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

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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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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

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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.

Keywords: hydrophobic contaminants, continuous flow centrifugation, grain size distribution, particulate organic matter, particle trap, Rhône River

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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

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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, Russel et al. (2000) showed that the sediment collected by the PT described by Phillips et

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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.

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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 (~20000 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.

The duration of the PT deployments in the river was 2 weeks generally, in order to collect a sufficient amount of SPM for physico-chemical analysis (> 2 g d.w.). To compare SPM collected by PT with those collected by CFC (reference sampling method), each deployment of PT was systematically bordered with two SPM samplings by CFC carried out during the PT installation and recovery days. The recovery of a trap is normally followed by the re-installation of the emptied trap; the sampling of SPM by centrifugation is systematically carried out just beforehand.

2.2 SPM recovery and treatment

The PTs used in this study and in the OSR monitoring network were built identical to PTs described in Schulze et al. (2007). They consist of a high quality (type 316 L) stainless steel box with

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three holes on the front and back faces allowing water circulation inside (Fig. 2). Two baffles induce a decrease of the current velocity within the PT, firstly by overflow and secondly by underflow, allowing the decantation of SPM into two sedimentation tanks. At the Jons station, the PT was immersed on the river bank at ~4-5 m above the bottom at a cross-section with well-mixed suspension, with fairly homogeneous SPM concentrations (Launay, 2014). Particles trapped in the two tanks were collected and mixed together in the largest tank using a clean Teflon spatula, then conditioned in an amber glass bottle (for chemical analysis) and in a polypropylene (PP) tube (for grain size determination).

Sampling using CFC was achieved with a stationary CEPA Z61 high speed centrifuge or a mobile Westfalia KA-2 centrifuge. Water was directly pumped from the Rhône River (50-100 cm below the water surface) to the centrifuge with a flow of ~700-800 L h^{-1}. The end of the pumping pipe was installed approximately 5 m downstream of the PT in order to avoid issues related to the possible non-homogeneity of SPM throughout the river cross-section. During base flow periods, approximatively 3000 L of river water were sampled, while during floods, lower water volumes were adjusted (depending on the turbidity) in order to collect more than 2 g (d.w.) of particles. After centrifugation, particles deposited on a Teflon sheet (for the stationary CFC) or in a Teflonated bowl (for the mobile CFC) were collected for the same analyses as the PT samples.

Suspended particulate matter collected in the glass bottles were deep-frozen and freeze-dried as soon as brought to the laboratory. The freeze-dried samples were grinded and homogenized with an agate ball mill (PM200, Retsch), then stored in the dark in dry atmosphere until chemical analysis. Suspended particulate matters collected in PP tubes were stored at 4°C in the dark until grain size distribution analysis.

2.3 Analytical methods

Volumetric grain size distribution of SPM was assessed by laser diffraction using a Cilas 1190 particle size analyzer according to the ISO 13320 standard method (AFNOR, 2009). A representative

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wet sub-sample was introduced into the analyzer respecting good obscuration rate (typically 15%). The volumetric grain size distribution of the sample was computed using the Fraunhofer optical model (AFNOR, 2009).

The determination of POC in SPM samples collected before December 2014 was performed using a carbon analyzer (Thermo Electron, CHN Flash 2000) by INRA laboratory (Arras, France). Decarbonation was completed using hydrochloric acid according to the NF ISO 10694 standard method (AFNOR, 1995). The limit of quantification (LOQ) was estimated to be 0.05 g kg^{-1} and analytical uncertainty varied between ~3% and ~6% (k=2), depending on the POC concentration. For samples collected after December 2014, POC analyses were conducted by Irstea laboratory using a similar carbon analyzer (Thermo Electron, CN Flash 2000) and a method adapted from the NF ISO 10694 standard method (AFNOR, 1995) and manufacturer recommendation. The LOQ was estimated to be 0.5 g kg^{-1}. A reference material from a proficiency interlaboratory testing (Aglae, 15M9.1; 40 g kg^{-1}) was systematically used to control analytical accuracy (93%) and uncertainty (8%; k=2).

The determination of total Hg in SPM was performed using an automated atomic absorption spectrophotometer, DMA 80 (Milestone), according to EPA method 7473 (EPA, 2007). The LOQ of Hg in SPM was 10 µg kg^{-1}. Blanks and certified reference materials (IAEA 433, marine sediment; LGC 6187, river sediment) were systematically used to control analytical accuracy (94%) and uncertainty (14%; k=2).

The contents of the so-called indicator PCBs (congeners 28, 52, 101, 118, 138, 153, and 180) were analyzed in SPM according to the French Standard XP X33-012 (AFNOR, 2000). Approximately 1.0 g (d.w.) of sample was extracted with a cyclohexane/acetone 90:10 v/v mixture, concentrated by evaporation and purified on a 1 g Florisil SPE cartridge. A small amount of copper powder was finally added in order to avoid sulfur interferences prior to gas chromatography analysis with a 63Ni electron capture detector (GC-ECD). Samples were analyzed on two different columns (RTX®-5, 30 m x 0.25 mm x 0.25 µm and RTX®-PCB, 30 m x 0.25 mm x 0.25 µm) to confirm the results. The accuracy of measurements was checked via intercomparison exercises and the analysis of a

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reference material (BCR 536). A sample of sediment from the Bourbre River, a tributary of the Rhône River, was used to determine analytical uncertainties, as no certified reference material exists for such low levels of PCBs in equivalent matrix. The LOQs were estimated between 0.5 and 2.5 µg kg-1 depending on the current analytical conditions (e.g. condition of the radioactive beta particle emitter) and on the congeners. Analytical uncertainties were estimated to be 60% (k=2) for concentrations lower than 3-times the LOQ and to be 30% (k=2) for concentrations higher than 3-times the LOQ.

2.4 Data treatment and statistical analysis

2.4.1 Grain size distribution

The grain size distribution of SPM collected in the Rhône River is multimodal, as is the case in most rivers of this size (Launay, 2014). As a consequence, the traditional summary of grain size distribution by some percentile diameters (e.g., d50, d10, d90) may not be representative of the dominant particle populations in the samples. The particle size distribution of a homogeneous population of SPM is generally regarded as a lognormal distribution due to the sorting process applied to the particles during their transport in the stream (e.g. Blott and Pye 2001). The mixture of different homogeneous sub-populations is expected to yield a mixture of Gaussian distributions for the logarithms of diameters, which can be identified in measured grain size distributions using a calibration procedure (Launay, 2014). The normalmixEM function included in the R Package Mixtools (Benaglia et al., 2009) was applied to identify the parameters of the mixture of normally distributed populations. The calculation is done iteratively by the method of maximum likelihood with the Expectation Maximization algorithm suggested by Dempster et al. (1977). The user provides the population to be studied and the number of Gaussian distributions to be identified in the combined probability density function. For the studied SPM samples, between 2 and 4 (3 in most cases) gaussian laws were generally observed. The normalmixEM function returns i) the mode (µ; in µm), ii) the standard deviation (σ; in µm), and iii) the proportion (λ; in %), of each fitted Gaussian distribution

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(Fig. 3). A Gaussian distribution was discarded as spurious in case any of the following conditions was not met: μ<1 μm, σ>0.5 μm or λ<1%.

2.4.2 Statistical tests

Statistical tests were used for data comparison and correlation determination. For each test, a preliminary study of the data was performed to determine whether the data sets were normally distributed (using Shapiro-Wilk test) with equal variances. As all the data sets tested do not meet these conditions, non-parametric tests were used: Wilcoxon test (two-tailed) for the comparison of mean values and Kendall test for correlation determination. A summary of each statistical test (conditions and results) is presented in Table 1 with conclusions given on the basis of a significance level of 0.05.

