FIGHT AGAINST CHEMICAL WATER POLLUTION: SETTING UP A MONITORING SYSTEM IN RIVERS OF THE LAKE GENEVA BASIN TO SUPPORT AUTHORITIES IN DECISION-MAKING

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Abstract: Water pollution by chemicals (e.g. persistent organic pollutants) impacts biodiversity as well as human health, economy and life quality. With the increase of population and human activities, it has become an urgent security issue. By introducing the water pollution-related traces into an intelligence process, we are convinced that forensic science can support authorities in decision-making to tackle this security issue. By taking the example of the Lake Geneva basin, this study identifies the limitations of current approaches to monitor chemical pollutants (hardly comparable data, insufficient sensitivity and low temporal representativeness). To overcome these limitations, a passive sampling-based acquisition process was elaborated. Relevant features were extracted (concentrations, loads and 'chemical signatures' of pollutants) and enabled pattern detection. The analysis of these patterns in combination with alternative information (e.g. field knowledge from environmental agencies) resulted in intelligence products that can support authorities in preventing current chemical releases from being repeated (or continued) or similar releases from being committed.

Keywords: pollution sources, passive sampling, pattern detection, intelligence, decision-making

INTRODUCTION

Water security has become an urgent issue because water resources are affected by population increase, economic development, climate change and other global to local drivers (Bakker, 2012; Sandford, 2012; Pahl-Wostl et al., 2016; Estoppey et al., 2019a; Wheater, 2019). Water pollution is one of the main stress-

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ors (Vörösmarty et al., 2010). In a regulatory context, it can be defined as 'the introduction of anthropogenic contaminants into water at a level that produces adverse effects to the receiving environment' (Tarazona, 2014). In this paper, we tackle the issue of 'chemical pollution', which is as worrisome as 'pathogen pollution' because of unknown long-term effects on aquatic life and on human health. Hundreds of millions of tons of industrial chemical (e.g. additives, lubricants, flame retardants) and consumer products (e.g. pharmaceuticals, cosmetics, detergents) are annually used worldwide and partially find their way into natural waters. Although most of these chemicals are found at very low concentrations (micropollutants), some are of concern because of their high toxicity (Schwarzenbach et al., 2006). During the last decades, international and national legislations have been developed to protect water, setting thresholds and penalties, among others (Kurukulasuriya and Robinson, 2006).

Similar to crimes against person or property, when water pollution cases occur (e.g. pollutant concentration in fishes exceeding legal thresholds), forensic science can support investigations and/or provide expert opinion in court decisions (Estoppey, 2017). However, forensic science can go beyond such a case-by-case approach (Ribaux et al., 2013) by introducing 'pollution traces'[2] in a solving problem process to acquire a better understanding of the security issue caused by water pollution. We hypothesize that setting up a monitoring system as described by Ribaux (2014) (acquisition of comparable data, extraction of relevant features, pattern detection, pattern analysis) can provide intelligence products. Those may support authorities in decision-making to prevent water pollution offences from being committed or repeated.

By taking the example of the Lake Geneva basin, the aim of this study is to identify the limitations of current approaches to monitor micropollutants and to assess a passive sampling-based acquisition process to provide comparable data, enabling the detection of most problematic sites and helping authorities to prioritize security actions.

LIMITATIONS OF CURRENT APPROACHES TO MONITOR MICROPOLLUTANTS

Lake Geneva is shared by two countries (France and Switzerland) and four regions (the French department of Haute-Savoie and the Swiss cantons of Vaud, Valais and Geneva). Pollution of the lake and the rivers of its basin implies a wide range of agencies, all of which have their own practices. The International

2 In a strictly legal-procedural approach, only traces related to pollution cases (exceedances of legal thresholds) should be introduced in the process. However, environmental law is unique in that a specified amount of harmful activity is permitted (Gibbs and Boratto, 2017). In our opinion, understanding "water pollution" problems also requires exploiting information conveyed by anthropogenic contaminants that are not legally classified as pollutants at the measured concentrations.

