

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

Echantillonnage de matières en suspension à l'aide de pièges à particules dans le Rhône : pertinence et représentativité pour la surveillance des contaminants

Matthieu Masson¹ ; Hélène Angot^{1,3} ; Chloé Le Bescond¹ ; Marina Launay² ; Aymeric Dabrin¹ ; Cécile Miège¹ ; Jérôme Le Coz² and Marina Coquery¹

¹ Irstea, UR MALY, Centre de Lyon-Villeurbanne, 5 rue de la Doua, CS 20244, F-69625, Villeurbanne Cedex, France (corresponding author: matthieu.masson@irstea.fr). ² Irstea, UR HHLY, Centre de Lyon-Villeurbanne, F-69625 Villeurbanne, France. ³ Now at Institute for Data, Systems and Society, Massachusetts Institute of Technology, Cambridge, MA, USA.

RÉSUMÉ

La surveillance des contaminants hydrophobes dans les eaux de surface nécessite la mesure des contaminants dans la fraction particulaire de la colonne d'eau. Des pièges à particules (PàP) ont récemment été développés pour échantillonner les matières en suspension (MES). Ces outils intégratifs ont l'avantage d'être facilement utilisable avec un faible coût. Le but de cette étude est d'évaluer la représentativité des MES et des contaminants associés dans des échantillons collectés à l'aide de PàP dans une grande rivière. 74 échantillons de PàP sont comparés à des échantillons collectés aux mêmes périodes par centrifugation. La granulométrie des échantillons de PàP est plus grossière quand le débit augmente. Les teneurs en carbone organique particulaire (COP) sont différentes principalement à cause de la dégradation de la matière organique et/ou de la production bactérienne à l'intérieur des PàP durant leur déploiement. Les différences de concentrations en polychlorobiphényles et mercure sont plutôt attribuées aux erreurs analytiques et ne sont pas liées aux modifications de la granulométrie ou du COP. Nos résultats montrent que les PàP sont des outils intéressants pour évaluer de façon fiable les tendances temporelles et spatiales des contaminants particuliers dans le cadre de réseaux de surveillance des rivières.

ABSTRACT

Monitoring hydrophobic contaminants in surface freshwaters requires measuring contaminant concentrations in the particulate fraction of the water column. Particle traps (PTs) have been recently developed to sample suspended particulate matter (SPM) as a cost-efficient, easy to operate and time-integrative tool. The aim of this study was to evaluate the representativeness of SPM characteristics and associated contaminants in samples collected in a large river using PTs. 74 samples collected using PTs were compared with samples collected during the same time period by continuous flow centrifugation. The grain size distribution of PT samples was coarser with increasing water discharge. Regardless of water discharge, particulate organic carbon (POC) contents differed likely due to the degradation of organic matter and/or bacterial growth within the PTs during their deployment. Differences in polychlorinated biphenyls and mercury concentrations were usually within the range of analytical uncertainties and could not be related to grain size or POC content shifts. Our findings suggest that PT is a valuable technique to assess reliable spatial and temporal trends of particulate contaminants within a river monitoring network.

KEY WORDS

Continuous flow centrifugation, grain-size distribution, hydrophobic contaminants, particle trap, particulate organic matter

1 CONTEXT AND OBJECTIVE

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. Particle trap (PT) provide a low-cost, practicable and usable technical solution for monitoring of contaminant concentrations and fluxes in surface waters. Since 2009, within the Rhône Sediment Observatory (OSR) program, PTs have been routinely used for the monitoring of particulate contaminants throughout the Rhône River. Whereas the representativeness of SPM samples collected by continuous flow centrifugation (CFC) was investigated and validated as early as 25 years ago, the representativeness of the particles collected with PTs is still questionable and not fully understood (Pohlert et al., 2011).

The objective of this study was to determine the physico-chemical representativeness of SPM samples collected by PT in a large river under a wide range of flow velocities and SPM concentrations. To fulfil this objective, we compared physico-chemical characteristics (grain size distribution, particulate organic carbon [POC], polychlorinated biphenyls [PCBs] and mercury [Hg]) of SPM collected in the Rhône River using both PT and CFC (reference sampling method) over a period of four years.

2 METHODS

The PTs used in this study and in the OSR monitoring network consist of a high quality (type 316 L) stainless steel box with three holes on the front and back faces allowing water circulation inside (Fig. 1) (Schulze et al., 2007). Two baffles induce a decrease of the current velocity within the PT, firstly by overflow and secondly by underflow, allowing the decantation of the SPM into two sedimentation basins.

The comparison of SPM sampling methods is 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 (Upper Rhône River watershed, upstream of Lyon urban area). The evaluation of the representativeness of SPM collected by PTs was performed by the comparison of the grain size distribution and POC, PCBs and Hg concentrations, with those measured on SPM collected by CFC (reference samples). The relevance and representativeness of SPM collected in rivers with PT were studied with consideration of i) the integrative effect of PT compared to CFC, the latter being assimilated to spot sampling, and ii) the chemical analytical uncertainties.