2.4.2 Temporal comparison of PT and CFC sampling

The evaluation of the representativeness of SPM collected by PT was performed by the comparison of the physico-chemical parameters (grain size distribution, POC) and contaminants (Hg, PCBs) with those measured on SPM collected by CFC (reference samples). To allow an accurate comparison of the concentrations measured in SPM collected by an integrative sampler (PT) and by punctual sampling (CFC), and thus reduce the time-integration effects, a mean concentration of each parameter i ($C_{ref,i}$) was calculated from the two CFC samples bordering a PT period (i.e. the corresponding reference samples). To take into account the variation of SPM concentration during the PT deployment, $C_{ref,i}$ was calculated as the mean concentration of the parameter i measured in the two CFC samples ($C_{start,i}$ at the installation and $C_{end,i}$ at the recovery of the PT) weighted by the SPM masses (m_1 and m_2) transported at the sampling site during each half-period of PT deployment:

$$C_{ref,i} = \frac{m_1 \times C_{start,i} + m_2 \times C_{end,i}}{m_1 + m_2} \quad (1)$$

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The SPM masses m_1 and m_2 were computed from hourly discharges and hourly SPM concentrations during each half-period of PT deployment. The relative error (in %) was calculated to compare the concentration of a parameter i obtained after PT sampling ($C_{PT,i}$) with its reference concentration ($C_{ref,i}$) :

$$relative\ i\ error = \frac{C_{PT,i} - C_{ref,i}}{C_{ref,i}} \quad (2)$$

A statistical approach was used to determine any significant difference among the concentrations of physico-chemical parameters in SPM sampled by PT and CFC. For each parameter, the difference between $C_{PT,i}$ and $C_{ref,i}$ was compared with the analytical uncertainty expressed as one standard deviation (which corresponds to the 68% confidence interval for a Gaussian distribution), respectively $s_{PT,i}$ and $s_{ref,i}$ (estimated using error propagation approach from Eq. 1 and taking a precision on the estimation of SPM fluxes estimated to be 20%; Launay, 2014). In this way, the difference of concentrations measured between SPM sampled by PT and CFC may be included in the analytical uncertainties if the following equation is verified:

$$\left|C_{PT,i} - C_{ref,i}\right| \leq 1.96\sqrt{s_{PT,i}^2 + s_{ref,i}^2} \quad (3)$$

Therefore, this approach includes both the analytical uncertainties and time integration effect of PT.

2.4.3 Estimation of contaminant fluxes

Mercury and PCB 138 fluxes were estimated at the annual scale using mean hourly discharges and mean hourly SPM concentrations in order to estimate hourly SPM fluxes. In case of SPM concentration gaps, hourly SPM concentrations were estimated from a robust relationship between discharge and SPM concentrations obtained at the Jons station (Poulier et al., submitted to this issue). Hourly contaminant fluxes were calculated by multiplying hourly SPM fluxes by hourly contaminant concentrations estimated either from PT samples (the Hg or PCB concentration

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measured in a PT sample was applied throughout the deployment period at the hourly scale) or from CFC samples (the Hg or PCB concentration measured in a CFC were applied on both sides of the two half periods of PT deployments). In case of Hg or PCB concentration gaps, contaminant concentrations were set depending on hydrological conditions (base flow or flood periods) (Poulier et al., submitted to this issue). All PCB concentrations below the LOQ were replaced by the LOQ value. Hourly contaminant fluxes were finally summed up over the period of interest.

3. Results

3.1 Water discharge and SPM concentrations

During the studied period (August 2012 to July 2016), the daily water discharge varied from 181 to 2147 $m^3 s^{-1}$ (Fig. 4a). Generally, wet seasons with several floods occurred during late fall, winter and spring (November-April), and a dry period was observed during summer and early fall (August-October). In contrast, the discharge remained exceptionally low from May 2015 to December 2016 with only one short flood event, and important flood events were recorded during summer 2014. Suspended particulate matter concentration was highly variable, ranging from <2 mg L^{-1} (i.e. <LOQ) to 668 mg L^{-1} (Fig. 4b), in relation with the discharge variations. The comparison of SPM concentration during the different periods (i.e. PT deployment period and the two days of CFC sampling) was achieved through the discharge-weighted average SPM concentration (SPM_{wa}), i.e. calculated as the ratio of the SPM flux to the water flux estimated during the corresponding periods (deployment period for PT and the day of the CFC was achieved). The SPM_{wa} concentration varied from <2 mg L^{-1} to 285 mg L^{-1} during PT deployment periods (S.I.1) and from <2 mg L^{-1} to 500 mg L^{-1} for SPM sampling by CFC (S.I.2).

3.2 Grain size distribution

The grain size distribution of SPM collected by PT ranged from ~0.1 to 400 µm (e.g. Fig. 3a) and was composed of three sub-populations of particles (i.e. three Gaussian modes were observed;

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Fig. 5). For SPM collected by CFC, the grain size distribution ranged from ~0.1 to 112 μm (Fig. 3b). Three modes were also observed in two-thirds of the samples but only two modes were observed in the remaining samples (Fig. 5). All these modes may be classified in three classes (Fig. 5), corresponding to very fine silts for the finest mode (median diameters, μ_1, ranging from 2.0 to 6.0 μm), medium silts for the intermediate mode (median diameters, μ_2, ranging from 9.4 to 20.7 μm) and very coarse silts for the coarser mode (median diameters, μ_3, ranging from 27.3 to 74.1 μm), according to the classification of Friedman and Sanders (1978). While the mean proportions of the medium silts (λ_2) were similar for SPM collected by PT (55 ± 9%) and CFC (52 ± 12%) (Wilcoxon test #1, Table 1), significant differences were observed for the finest (λ_1) and coarsest (λ_3) modes (Wilcoxon test #2 and #3, Table 1): on average, the PT samples contained -20% of very fine silts and +16% of very coarse silts than those collected by CFC (Fig. 5). Additionally, the mean diameters of the 2nd and 3rd modes (μ_2 and μ_3) were coarser for the PT samples (16.4 μm and 48.6 μm, respectively) than for the CFC samples (12.7 μm and 35.2 μm, respectively). These results, and the absence of the 3rd mode in one third of SPM samples collected by CFC, demonstrate that SPM sampled by the PT were clearly coarser than those sampled by the CFC.

To simplify the description of the grain size distributions, proportions obtained for the finest two modes were added (λ1 + λ2). These proportions varied between 53% and 97% for the PT samples and between 78% and 100% for the CFC samples (Fig. 4c, S.I.3) with mean values significantly different (Wilcoxon test #4, Table 1). The proportions of fine particles were clearly lower for the PT samples than for the CFC samples as suggested by the box plots (Fig. 4c).

3.3 Chemical composition

Particulate organic carbon concentrations measured in SPM collected by the PT varied between 14 and 50 g kg^{-1} and those measured in the CFC samples varied between 12 and 70 g kg^{-1} (Fig. 4d; S.I.3). The mean POC concentrations measured in PT (26 g kg^{-1}) and CFC samples (29 g kg^{-1}) were not significantly different (Wilcoxon test #5, Table 1) as shown by the box plots. These concentrations are

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well within the range of values observed in the downstream part of the Rhône River: 30-60 g kg^{-1} (Cauwet et al., 1990) and 8-27 g kg^{-1} (Cathalot et al., 2013).

Mercury concentrations measured in SPM collected by PT and CFC varied from 0.029 to 0.190 mg kg^{-1} and from 0.034 to 0.112 mg kg^{-1}, respectively (Fig. 4e; S.I.3). Mean Hg concentrations measured in PT (0.056 ± 0.023 mg kg^{-1}) and CFC samples (0.057 ± 0.015 mg kg^{-1}) were not significantly different (Wilcoxon test #6, Table 1) as shown by the box plots. Except for one PT sample, these values were below the threshold effect concentration (TEC; 0.18 mg kg^{-1}) that should not be exceeded to avoid negative effects on aquatic wildlife (MacDonald et al., 2000). Mean Hg concentrations were close to the average Hg concentration observed in the upper continental crust (i.e. 0.056 mg kg^{-1}; Wedepohl, 1995).

