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Sampling of suspended particulate matter using particle traps in the Rhône River: Relevance and representativeness for the monitoring of contaminants

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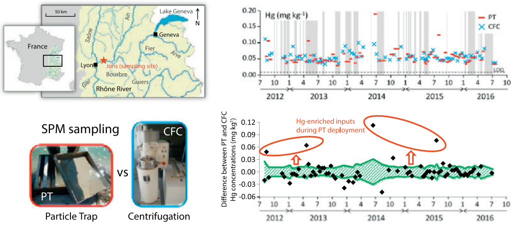
HIGHLIGHTS

- Particle traps (PTs) collect coarser particles than centrifugation (CFC) reference.
- Hg and PCB differences between PT and CFC come mainly from analytical uncertainties.
- PTs allow integrating variable contaminant concentrations during their deployment.
- PTs are a reliable SPM sampling tool to assess contaminant fluxes at annual scale.

GRAPHICAL ABSTRACT



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ABSTRACT

Monitoring hydrophobic contaminants in surface freshwaters requires measuring contaminant concentrations in the particulate fraction (sediment or suspended particulate matter, SPM) of the water column. Particle traps (PTs) have been recently developed to sample SPM as cost-efficient, easy to operate and time-integrative tools. But the representativeness of SPM collected with PTs is not fully understood, notably in terms of grain size distribution and particulate organic carbon (POC) content, which could both skew particulate contaminant concentrations. The aim of this study was to evaluate the representativeness of SPM characteristics (i.e. grain size distribution and POC content) and associated contaminants (i.e. polychlorinated biphenyls, PCBs; mercury, Hg) in samples collected in a large river using PTs for differing hydrological conditions. Samples collected using PTs ($n = 74$) were compared with samples collected during the same time period by continuous flow centrifugation (CFC).

The grain size distribution of PT samples shifted with increasing water discharge: the proportion of very fine silts (2–6 μm) decreased while that of coarse silts (27–74 μm) increased. Regardless of water discharge, POC contents were different likely due to integration by PT of high POC-content phytoplankton blooms or low POC-content flood events. Differences in PCBs and Hg concentrations were usually within the range of analytical uncertainties and could not be related to grain size or POC content shifts. Occasional Hg-enriched inputs may have led to higher Hg concentrations in a few PT samples ($n = 4$) which highlights the time-integrative capacity of the PTs. The differences of annual Hg and PCB fluxes calculated either from PT samples or CFC samples were generally below 20%. Despite some inherent limitations (e.g. grain size distribution bias), our findings suggest that PT sampling is a valuable technique to assess reliable spatial and temporal trends of particulate contaminants such as PCBs and Hg within a river monitoring network.

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1. Introduction

The monitoring of contaminant concentrations and fluxes in surface waters is necessary for assessing and managing environmental pollution in continental hydro-systems. Typical examples of challenging regulations are the European Union Water Framework Directive (WFD) (European Commission, 2000) which aims at achieving the good ecological and chemical status of European water bodies, and the Barcelona Convention (UNEP, 1976) which encourages the contracting parties to evaluate the pollution discharge delivered by watercourses to the Mediterranean Sea. As hydrophobic and lipophilic substances tend to preferentially accumulate in suspended particulate matter (SPM) rather than in the dissolved phase, SPM sampling is recommended as an alternative method to water sampling for the monitoring of these contaminants in rivers (Lepom et al., 2009; Schubert et al., 2012; Schulze et al., 2007). Suspended particulate matter sampling is preferred to bed material sampling as particle deposition is often spatially heterogeneous and includes bed materials.

Various sampling techniques can be used to collect SPM including direct water sampling (manual grab sampling or use of automatic samplers) followed by filtration (Duinker et al., 1979; Mahler and Van Metre, 2003) or settling (Etcheber and Jouanneau, 1980), in-line filtration (Horowitz, 1986), continuous flow centrifugation (CFC; Burrus et al., 1989; Rees et al., 1991; Schäfer and Blanc, 2002) or the deployment of particle traps (PT; Gardner, 1980; Phillips et al., 2000; Pohlert et al., 2011). Under usual SPM concentrations in rivers (1–100 mg L^{-1} typically), direct water sampling requires collecting too huge volumes of water, in order to provide enough material (>2 g dry weight, d.w.) for the analysis of a set of elements and contaminants including major parameters, metals, organic contaminants and radioelements. The deployment of most SPM sampling methods in the field is expensive, difficult, labor intensive and not always adequate. For instance, CFC requires permanent technical attendance for several hours typically, which is difficult and costly to implement to document the spatial and temporal trends of contamination throughout a large river network. Furthermore, SPM sampling frequency (typically 4–6 samples per station and per year) is usually far too low to record the high temporal variability of the hydrological regime with variable SPM sources and contaminant concentrations (Schulze et al., 2007).

