

Intensive monitoring of conventional and surrogate quality parameters in a highly urbanized river affected by multiple combined sewer overflows

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ABSTRACT

The paper reports results of four intensive campaigns carried out on the Seveso River (Milan metropolitan area, Italy) between 2014 and 2016, during intense precipitation events. Laboratory analyses were coupled with on-site, continuous measurements to assess the impact of pollutants on water quality based on both conventional and surrogate parameters. Laboratory data included total suspended solids, caffeine, total phosphorus and nitrogen, and their dissolved forms. Screening of trace metals (Cr, Cu, Pb, Ni, Cd) and PBDEs (polybromodiphenylethers) was carried out. Continuous measurements included water level, physico-chemical variables and turbidity. Nutrient concentrations were generally high (e.g. average total phosphorus > 1,000 µg/L) indicating strong sewage contributions. Among monitored pollutants Cr, Cu, Pb, and Cd concentrations were well correlated to TSS, turbidity and discharge, being bound mostly to suspended particulate matter. A different behavior was found for Ni, that showed an early peak occurring before the flow peak, as a result of first flush events. PBDEs correlated well to nutrient concentrations, showing the highest peaks soon after activation of the combined sewer overflows, likely because of its accumulation in sewers. In addition to showing the existing correlations between quality parameters, the paper highlights the importance of surrogate parameters as indicators of anthropic pollution inputs.

Key words | caffeine, combined sewer overflows, contaminants, monitoring, surrogate parameters, PBDEs

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INTRODUCTION

The water quality of rivers and water bodies in general, in highly anthropized basins is often compromised to some degree (Bendoricchio *et al.* 1993; Capodaglio *et al.* 2003; Lestel & Carrè 2017), in particular when urban areas are served by combined sewer systems (CSS) draining a mixture of urban runoff and municipal waters (Capodaglio *et al.* 2005a; Gasperi *et al.* 2010). During high precipitation events, the transport capacity of the sewer may become

insufficient and these waters are discharged into the natural receptors through the activation of combined sewer overflows (CSOs), allowing to preserve the operation of local wastewater treatment plants (Harremoes *et al.* 1993). CSO events may determine sudden reductions of dissolved oxygen in receiving river waters and contribute additional pollutant (metals, organics, trace elements, etc.), pathogens and nutrient loads to aquatic ecosystems (Gasperi *et al.*

2008; Passerat *et al.* 2011; Viviano *et al.* 2014). The solution to the problems originated by CSOs is not simple. Researchers have postulated the combined use of modelling and hardware solutions (Capodaglio *et al.* 2005b) or, in recent times, a total paradigmatic shift for the management of urban waters (Novotny 2008; Capodaglio *et al.* 2016a; Capodaglio *et al.* 2017).

Recently, the problem of emerging and trace pollutants, generally present at low concentrations in urban wastewater, has also been highlighted (Ceconet *et al.* 2017), which, in addition to the uncertainty about their effects, also poses questions about their early detection (Capodaglio *et al.* 2016b). The use of surrogate measurements can, to some degree, substitute specialized monitoring of pollutants that cannot be easily detected during high flow events (Viviano *et al.* 2014; Capodaglio 2017; Viviano *et al.* 2017).

Even detailed monitoring of nutrients requires relevant logistic and economic efforts that usually cannot be satisfied through ordinary monitoring campaigns (Jones *et al.* 2012; Copetti *et al.* 2017a). Therefore, trends of nutrients and other pollutants in water courses during strong precipitation/discharge events are scarcely described in detail in the scientific literature, despite the fact that the highest pollutant loads are normally generated under these extreme conditions. In small anthropized environments most of the annual phosphorus load is generated during few, high flow events (Grayson *et al.* 1996; Demars *et al.* 2005). In this context, different studies underlined the importance to integrate traditional grab samplings and laboratory analysis with high frequency continuous monitoring to improve the estimation of pollutant loads (Quilbé *et al.* 2006; Viviano *et al.* 2014). Turbidity, in particular, showed to be a good surrogate for total phosphorus (TP) (Salerno *et al.* 2014a), and in general for water quality variables linked to the dynamics of suspended solids (Grayson *et al.* 1996; Stubblefield *et al.* 2007). Viviano *et al.* (2014) underlined the need of more detailed knowledge on the dynamic of nutrients in urban systems, with particular reference to the identification of the sources of P loads generated in a catchment (Copetti *et al.* 2017b). Caffeine was shown to be a good tracer of phosphorus of anthropogenic origin (Buerge *et al.* 2003; Musolff *et al.* 2009; Viviano *et al.* 2014; Viviano *et al.* 2017).

In this study, the results of four intensive field campaigns carried out on the Seveso River, a watercourse

strongly influenced by human activities, located in the Milan (Italy) metropolitan area, are presented. Measurements of both conventional and surrogate parameters during intense storm events were conducted, just upstream of the immission of the river into the Milan city limits. The paper describes in details the monitored trends of phosphorus and other nutrients, and presents insights related to the flow-related dynamics of other typically anthropic pollutants, such as trace metals and polybromodiphenylethers (PBDEs). These have been observed in the river, and their dynamics defined for the specific case through relatively elaborated statistical analysis. The approach used herein, applied to other watersheds, could provide similar critical information with reduced monitoring efforts.