The concentrations of PCBs were measured in 80% of the collected samples (S.I.4 and 5). Concentrations of PCB 28 and PCB 52 measured in SPM collected by PT and CFC were almost always below the LOQ (less than 5% of quantified values; S.I.3). The congener 118 was quantified in 30% and 37% of samples collected by PT and CFC, respectively. The percentages of quantified values for the four other congeners (101, 138, 153 and 180) were higher and varied from 69% to 88% (S.I.3). The minimum PCB concentration measured in SPM was <0.5 µg kg^{-1} (lowest LOQ) for all congeners (S.I.3). The maximum PCB concentration measured in SPM was higher for the four PCB congeners with the highest quantification frequency (congeners 101, 138, 153 and 180; between 3.14 and 5.16 µg kg^{-1}) than for the others (congeners 28, 52 and 118; between 0.54 and 2.13 µg kg^{-1}). The sum of the seven indicator PCBs (for values lower than the LOQs, concentrations equal to the LOQs were used) ranged between 4.0 and 18.2 µg kg^{-1} and did not exceed the TEC value (59.8 µg kg^{-1}; MacDonald et al., 2000). These concentrations are similar to those measured in sediments of the Rhône River sampled upstream of the Lyon agglomeration from mid-1990s to 2010 which are still considered as contaminated, despite a decrease in concentrations since 1980s (Desmet et al., 2012). Strong correlations were found between the four PCB congeners (data below LOQ were excluded) with the highest quantification frequency, i.e. PCB 101, PCB 138, PCB 153 and PCB 180 (Kendall test #7,

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Table 1; Table 2). This suggests that these 4 congeners have a similar behavior in SPM, even if the concentrations of PCB 101 and 180 are lower than those of PCB 138 and 153 (S.I.3). For this reason, we decided to simplify the study by focusing on PCB 138 thereafter, as this congener was well quantified in SPM and has one of the best correlation factors with the other congeners. The mean PCB 138 concentrations measured in CFC (1.95 ± 0.78 µg kg^{-1}) and PT samples (2.31 ± 0.79 µg kg^{-1}) were not significantly different (Wilcoxon test #8, Table 1) as suggested by the box plots (Fig. 4f) and similar median values (less than 5% difference; S.I.3).

4. Discussion

4.1 Representativeness of the grain size distribution of SPM sampled by PT

The grain size distributions of SPM collected by CFC during base flow and flood periods were similar (Fig. 5) as confirmed by statistical tests (Wilcoxon test #9, Table 1) carried out on the coarser particle class proportions (λ3). For SPM collected by PT, very coarse silts prevailed during flood periods (Wilcoxon test #10, Table 1) with a mean proportion of 34% vs. 19% during base flow periods. Consequently, the differences between SPM sampled by PT and CFC seem to be amplified during flood periods. The relative error of fine particle proportion (λ1 + λ2) in PT samples (vs. CFC) varied between -4% and -44% (S.I.1) with mean values significantly different (Wilcoxon test #11, Table 1) between base flow periods (-15%) and flood periods (-29%). Moreover, a strong negative relationship was observed between the relative fine particle proportion (λ1 + λ2) error (see Eq. 2) and the mean discharge during PT deployment periods (Fig. 6). Thus, the grain size distribution of SPM sampled by PT was highly dependent on hydrological conditions. This phenomenon has already been reported by Phillips et al. 2000 who showed that SPM trapped in the Phillips PT became significantly coarser than SPM of the water flow when the current velocity reached 0.6 $m.s^{-1}$. It is however unclear whether the PT induced a loss of finest particles and/or a gain of coarsest particles. The potential loss of finest particles by PT has already been reported in several studies (Phillips et al., 2000; Pohlert et al., 2011; Schubert et al., 2012). Schäfer and Blanc (2002) also suggested that an

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increase of flow energy induced a decrease of the trapping efficiency for fine particles that do not enter in the PT. 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; however their proportions may differ as a function of flow velocity. A better understanding of how this PT works should be provided by future hydraulic flume experiments based on protocols reported by Phillips et al. (2000) or Smith and Owens (2014), for example.

4.2 Representativeness of the chemical composition of SPM sampled by PT

4.2.1 Organic Matter

Particulate organic carbon concentration decreased with increasing SPM_{wa} concentration (Fig. 7a) to reach values between 10 and 20 g kg^{-1} (Kendall test #12, Table 1). Similar trends are generally observed in surface waters (e.g. Paolini, 1995; Veyssy et al., 1998) and may be explained by a dilution of autochthonous particulate organic matter (e.g. phytoplankton) by less-enriched organic land-derived material during flood periods (Meybeck, 1982). This is supported by the range of total organic concentrations (4 and 8 g kg^{-1}) measured in the subsoil of the region of interest (Salminen et al., 2005).

The relative error of POC concentrations in PT samples (vs. CFC) varied between -56% and +57%, except one outlier reaching +98% during base flow. No correlation was observed between relative POC error and SPM_{wa} concentration (Fig. 7b), which suggests that the origin (i.e. autochthonous or land-derived material) of particulate organic matter does not explain the differences in POC concentrations measured in SPM sampled by PT and CFC. Furthermore, no correlation was observed between relative POC error and the relative fine particle proportion (λ1 + λ2) error (Fig. 7c). The general coarsening of grain size distribution of SPM sampled by PT is unlikely to influence POC concentration directly. Therefore, POC was probably distributed evenly among the three main classes of particles composing the grain size distribution of SPM sampled in the Rhône River at the Jons station. This hypothesis is reinforced by the results of an experiment in which similar POC

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concentrations were measured in sub-fractions of SPM samples fractionated as a function of particle size (granulometric sorting according to gravity; Launay, 2014). Moreover, excluding the most extreme value (98%), relative POC errors were normally distributed around 2% (Shapiro–Wilk test #13, Table 1). The presented results do not support the hypothesis of a loss of fine-particulate matter and light organic material with the overflow as proposed by Schubert et al. (2012).

Alternatively, the degradation of rapidly biodegradable organic matter in the PT during the sampling period could influence SPM quality (Schubert et al., 2012). Figure 7d shows the relative POC error as a function of time: 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. From July 2012 to June 2014, positive POC errors were observed during summer and early fall, while negative values were observed during winter and spring (Fig. 7d). This trend was not clearly observed thereafter. Variations of relative POC errors may be due to a balance between two processes inside the PT: (i) degradation of the organic matter trapped during the PT deployment period (Pohlert et al., 2011), and (ii) production of organic matter such as bacterial growth. However, the fact that seasonal variations were not systematically observed along years suggests that other phenomena should contribute to the differences of POC concentrations between PT and CFC samples. In particular, PT may integrate variations of organic matter quality such as phytoplankton blooms characterized by an increase of POC concentrations, or flood events characterized by a decrease of POC concentrations as mentioned above.

4.2.2 Particulate mercury

Mercury concentration increased with POC concentration in SPM samples collected by PT and CFC (Fig. 8a; Kendall test #14, Table 1). This trend is due to the well-known strong affinity of Hg for organic matter (e.g. Mason and Sullivan, 1998). Hence, Hg is also affected by the dilution of POC by less-enriched organic land-derived material during flood periods. This is supported by the decrease of Hg concentration with increasing SPM concentration (Fig. 8b). The mean Hg concentrations (S.I.3) of

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the PT and CFC samples during flood periods, i.e. 0.047 and 0.051 mg kg^{-1}, respectively, were significantly different (Wilcoxon test #15 and #16, Table 1) from the mean concentrations measured during base flow periods, i.e. 0.056 and 0.057 mg kg^{-1}, respectively. During flood periods and for SPM_{wa} concentrations above 100 mg L^{-1}, Hg concentrations of PT and CFC samples (n=10) tend toward 0.03-0.05 mg kg^{-1} (Fig. 8b); these concentrations correspond to the Hg geochemical background level estimated between 0.03 and 0.04 mg kg^{-1} from soil samples in this region (Salminen et al., 2005). This suggests that SPM carried during the flood periods at the Jons station were not Hg-enriched. In contrast, increases of particulate Hg concentrations were measured during floods in the Lower Rhône at the Arles station (in November 2008). This could be attributed to Cevenol Rivers that drain Hg rich-areas (Launay, 2014).