To overcome these problems, PTs are an alternative tool to sample SPM, since they are cost-efficient, easy to operate and time-integrative (Phillips et al., 2000; Schulze et al., 2007). A PT can be deployed regardless of SPM concentrations in the river, since the frequency at which the PT is emptied can be adjusted. A monitoring network can thus be spatially and temporally extended using PTs: more stations can be equipped for the same cost. Moreover, integrative-sampling over long periods of time accounts for all flood events, during which the main part of the annual particulate flux is transported. A standardized model of PT (Schulze et al., 2007) is already used to collect SPM samples in rivers as part of the German Environmental Specimen Bank, to support the assessment of long-term trends in contaminant concentrations (Koschorreck et al., 2015). Based on this technique, retrospective studies of metals, arsenic (Fliedner et al., 2014), triclosan, methyl-triclosan residues (Rüdel et al., 2013), polychlorobiphenyls (PCBs), and hexachlorobenzene (Schubert et al., 2012) in SPM of different German rivers have recently been published.

Whereas the representativeness of SPM samples collected by CFC was investigated and validated as early as 25 years ago (e.g. Burrus et al., 1989; Horowitz et al., 1989; Rees et al., 1991), the representativeness of the particles collected with PTs is still questionable and not fully understood. This question is arguably the main obstacle to a wider use of PTs in river pollution monitoring programs. Some studies suggested that SPM sampled by PT may differ from SPM in the river, which was reflected by a modification of SPM parameters such as grain size distribution (particle fractionation effects) or organic carbon content (Allan et al., 2009; Ciffroy et al., 1999; Pohlert et al., 2011; Schubert et al., 2012). This representativeness issue is a serious concern because it could lead to biased concentrations for contaminants (e.g. Laceby et al., 2017) that usually have a strong affinity for fine particles, due to an increasing specific area with decreasing grain size (Duinker, 1986; Olsen et al., 1982; Pierard et al., 1996), or for organic rich particles (Karickhoff et al., 1979; Olsen et al., 1982). Also, Russell et al. (2000) showed that the sediment collected by the PT described by Phillips et al. (2000) provided representative SPM samples of the river in terms of major elements (total carbon and phosphorous) and metals (e.g. Fe, Mn, As, Pb, Zn) concentrations (with respect to the laboratory analytical errors). Pohlert et al. (2011) reported a systematic study that intended to address the representativeness of SPM samples collected with a PT, which unfortunately was also different in size and design (different inlets/outlets, slopped bottom, no baffles) from the German standardized model. Their study relied on SPM samples collected using this PT and two other systems, CFC and an in-situ isokinetic sampler. Their results showed similar PCB concentrations in SPM collected by the three systems, but differences in particle-size, organic carbon and hexachlorobenzene contents were observed. The relative importance of particle segregation and time-integration effects could not be clearly disentangled, since CFC samples are not time-integrative. Moreover, analytical uncertainties of contaminant concentrations were not reported and their potential contributions in the differences observed between sampling techniques were not considered.

Since 2009, within the Rhône Sediment Observatory (OSR) program, PTs designed according to the German PT described by Schulze et al. (2007) have been routinely used for the monitoring of particulate contaminants throughout the Rhône River (from Lake Geneva to the Mediterranean Sea). The objective of this study was to determine the physico-chemical representativeness of SPM samples collected by PT in a large river under various hydrological conditions, i.e. under a wide range of flow velocities and SPM concentrations. To fulfil this objective, we compared physico-chemical characteristics of SPM collected using both PT and CFC (reference sampling method) over a period of four years. The particle fractionation effects were investigated using an original method based on the deconvolution of the grain size distributions. Additionally, POC, PCBs and Hg concentrations were analyzed and analytical uncertainties evaluated, to assess the potential bias in particulate concentrations induced by the sampling method. To allow an efficient comparison of data obtained by integrative (PT) and punctual (CFC) sampling techniques, time-integration effects were considered in this study based on SPM fluxes during PT deployment.

2. Material and methods

2.1. Sampling strategy

The comparison of SPM sampling methods was based on SPM samples collected within the OSR program by both PT ($n = 74$) and CFC ($n = 85$) in the Rhône River at Jons, France (Fig. 1). The location of this sampling station is strategic as it integrates the upper part of the Rhône River watershed (~20,000 km^2) upstream of the Lyon urban area. Grain size distribution or POC content of SPM may differ depending on hydrological conditions (Allan et al., 2009; Ciffroy et al., 1999; Pohlert et al., 2011; Schubert et al., 2012). Therefore, this study covered a long period of time (August 2012–July 2016) characterized by base flow periods (discharge <800 $m^3\ s^{-1}$) and several flood events (discharge >800 $m^3\ s^{-1}$).

Since no hydrometric station exists at Jons, daily discharges at this station were computed using a 1-D hydrodynamical model (Dugué et al., 2015) from the discharge inputs of the Rhône River, the Bourbre River and the Ain River (Fig. 1). At the Jons station, mean daily SPM concentrations were computed from in situ turbidity measurements every 15 min using a Hach Lange SC200 turbidity probe, with turbidity-SPM concentration curves calibrated using frequent water sampling and filtration.