Commission for the Protection of the Water of Lake Geneva (CIPEL) performs an extensive coordination role. Three main limitations of current approaches to monitor micropollutants in the lake basin have been identified (Estoppey et al., 2019b):

1. Difficulty in obtaining comparable data. A homogeneous global view of micropollutant levels in the Lake Geneva basin is complicated because sampling methods and frequencies as well as target substances differ across regions and agencies.

2. Difficulty in achieving sufficient sensitivity. Some of the micropollutants, such as hydrophobic compounds, are present at particularly low concentrations in water (ng/L or even pg/L) and are difficult to measure with usual methods based on (grab or automatic) active sampling.

3. Difficulty in acquiring a temporal representativeness. In many rivers of the lake basin, only grab samples are collected, thus providing only a snapshot of the concentration at the moment of the sampling.

These limitations make the understanding of the problem of pollution by micropollutants in the Lake Geneva basin difficult. The prioritization of actions in space (e.g. at the most polluted rivers) and in time (e.g. at key times of year) by authorities is thus largely compromised.

AQUIRING RELIABLE DATA THROUGH A COMMON SAMPLING PROTOCOL

Traces related to chemical pollutions of water (i.e. the remnants of the chemical releases) are often latent[3]. The acquisition of these traces requires a method that can be systematically and regularly applied; as the possibility to subsequently detect spatiotemporal patterns depends on it. Those patterns may help to understand past and present water pollutions and prevent future pollutions (Ratcliffe, 2011; Morelato et al., 2014). The acquisition method should be simple and cost-effective enough to be used at large-scale, but at the same time needs to be sensitive and representative enough to overcome the limitations highlighted in the previous section. Passive sampling – which is based on the free flow of contaminants from water to a polymer (Vrana et al., 2005) – has shown to possess the essential traits for local and global monitoring of nonpolar organic compounds in water (Lohmann et al., 2012; Lohmann et al., 2017), therefore overcoming the limitations described in the previous section:

The comparability of provided data offers a global view of micropollutant levels. Samplers can indeed be deployed at large scale at low cost, enabling a

3 In certain cases of chemical pollutions (oil spills, release of oxygen demanders,…), traces are however visible with the naked eyes (oil sheens, dead fishes,…). For such cases, a higher number of stakeholders (including for example fishermen's associations or even the population in general) could contribute to the detection of new pollution events.

sequestration of pollutants in a same matrix (polymer) followed by a centralized chemical analysis (Lohmann et al., 2017).

The pollutant accumulation in samplers allows achieving low limits of quantification. For nonpolar compounds, sampling rates (R_S) of several dozen of liters per day are achieved, enabling to reach high sensitivity over a typical sampling period (t) of 4 to 6 weeks (Smedes and Booij, 2012; Jacquet et al., 2014).

The integrative sampling provides time-weighted average (TWA) concentrations. When samplers operate in the linear phase of the uptake, they sequester pollutants from episodic pollution, improving the representativeness of results (Vrana et al., 2005).

In a first instance, a monitoring system was set up for three classes of nonpolar compounds (PCBs, PBDEs, and PAHs). For these compounds, exchanges between water and (absorption-based) passive samplers are well understood (Mills et al., 2014) and the two required compound-specific parameters - i.e. the sampler-water partition coefficient (K_{SW}) and the sampling rate (R_S) - have been determined/modeled (Booij et al., 2007; Smedes et al., 2009; Rusina et al., 2010; Smedes, 2019). In addition, performance reference compounds (PRCs) can be used to correct the impact of exposure conditions (typically water flow rate) on R_S (Booij and Smedes, 2010; Lohmann et al., 2012; Smedes and Booij, 2012). Proficiency tests are regularly organized (Booij et al., 2017) for the often-used single-phase silicone rubber (SR) samplers. The latter offer high robustness (resistance in river conditions) and a linear phase of uptake (integrative window) for most of the studied compounds (Estoppey, 2017).