The relative error of Hg concentration in PT samples (vs. CFC) varied from -52% to +42% (Fig. 8c), except for five values between +69% and +154% that correspond to PT samples with the highest Hg concentrations. No correlation was observed between the relative Hg and POC errors (Fig. 8c) despite the correlation observed between COP and Hg concentrations. This suggests that the potential changes in POC concentration inside the PT did not directly affect Hg concentration. Bias-correction attempts of Hg concentration measured in the PT by relative POC error were unsuccessful as they did not allow the reduction of the relative Hg errors. Other hypotheses may explain differences between Hg concentration measured in SPM sampled by PT and CFC:

(1) Variation of grain size distribution: coarse particles generally support lower levels of metals and organic contaminants (e.g. Klamer et al., 1990). However, the variations in grain size distributions, which are coarser for the PT samples than for the CFC samples, especially during flood periods, do not seem to contribute to the relative Hg errors (Fig. 8d). Again, bias-correction attempts of the Hg concentrations measured in the PT by grain size distribution (for example by the finest particle proportion errors) were unsuccessful.

(2) Time-integration effects of the PT may be important if Hg concentration of SPM changes over time. This for instance occurred between April, 23rd and May,6th 2013: a flood was recorded on the

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Bourbre River on April, 27th. The Bourbre River is known to have high Hg concentrations in SPM, generally exceeding 0.100 mg kg^{-1} (Thollet et al., 2015). This flood event is the reason why Hg concentration measured in SPM sampled at the Jons station using PT (0.107 mg kg^{-1}) was higher than Hg concentration measured in the two corresponding CFC samples (0.042 and 0.044 mg kg^{-1}; Fig. 4e). In the same vein, a substantial contribution of the Bourbre River to the SPM flux at the Jons station from the 14th to 28th of August 2012 (Dabrin et al., submitted to this issue) may explain the high Hg concentration measured in the PT sample at Jons (0.107 mg kg^{-1}) and the high relative Hg error of 82%.

(3) The analytical uncertainties may be another explanation as they are 2-4 times greater for Hg analysis (14%) than for POC analysis (3-8%). Larger analytical uncertainties may add noise to the relative Hg errors and may explain the absence of correlation between relative Hg errors and POC errors. It is therefore critical to account for analytical uncertainties when comparing Hg concentrations between PT and CFC samples (see section 4.3)

4.2.2 PCB 138

Unlike Hg concentration, no clear correlation was observed between PCB 138 and POC concentrations (Fig. 8f). This suggests that particulate organic matter was not the main carrier phase of PCB 138 in the Upper Rhône River. During periods with the highest SPM_{wa} concentrations (typically >100 mg L^{-1}), PCB 138 concentrations tend towards low values (0.67-1.35 µg kg^{-1}; Fig. 8g) as observed for Hg. This may indicate that resuspension of bed and bank materials by floods induced input of less contaminated sediments. Moreover, the main sources of PCBs to the Rhône River are reported to be located downstream of the sampling station, in Lyon urban area and some tributaries of the Lower Rhône River (Mourier et al., 2014).

The relative error of PCB 138 concentration in PT samples (vs. CFC) was estimated only if the concentrations measured in the PT and the two corresponding CFC samples were above the LOQ (50% of the situations; n=35). The relative PCB 138 error varied from -45% to +60% (Fig. 8h), except

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for three PT samples (between +123% and +161%) which were sampled during a limited period, from November 2012 to February 2013. These 3 samples were different from the 5 PT samples with the highest Hg error values, suggesting that potential Hg and PCB sources are different. The relative PCB 138 errors were related neither to relative POC errors (Fig. 8h) nor to fine particle proportion errors (Fig. 8i).

4.3 Accounting for analytical uncertainties in the comparison

In this study, the concentrations of contaminants measured in SPM sampled by PT and CFC were compared with consideration of analytical uncertainties, which had not been the case in most other studies (e.g. Pohlert et al., 2011; Shubert et al., 2012). Russel el al. (2000) indicated than the differences of metals (such as As, Pb, Zn) concentrations between SPM samples collected by PT (Philipps device) and manually were generally below analytical uncertainties. The comparison of absolute contaminant concentrations with their analytical uncertainties (see Eq. 3) allowed determining if there was any significant difference among the concentrations of contaminants in SPM sampled by PT and CFC. For Hg, 51 pairs of samples (PT and CFC) out of 70 in total (i.e. 73%) had Hg concentrations that were not significantly different with respect to the analytical uncertainties (Fig. 8e). This proportion was higher during base flow periods (80%) than during flood periods (53%). For PCB 138, 31 pairs of out of 35 (i.e. 89%) had PCB concentrations that were not significantly different with respect to the analytical uncertainties (Fig. 8j). This proportion was greater than those observed for Hg and may be partly explained by a higher analytical uncertainty for PCB 138 (30-60% depending on the concentration; k=2) than Hg (14%; k=2). As for Hg, the proportion of sample pairs for which the difference in PCB 138 concentration can be explained by the analytical uncertainties was higher during base flow periods (96%) than during flood periods (67%).

During base flow periods, most of Hg and PCB 138 concentrations measured in PT samples are comparable with those measured in CFC samples when analytical uncertainties are taken into account. However, some differences, not fully attributable to analytical uncertainties, were observed

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mostly during flood periods. Moreover, we observed the absence of correlation between relative contaminant (Hg or PCB 138) errors and SPM characteristics (POC or fine particle proportion) errors. These results suggest that the differences in Hg and PCB 138 (and other PCB congeners, by extension) between PT and CFC samples concentrations are due to integrative effect of the PT. In other words, the differences of contaminants observed between PT and CFC samples are attributed to: i) analytical uncertainties (whose effect was estimated), ii) differences in terms of grain size and POC contents (whose effects seemed negligible), and iii) the integrative capacity of the PT (whose effects were demonstrated during specific hydrological events). This emphasizes the capacity of SPM sampling by PT to integrate the whole peak of Hg and PCB concentrations, which may be limited in duration and thus easily missed by punctual sampling by CFC.

4.4 Relevance of PT sampling to assess annual SPM and contaminant fluxes

One of the main objectives of OSR program is the estimation of annual contaminant fluxes transported with SPM along the river. Annual Hg and PCB 138 fluxes at Jons station were estimated from Hg and PCB 138 concentrations measured in either PT or CFC samples for 2013, 2014 and 2015 (Table 3). Annual Hg fluxes varied between 25.8 and 38.5 kg y^{-1} for PT data and between 30.2 and 42.5 kg y^{-1} for CFC data. Annual PCB 138 fluxes varied between 1.25 and 2.16 kg y^{-1} for PT data and between 0.94 and 1.79 kg y^{-1} for CFC data. The differences of annual Hg and PCB 138 fluxes estimated using PT or CFC data were below 20% (Table 3), except for PCB 138 fluxes in 2015 where the difference reached 48% (mainly due to PCB 138 concentrations below the LOQ measured in three CFC samples during flood periods in April and May, while concentrations measured in the PT samples were close to 3 µg kg^{-1}; Fig. 4f). Again, this result highlights the advantage of the integrative capacity of PTs for the monitoring of contaminants in SPM.

Mercury and PCB fluxes were also estimated for two distinct periods of about 7 to 8 months (periods chosen to avoid as many gaps as possible) with contrasted hydrological regimes: the first period (from 9th April to 22th October 2013) is characterized by 3 flood events; the second period

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(from 7th May to 22th December 2015) may be described as a dry period with low discharge. For these two periods, the differences of Hg and PCB fluxes estimated from PT and CFC data were below 20% (between 3% and 18%; Table 3).

These results demonstrate that cumulated contaminant fluxes estimated from either PT or CFC samples are similar at the annual scale. This is due to i) the good agreement between Hg/PCB 138 concentrations measured in SPM sampled by PT and CFC, with relative Hg and PCB 138 errors generally centered around the null value, and especially to ii) the low range of variation of contaminant concentrations compared to that of discharge and SPM concentrations (Fig. 4a, e and f). Therefore, we conclude that PT can be considered as a reliable SPM sampling technique for the long-term monitoring of Hg and PCB cumulated fluxes in rivers at the annual or multi-month scale. In fact, annual budgets of SPM and associated contaminants (Hg and PCBs) in the Rhône River have recently been estimated using contaminant concentrations measured in PT samples (Poulier et al., submitted to this issue).