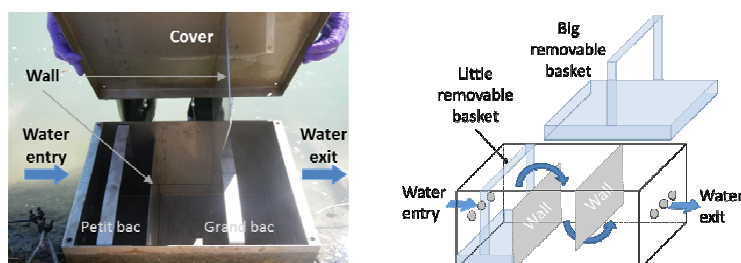


Figure 1: Photo and schematic drawing of the PTs used in this study and in the OSR monitoring network

3 RESULTS AND DISCUSSION

The SPM sampled in the Rhône River at the Jons station consisted of a mixture of three classes of particles: very fine silts, medium silts and very coarse silts. The grain size distribution was coarser in PT than in CFC samples. A strong negative relationship was observed between the relative grain size error (i.e. the difference in the proportion of the two finest classes of particles between a PT sample and the two CFC samples collected at the installation and recovery of the PT) and the mean discharge during PT deployment periods (Fig. 2a). It is unclear whether the PT induced a loss of finest particles and/or a gain of coarsest particles. However, the present study clearly shows that all particles sizes were captured by PT, including the smallest ones: the properties of the sub-populations were conserved but their proportions may differ as a function of flow velocity.

The relative errors (from -52% to +42%) of POC concentrations in PT samples vs. CFC cannot be attributed to either hydrological conditions (water discharge and SPM concentrations) or differences in grain size distribution. In reality, alternating episodes with positive (i.e. over-estimation of POC by the PT) and negative (i.e. under-estimation of POC by the PT) errors can be observed (Fig. 2b). A shift of POC concentration in PT due to production and/or degradation of organic matter is strongly

suspected. Consequently, we suggest that, whenever possible, long duration of PT deployment (longer than to 2 weeks) must be avoided, especially when POC concentration is high (typically $>30 \text{ kg}^{-1}$), i.e. when organic matter may be considered as rapidly biodegradable.

The relative errors (between -52% to +42%, typically) of Hg concentrations in PT samples vs. CFC were acceptable. An increase in grain size or a POC shift did not influence Hg concentration in PT samples. In fact, analytical uncertainties could mainly explain the differences of Hg concentrations measured in the PT and CFC samples (Fig. 2c). The highest relative Hg errors were observed during flood periods and were related to the highest Hg concentrations measured in PT samples. This result was explained by the transitory contribution of a Hg-enriched tributary during the PT deployment period.

Only 4 out of the 7 indicator PCBs (congeners 101, 138, 153 and 180) were quantified in more than 50% of the PT and CFC samples. These congeners showed a similar behavior: an increase in grain size or a POC shift did not influence their concentration in PT samples. The relative errors of PCB concentrations (typically from -45% to +60%) were acceptable. For the vast majority (89%) of samples, the relative error was in the range of analytical uncertainties (Fig. 2d). Outliers, mainly observed during flood periods, were attributed to the time integration effect of PT.

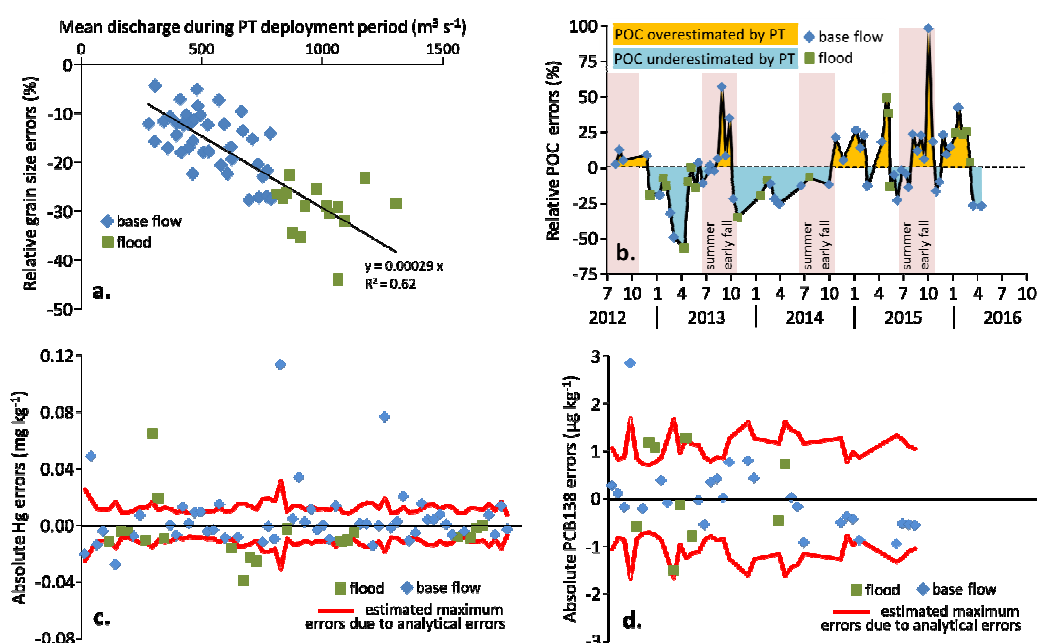


Figure 2: a) Relative fine particle contribution errors vs. mean discharge during PT deployment period; b) Relative POC errors vs. time; c) and d) Comparison of absolute Hg and PCB138 concentration errors, respectively, with analytical errors (data are ordered by sampling date).

4 CONCLUSIONS

Despite the grain size distribution bias towards coarser particles and/or potential organic matter production/degradation, PTs can be considered as a reliable tool for SPM sampling with the aim of Hg and PCBs monitoring. The concentrations of pollutants other than those studied in this work, such as metals or polycyclic aromatic hydrocarbons, should be similar, with respect to analytical uncertainties, whether they are measured in SPM collected by PT or by CFC. Furthermore, this study highlights the main advantage of the SPM sampling by PTs: samples are time integrative and are thus representative of the SPM and associated pollutants transported in the river during periods of time with varying hydrologic conditions.

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