Even though it is not a prerequisite (see section below), the chances of success of a systematic monitoring by passive sampling are maximized, in our opinion, when lab and field tasks are distributed as presented in Figure 1. In this process, a central laboratory (with expertise in passive sampling) manages the preparation of samplers (step 1 on *Figure 1*), loading PRCs on cleaned samplers and distributing them into jars. The ready-to-use samplers are supplied (ideally by mail) to partners around the lake (mainly environmental protection agencies) who manage the installation (step 2) and the retrieval (step 3) by following a common protocol. During the first campaign, partners have been trained by our care (in the field) to ensure that key manipulations (e.g. exposition of procedural blank to air) are done correctly. Exposed samplers are then transmitted back to the central laboratory, which carries out a Soxhlet extraction and quantifies the amount of pollutant in samplers (N_S) by gas chromatography coupled with mass spectrometry in tandem (step 4). TWA concentrations of pollutants can then be determined from N_S, R_S, K_{SW} and t.

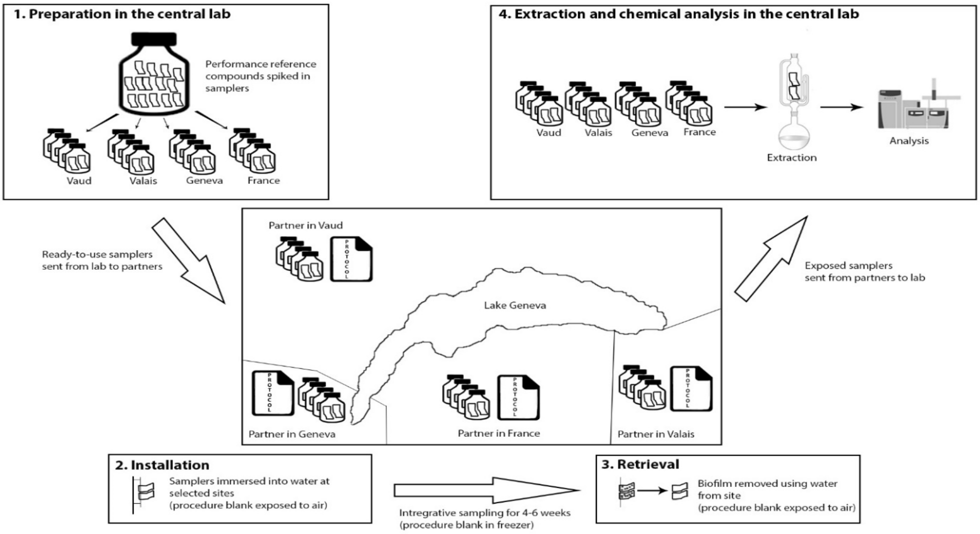

Figure 1: *Passive sampling-based monitoring of nonpolar contaminants in rivers of Lake Geneva basin.*

SELECTION OF FEATURES AND PATTERN DETECTION

As underlined by Lohmann et al. (2017), a global monitoring does not ultimately require analysis of all samplers by a single laboratory, as long as the implied laboratories provide comparable results (testable through proficiency tests). It is however essential that a selection of features is systematically measured/reported to enable subsequent comparisons among sampling sites and among sampling periods. This selection of features (often referred as 'profile' in forensic literature) should be relevant to the intelligence process objectives (Morelato et al., 2014). In this project, three features have been considered as relevant:

Aqueous concentration of pollutants (C_W), i.e. the amount of pollutants per volume of water (e.g. in pg/L). Comparing this feature among sampling sites enables the identification of the rivers with the highest risks for organisms and humans (regarding the exposure to studied pollutants). *Figure 2* shows C_W of PCBs obtained in the first campaign. The highest concentrations were measured in relatively small rivers (< 1 m^3/s during the sampling period). The same rivers are of concern for PBDEs, whereas the rivers presenting the highest C_W of PAHs are the two biggest studied rivers (> 25 m^3/s).