5. Conclusion

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 punctual sampling, and ii) the analytical uncertainties. The comparison of physical and chemical characteristics of SPM collected by PT and CFC allowed drawing the following conclusions:

i) A deconvolution method of grain size distributions into Gaussian distributed sub-populations showed that 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. However, all classes of particles were captured by PT with a shift – highly dependent on water discharge – from very fine silts towards coarser silts.

ii) Particulate organic carbon concentrations measured in the PT and CFC samples depended on the origin of SPM: less-enriched organic land-derived material (mainly during flood periods) or

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autochthonous more-enriched material (mainly during base flow periods). The relative errors (from -52% to +42%) of POC concentrations in PT samples vs. CFC cannot be attributed to differences in grain size distribution. Instead, integration of events such as phytoplankton blooms or floods by the PT contributed to an increase or a decrease, respectively, of POC concentrations in the PT samples compared to the CFC samples. Hypothetical variations of POC concentrations by production and/or degradation of organic matter inside the PT during its deployment remain to be demonstrated.

iii) Mercury concentrations measured in PT and CFC samples were correlated with POC concentrations and thus affected by hydrological conditions. The relative errors for Hg concentration (between -52% to +42%, typically) were acceptable and can be explained by analytical uncertainties. The highest relative Hg errors were related to the highest Hg concentrations measured in PT samples and were explained by the punctual contribution of a Hg-enriched tributary during the PT deployment period.

iv) 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 concentrations in the PT samples. The relative errors for 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. Outliers, mainly observed during flood periods, were attributed to the time integration effect of PT sampling.

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 within the aim of Hg and PCBs concentration/flux monitoring. It is however important that PTs are well positioned in the river flow, i.e. a few meters above river-bottom and in a cross-section with homogeneous SPM concentrations. As i) all classes of particles are captured and ii) grain size distribution of SPM is relatively fine (mainly silts), the concentrations of contaminants other than those studied in this work, such as polycyclic aromatic hydrocarbons, should be similar, with respect to analytical uncertainties, whether they are measured in SPM collected using PT or CFC techniques. A future

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study on the effect of particle size distribution bias on metal concentrations is planned using another field SPM data. Furthermore, this study highlighted the main advantage of SPM sampling by PTs: samples are time integrative and are thus representative of SPM and associated contaminants transported in the river during periods of time with varying hydrological conditions. Future experiments in controlled tilting flume are planned to improve our understanding of sampling processes within PT and possibly reduce grain size distribution bias through modification of PT shape.

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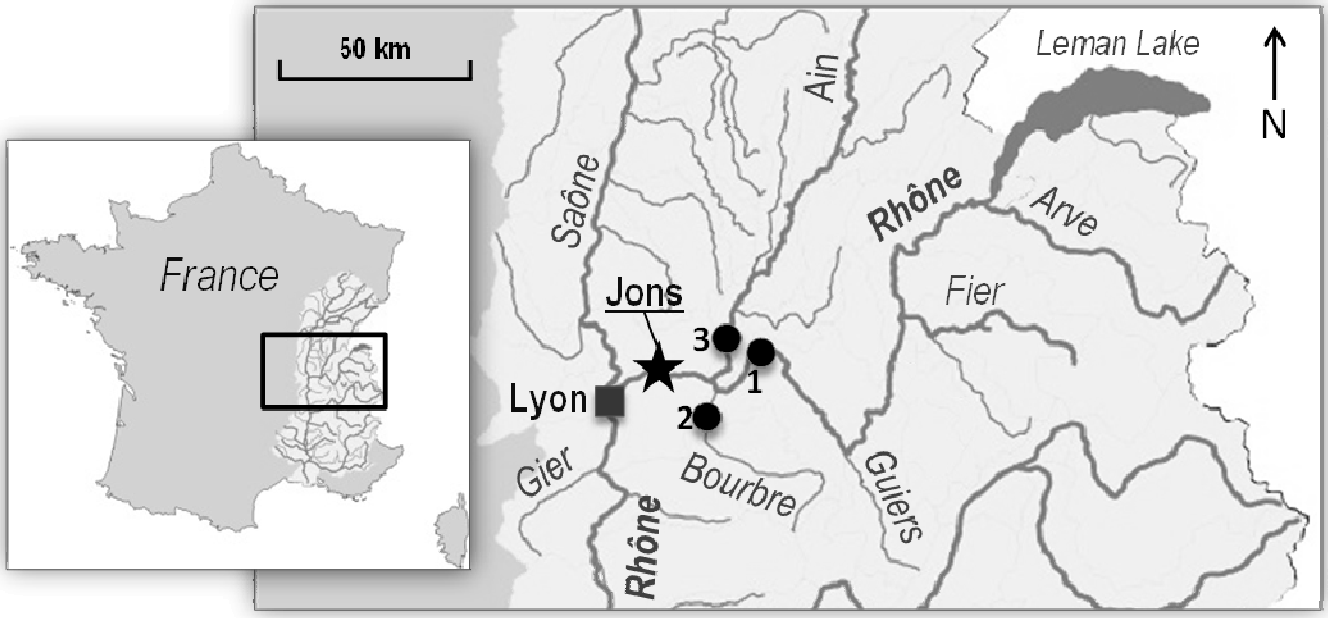

Figure 1*: Map of the Upper course of the French Rhône River: SPM sampling at Jons station (black star) and river discharge measurements stations (solid circles) at 1. Lagnieu (Rhône River); 2. Tignieu-Jameyzieu (Bourbre River); 3. Chazey (Ain River); (discharge stations operated by CNR "Compagnie Nationale du Rhône").*

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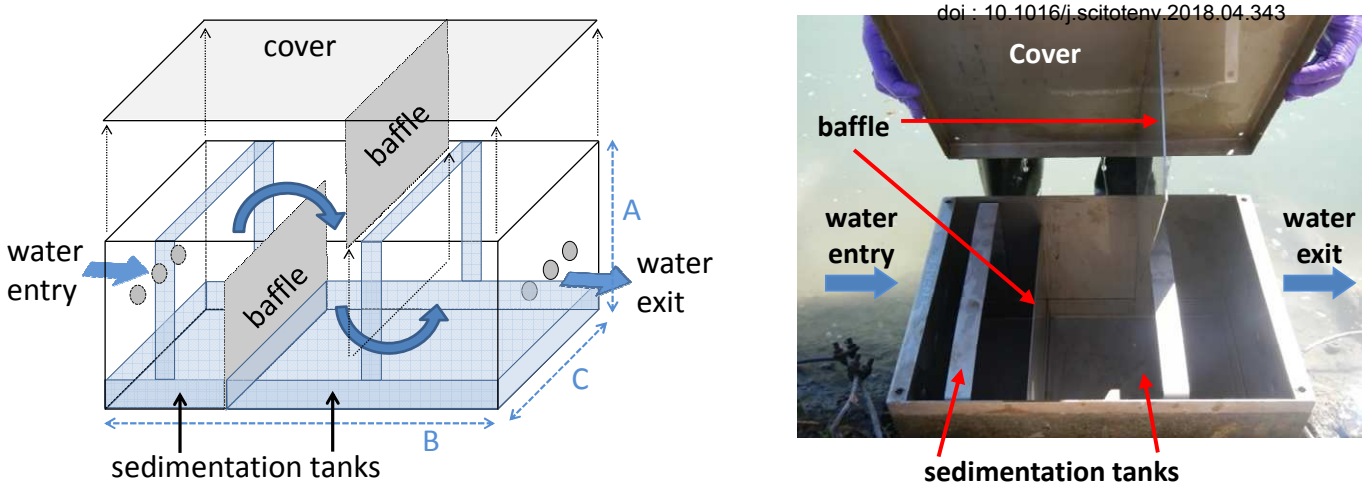

