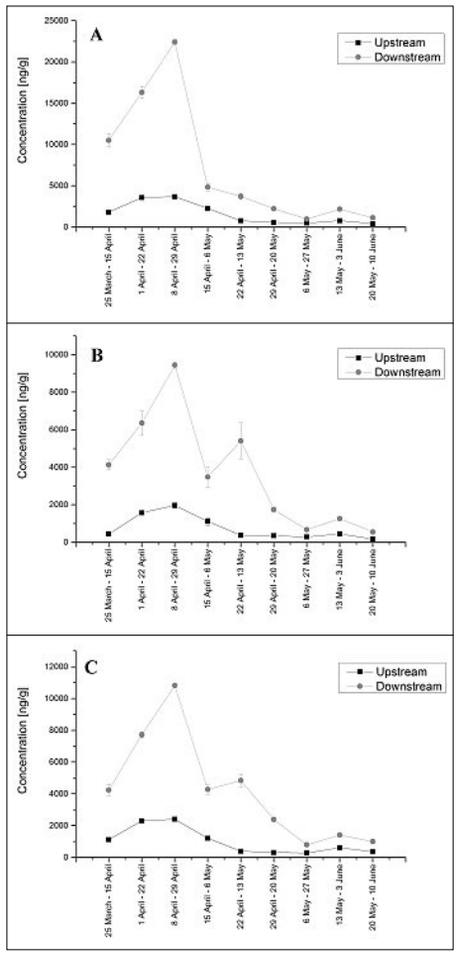

Fig. 3. Concentration of diuron (A), terbuthylazine (B) and linuron (C) on the POCIS during the monitoring in the Sion-Riddes canal.

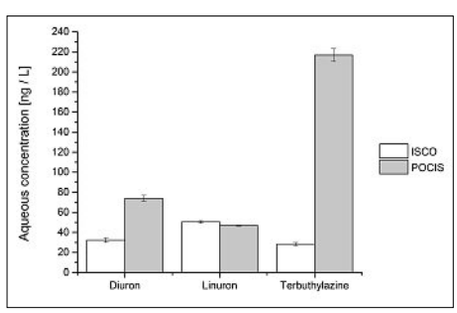

Fig. 4. Comparison between the aqueous concentration of diuron, terbuthylazine and linuron on the POCIS with the concentrations obtained by ISCO during the monitoring in the Sion-Riddes canal.

According to the strategy explained in the section 'Passive Sampling', a calibration of the POCIS was done. Rs_{cal} was calculated for the studied herbicides and ke_{cal} was determined for the PRC DIA-5. An autosampler was installed in the Sion-Riddes to confirm the TWA concentration obtained by POCIS. After 21 days, the retained fraction of DIA-5 was 0.78 and the resulting ke_{insitu} was 0.031. Rs_{insitu} of diuron, linuron and terbuthylazine were calculated using Eqn. (4). The resulting estimated aqueous concentrations are presented in Fig. 4 and are compared with the concentrations measured by active sampling (ISCO). POCIS and automatic sampling provided very similar aqueous concentrations in the case of linuron whereas the aqueous concentrations differed in the case of diuron and terbuthylazine. These differences may be due to several causes. As the aqueous concentrations of diuron and terbuthylazine were higher in the case of POCIS, it cannot be excluded that these samplers captured pollution peaks that could have been missed by the automatic sampler. The most likely hypothesis is however that DIA-5 does not follow exactly the same kinetics as diuron and terbuthylazine (anisotropic kinetics). Further experiments are needed to confirm these observations. Experiments using other PRCs are being conducted to assess if they satisfy the assumption of isotropic kinetics. A promising alternative could be to use more than one PRC to improve the quality of the estimation as done by Belles.[26]

POCIS revealed the herbicides released in the Sion-Riddes canal due to the studied agricultural area. Results obtained by these samplers showed that the impact was higher during herbicide application on the crops. The applied methodology revealed that the comparison of C_S between two sites enables the release of contaminants in a risk area to be confirmed.

Conclusion

Deployment of LDPE strips in the Venoge River and POCIS in the Sion-Riddes canal enabled industrial and agricultural pollution trends to be revealed. Regarding the Venoge River, this study showed that the impact of the studied WWTP was higher in summer than other seasons due to the low flow rate of the Venoge River during this season.

Concerning the Sion-Riddes canal, it was shown that the studied agricultural area released herbicides, particularly in April when herbicides were applied on the crops. This study showed that pollution trends can be pointed out using concentration in samplers (C_s) as long as variations of exposure conditions are taken into account. In order to do this, factors by which these exposure conditions influenced the uptake have to be systematically applied. To numerically estimate the variation of *in situ* sampling rate due to exposure conditions and to determinate aqueous concentration, the use of PRC seems to be promising.

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