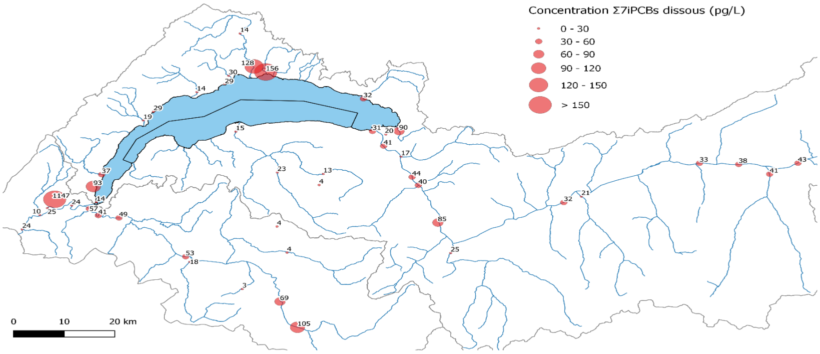

Figure 2: *Aqueous concentration of the sum of the studied PCBs (dissolved fraction) at the different studied sites (pg/L) (adapted from Estoppey et al., 2019b).*

Load of pollutants, i.e. the amount of pollutants per period of time (e.g. in mg/day). Measuring this feature requires to multiply C_W by the volumetric flow rate (e.g. in m^3/day) at each sampling site (obtained from hydrological stations or estimated from on-site measurements). Comparing this feature among lake tributaries reveals the main contributors to pollutants in the lake, whereas comparing loads among sampling sites along a single river may reveal increases due to the presence of pollution sources. *Figure 3* shows PCB loads obtained in the first campaign; the Rhône river (about 165 m^3/s at the sampling period) is the main contributor to PCBs in the lake (among studied tributaries), as it is also for PBDEs and PAHs.

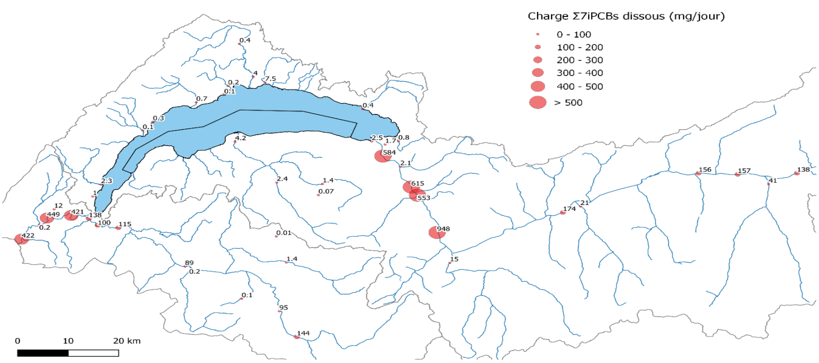

Figure 3: *Loads of the sum of the studied PCBs (dissolved fraction) at the different studied sites (adapted from Estoppey et al., 2019b).*

‘Chemical signature’, i.e. the proportion of compounds within a class of pollutants (e.g. in %). This feature may provide information on the kind of pollution sources affecting the rivers. *Figure 4* illustrates a few examples of PCB ‘chemical signatures’ observed in the first campaign. Some signatures are dominated by less hydrophobic congeners (e.g. PCBs 28 and 52 in the Venoge and Chamberonne rivers) whereas other signatures are dominated by much more hydrophobic ones (e.g. PCBs 138 and 153 in the Arve river).