***Figure 2**: Scheme and picture of the particle trap (PT) used to collect SPM; A=250 mm, B=400 mm, C=300 mm.*

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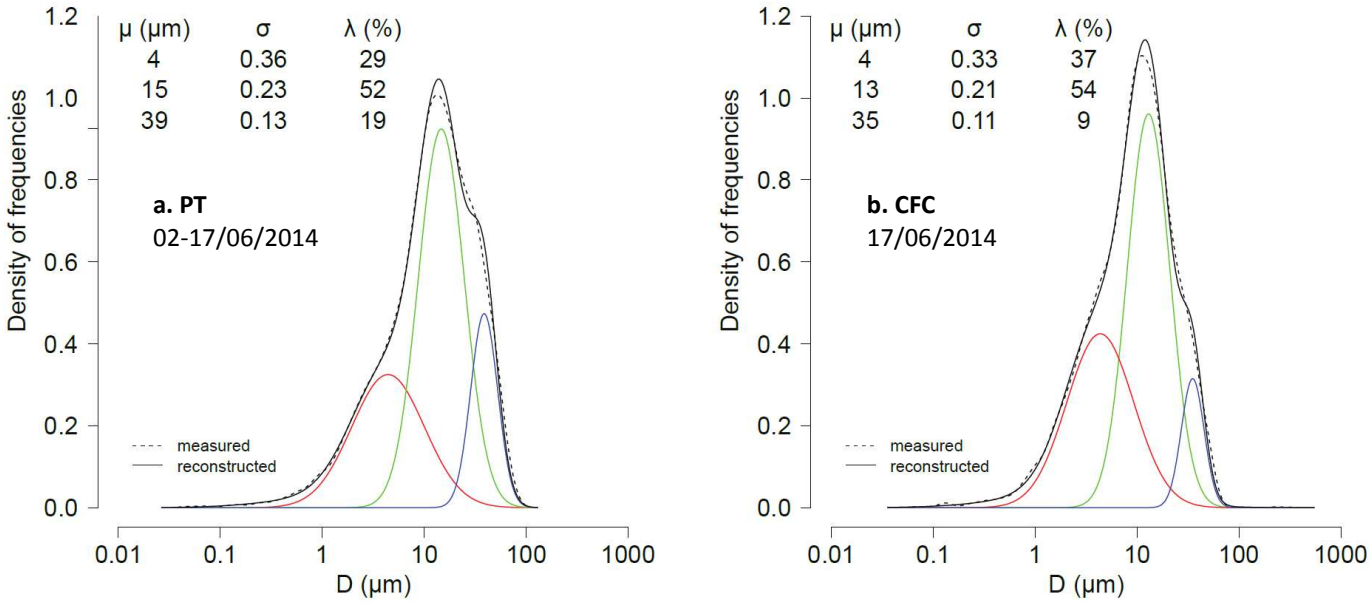

Figure 3: *Examples of decomposition in three Gaussian distributions (red, green and blue lines) of the volumetric grain-size distribution (dashed line) of SPM samples collected at Jons station by (a) PT and (b) CFC techniques. The black solid line is the sum of the 3 Gaussian distributions.*

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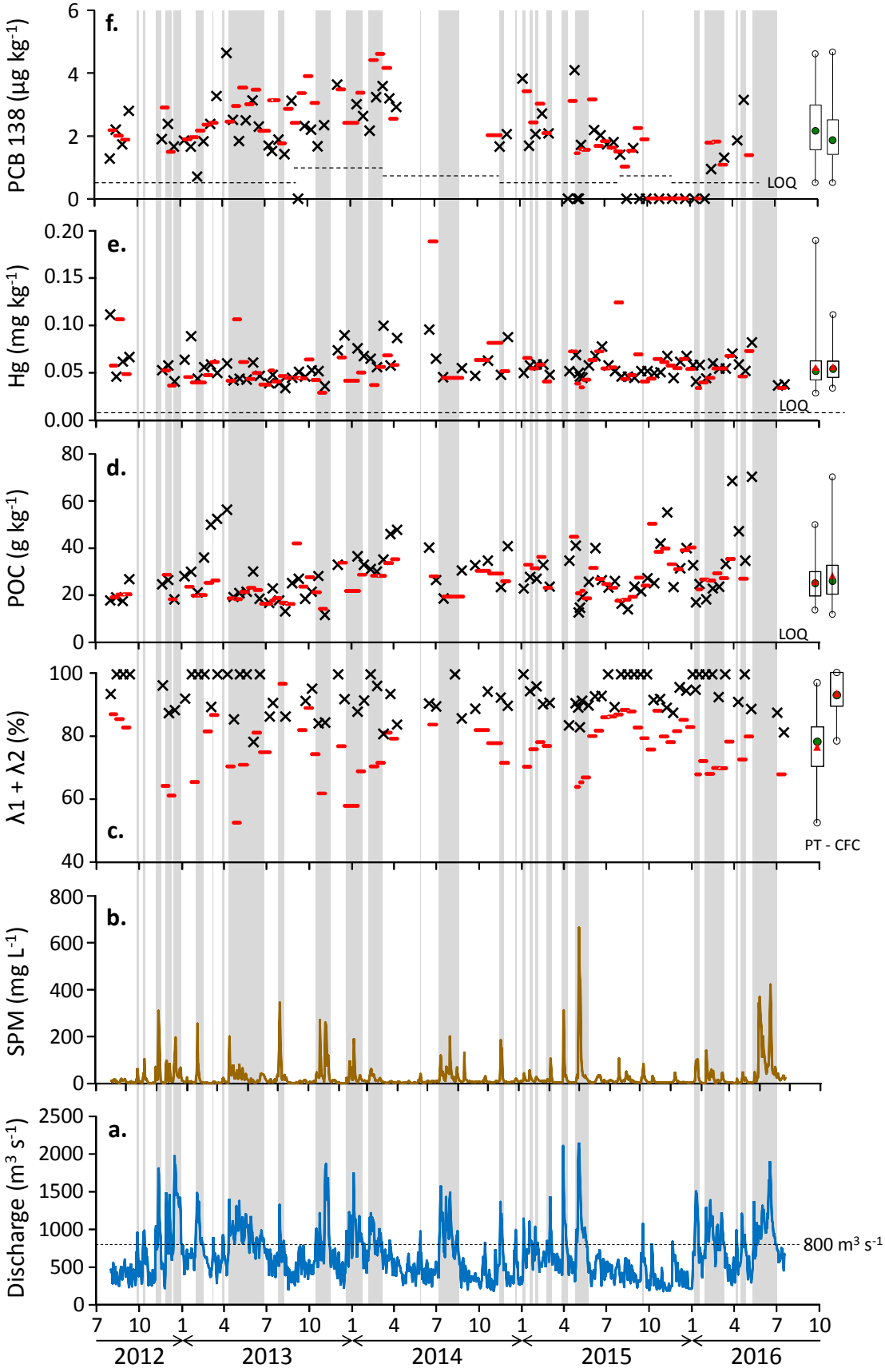

Figure 4: *Parameters measured at Jons station from August 2012 to July 2016 (x-axis : years and months expressed in numbers): (a) hourly water discharges, (b) SPM concentrations, (c) proportions of the finest particles (sum of λ1 and λ2), (d) POC, (e) Hg and (f) PCB138 concentrations measured in SPM samples collected by CFC (black crosses) and PT (red). The dashed lines represent the LOQ for Hg and PCB138. Symbols on the x-axis represent samples with concentrations below the LOQ. The box plots for PT values (left) and CFC values (right) represent minimum and maximum (black circles), 1st and 3rd quartiles (box), mean (red triangle) and median (green circle) concentrations. Grey areas represent the flood periods (daily water discharge >800 $m^3 s^{-1}$).*