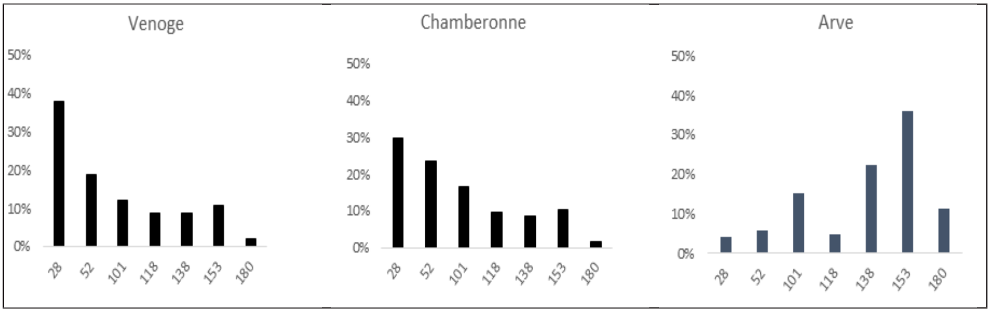

Figure 4: *Loads of the sum of the stdied PCBs (dissolved fraction) at the different studied sites (pg/L) (adapted from Estoppey et al., 2019b).*

UNDERSTANDING THE PROBLEM TO SUPPORT DECISION-MAKING

Analyzing the detected patterns leads to hypothesis generation that often requires alternative information (e.g. knowledge of partners about ‘history’ of the rivers and potential pollution sources or pollutant proprieties affecting their fate in the environment). Based on data provided by environmental agencies, it has been shown that a high number of industries and contaminated sites (landfills/backfills) were present along the rivers with the highest C_W and loads of pollutants. The information about past and present construction/maintenance works as well as remediation processes (occurring near some of these rivers) was provided by partners and also brought to the analysis. In addition, based on literature and information from previous investigations, the extracted ‘chemical signature’ was used to infer on the type of pollution sources which could mainly contribute to the pollution of certain rivers. For example, the signature obtained in the Chamberonne river was dominated by low-chlorinated PCBs and could suggest that the river is affected by releases from wastewater treatment plants or contaminated industrial sites (pollutants washed by rain). Those results are similar to the Venoge river, which also present this atypical signature (Schmid et al., 2010; Estoppey, 2017). The signature obtained in the Arve river on the other hand is dominated by more highly chlorinated PCBs, which could reflect the presence of combustion processes (Van Caneghem et al., 2014).

The resulting intelligence product should then be rapidly communicated to authorities in order to support their decision-making process (Morelato et al., 2014). It can for example help to:

- Prioritize reactive actions to prevent the highest pollutant releases to be continued/repeated. To effectively decrease the risks to which organisms and humans are exposed in rivers of the Lake Geneva basin, authorities should primarily investigate the rivers presenting the highest $C_{W,}$ based on a list of potential sources that can be provided. To reduce the inputs into the lakes, actions should be taken in the tributaries presenting the highest loads.
- Take proactive actions to prevent similar pollution types from being committed. Maintenance and constructions works are suspected to releases some of the studied pollutants into certain rivers. To prevent future pollution during such kinds of works, authorities can request more protective measures from companies. Raising industry awareness to cover potential contaminated sites can prevent pollutants to be washed by rain.

CONCLUSION

The first monitoring campaign described in this paper acts as a proof of concept. Comparable data obtained through the passive sampling-based acquisition process enables trends to be detected by using relevant extracted features. The analysis of those trends provides intelligence that can be rapidly transmitted to authorities to support them in decision-making (e.g. prioritization of reactive actions to prevent pollution to be continued/repeated or possibility to take proactive actions to prevent similar pollution types from being committed). This intelligence process is cyclical and thus subject to continuous development. The critical point is to organize all the acquired knowledge in a structured '*memory*'. Only in this way, newly integrated data can be efficiently compared to former data and allow the detection of new trends. Data provided by future campaigns are for example expected to make the detection of temporal trends which can be linked to natural (e.g. precipitations or temperature) or anthropogenic (e.g. constructions or maintenance works) parameters possible. The cycle-process thus leads to a better understanding of the water pollution problem. In addition, using a '*memory*' helps to improve the different steps of the process. In the acquisition step for example, the deployment strategy in rivers presenting high flow rates or strongly fluctuating water-levels has been improved after the first campaign.

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