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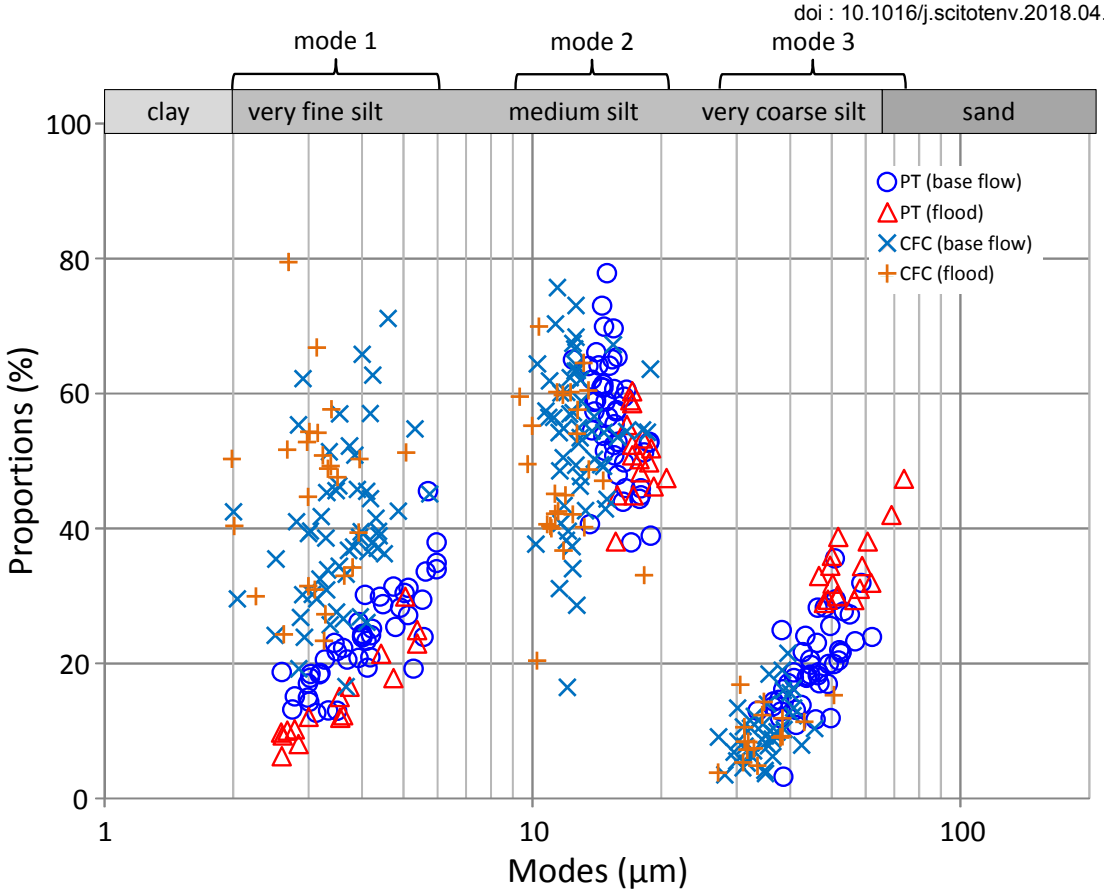

***Figure 5**: Modes and associated proportions of the Gaussian populations extracted for the grain size distributions of SPM sampled at the Jons station by PT and CFC for base flow and flood periods.*

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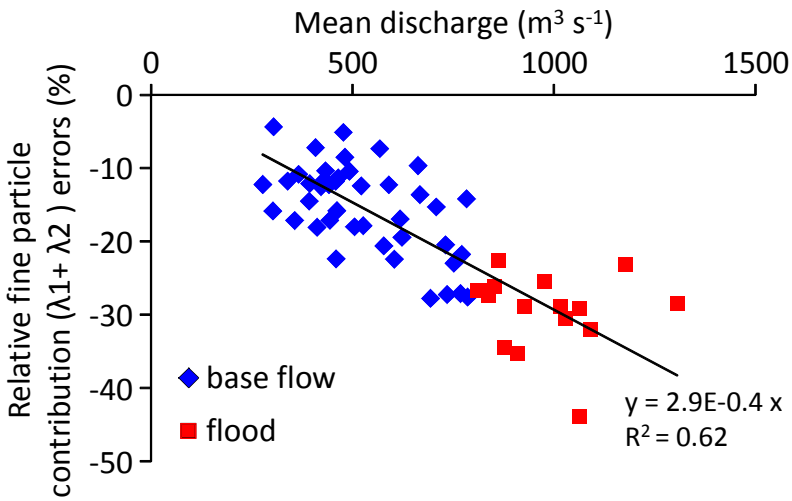

***Figure 6**: Relative errors of the fine particle proportions (expressed as the sum of the proportion of the two finest modes λ1 and λ2) as a function of the mean water discharge calculated during the PT deployment period at the Jons station from August 2012 to July 2016.*

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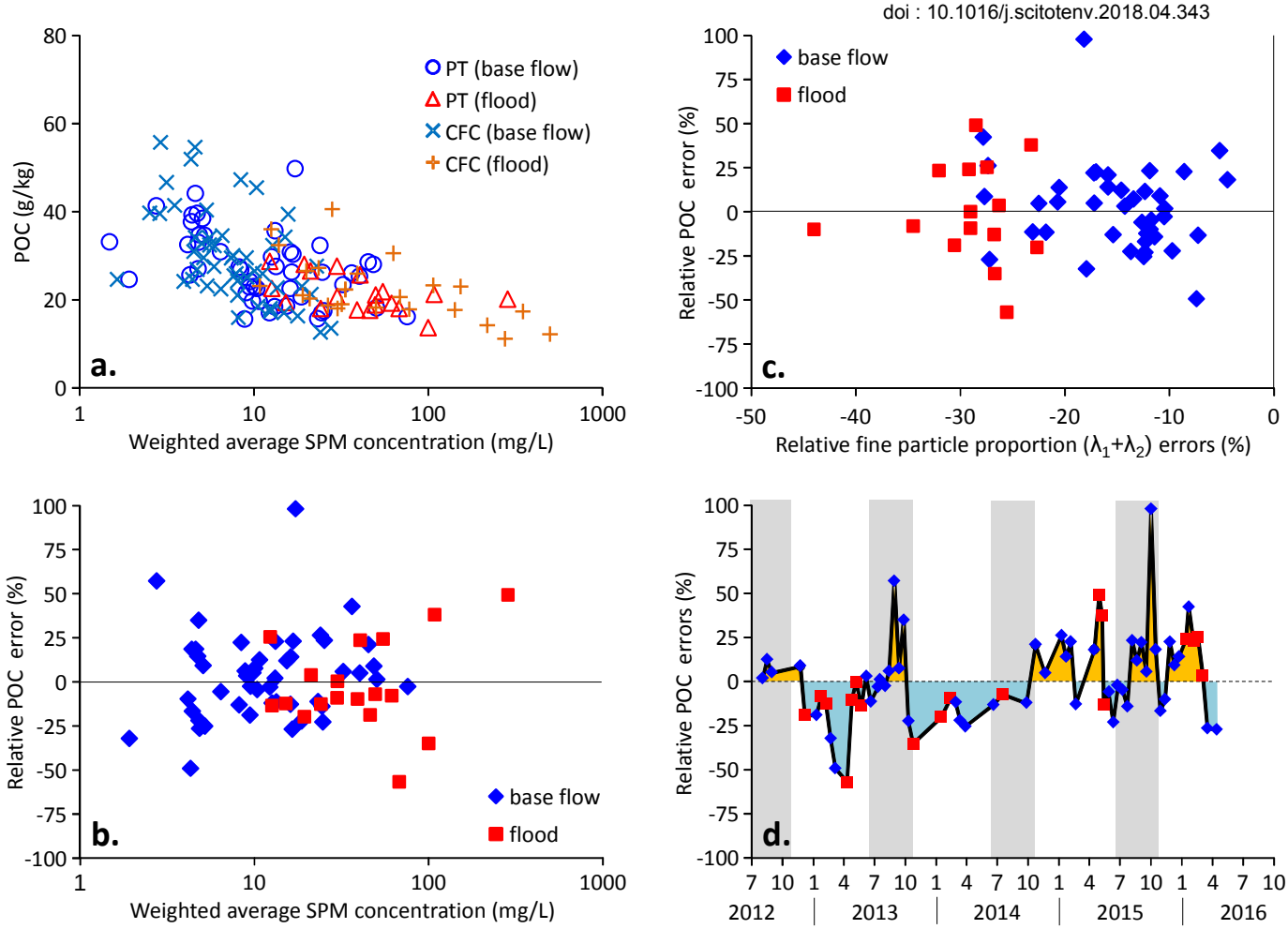

***Figure 7**: Trends in the POC concentrations measured in SPM samples collected by PT and CFC techniques at the Jons station from August 2012 to July 2016: (a) POC concentrations vs. weighted average SPM concentrations; (b) relative POC errors vs. weighted average SPM concentrations; (c) relative POC errors vs relative fine particle proportion ($\lambda_1+\lambda_2$) errors; (d) relative POC errors vs. time (grey areas show summer and early fall periods).*

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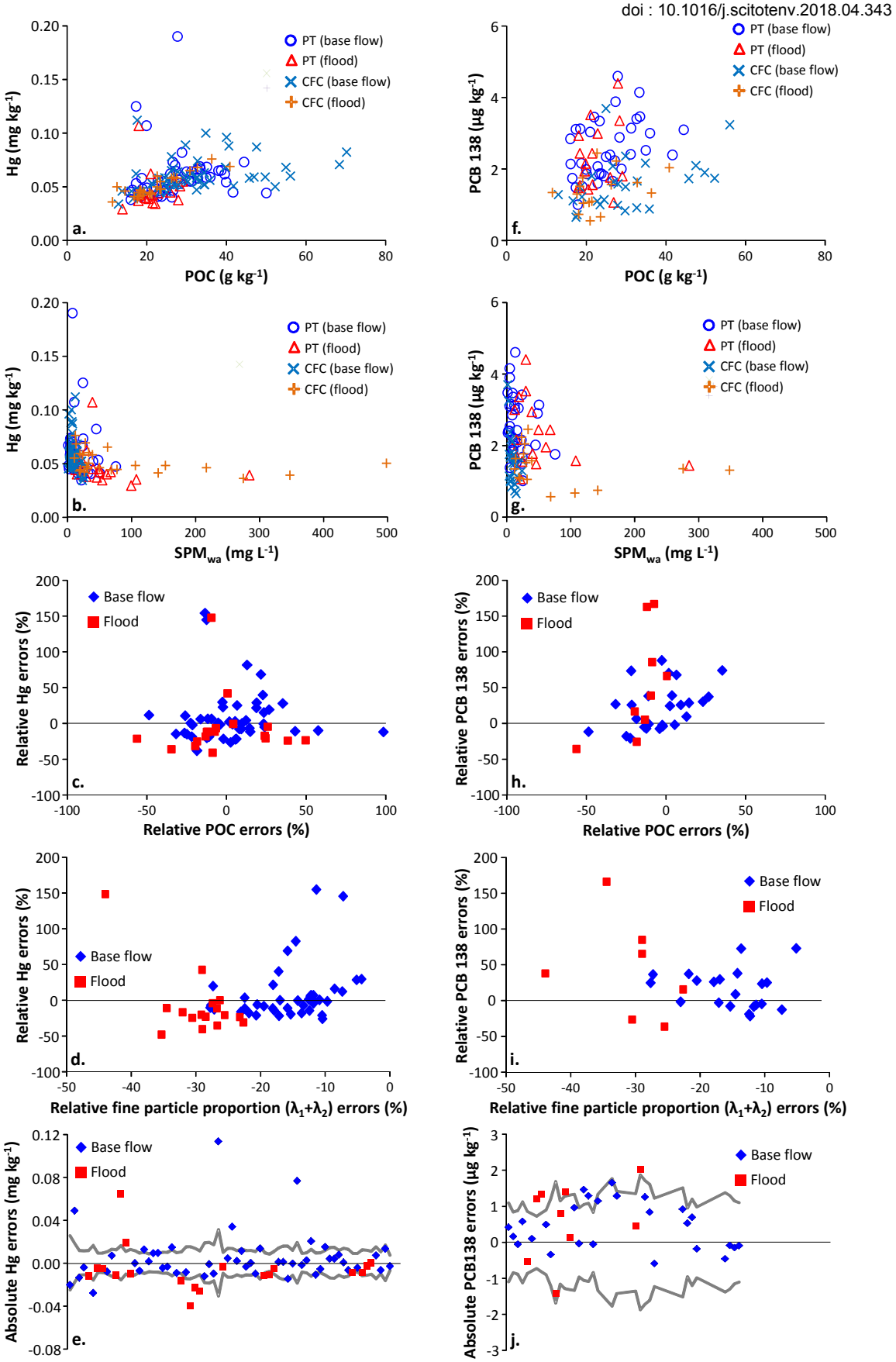

Figure 8: *Trends in Hg and PCB 138 concentrations measured in SPM samples collected by PT and CFC at the Jons station from August 2012 to July 2016: (a) Hg concentrations vs. POC concentrations; (b) Hg concentrations vs. weighted average SPM concentrations; (c) relative Hg errors vs. relative POC errors; (d) relative Hg errors vs. relative fine particle proportion ($\lambda_1+\lambda_2$) errors; (e) comparison of absolute Hg concentration errors with analytical errors (grey lines show estimated maximum errors due to analytical errors; data are ordered by sampling date). Same plots are shown for PCB 138 (f, g, h, i, j).*

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# test	Section	Description of the test	Type of test	p value	Conclusion
#1	3.2	λ2 : PT vs. CFC samples	Wilcoxon	0.149	not different
#2	3.2	λ1 : PT vs. CFC samples	Wilcoxon	< 2.2E-16	different
#3	3.2	λ3 : PT vs. CFC samples	Wilcoxon	< 2.2E-16	different
#4	3.2	λ1+λ2 : PT vs. CFC samples	Wilcoxon	< 2.2E-16	different
#5	3.3	POC : PT vs. CFC samples	Wilcoxon	0.2678	not different
#6	3.3	Hg : PT vs. CFC samples	Wilcoxon	0.1677	not different
#7	3.3	correlation between PCB 101, PCB 138, PCB 153 and PCB 180 (in all samples)	Kendall	all p-values : < 2.0E-08	positive correlations; Kendall corr.: 0.37 - 0.67
#8	3.3	PCB 138 : PT vs. CFC samples	Wilcoxon	0.289	not different
#9	4.1	λ3 in CFC samples : base vs. flood periods	Wilcoxon	0.665	not different
#10	4.1	λ3 in PT samples : base vs. flood periods	Wilcoxon	2.9E-08	different
#11	4.1	λ1+λ2 error : base vs. flood periods	Wilcoxon	7.5E-08	different
#12	4.2.1	correlation between SPMwa and POC (in all samples)	Kendall	9.0E-15	negative correlation; Kendall corr.: -0.44
#13	4.2.1	POC error : distribution test	Shapiro-Wilk	0.845	normal distribution
#14	4.2.2	correlation between POC and Hg (in all samples)	Kendall	4.9E-15	positive correlation; Kendall corr.: 0.44
#15	4.2.2	Hg in PT samples : base vs. flood periods	Wilcoxon	2.9E-04	different
#16	4.2.2	Hg in CFC samples : base vs. flood periods	Wilcoxon	0.0047	different

***Table 1**: Statistical tests used for data comparison (non-parametric test of Wilcoxon), correlation determination (non-parametric test of Kendall) and normal distribution evaluation (Shapiro-Wilk test). For each test, the paragraph section and a brief description of the test are indicated. The result of each test is indicated by the p-value and a brief conclusion is given on the basis of a significance level of 0.05.*

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	PCB 101	PCB 138	PCB 153	PCB 180
PCB 101	1.00			
PCB 138	0.52	1.00		
PCB 153	0.59	0.67	1.00	
PCB 180	0.43	0.37	0.46	1.00

***Table 2**: Kendall correlation coefficients between concentrations of PCB 101, PCB 138, PCB 153 and PCB 180 measured in SPM samples collected by PT and CFC (not calculated for PCB 28, PCB 52 and PCB 118 as quantified in less than 50% of samples; concentrations below the LOQ were excluded). For all PCB couples, the p-values of the Kendall test were largely under 0.05 showing strong correlations between PCB concentrations.*

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Periods	Hg (kg)		PCB 138 (kg)		Difference PT vs. CFC	
	PT	CFC	PT	CFC	Hg	PCB138
annual : 2013	35.2	37.7	2.16	1.79	-7%	19%
annual : 2014	25.8	30.2	1.25	1.17	-16%	7%
annual : 2015	38.5	42.5	1.54	0.94	-10%	48%
flood period : 09/04 - 22/10/2013	19.9	16.8	0.98	0.90	17%	9%
dry period : 07/05 - 22/12/2015	10.7	10.4	0.30	0.25	3%	18%

***Table 3**: Hg and PCB 138 fluxes estimated at the Jons Station for different periods using PT and CFC contaminant concentrations and associated percentage differences.*

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- 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

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