METHODS

Study site

The Seveso River originates at 490 m a.s.l. in an area close to the Italian-Swiss border, and flows for approximately 46 km entirely in the territory of the Lombardy Region of Italy (Figure 1), with a catchment area of about 226 km² and average discharge of about 1.8 m³ s⁻¹. The river has several minor tributaries, the most important of which is the Certesa Stream, joining it in the northeastern portion of its catchment (Figure 1, inset map). During its course, it crosses some of the most populated and industrialized regions of the Milan metropolitan area, with mixed land uses: about 55% urban, 24% forests and 21% agricultural (Figure 1). All local municipalities are served by combined sewer systems (CSSs), hence pollutant loads to the river are due to both direct inputs of sewer water, and to the inflow of polluted tributaries. The Seveso shows a highly modified hydro-morphology: during the past, it was channeled for most of its course and, just before entering into the inner city of Milan, buried into an underground culvert. During strong precipitation events, it often floods neighboring urban areas, inducing both direct infrastructural problems, and public hygiene concerns related to the poor water quality. At the end of its urban course, the Seveso enters the Martesana-Redefossi canal (a system built in 1460 A.D. with the dual purpose of transportation and water supply to the

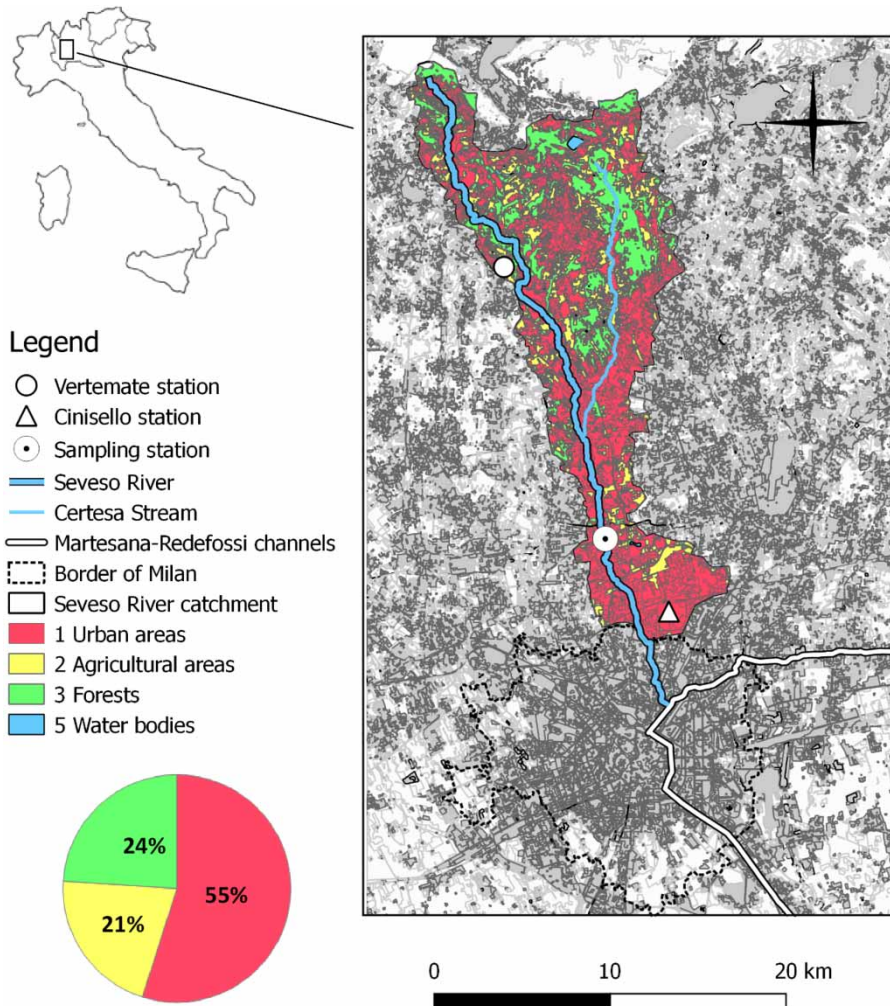


Figure 1 | Seveso River basin map with land use coverage, position of the sampling point and weather stations used in this study.

City of Milan), which in turn flows into the Lambro River, a tributary of the Po, the major Italian river.

Field and laboratory measures

The monitoring point is located about 5 km upstream of the buried stretch of the river (Figure 1), and is equipped to collect water samples at time-steps of 1 h, while continuously measuring several physico-chemical variables, with a continuous measurement system (YSI 6920 v2): water level (WL), temperature (Temp), electrical conductivity (Cond), pH, oxidation reduction potential (ORP), dissolved oxygen (DO) and turbidity (Turb). These sensors were calibrated in the IRSA-Water Research Institute laboratory

before field installation, following procedures reported in Viviano *et al.* (2014). Monitoring was active in the periods 15 March–15 July 2014 and 17 March–7 July. Meteorological data were collected from the two nearest weather stations, located upstream (Vertemate) and downstream (Cinisello) of the sampling point (Figure 1). Within the two measuring periods, four precipitation events were intensively monitored for about 24 h: 27–28 April 2014, 14–15 June 2014, 11–12 May 2016, and 2 July 2016. During these campaigns, water samples were collected hourly through a WS Porti 24 T automated, refrigerated sampler (Water-Sam GmbH & Co, KG). Collected samples were coded using a progressive number from 1 to 90 as follows: April 2014 event = 1–24; June 2014 event = 25–44;

May 2016 event = 45–68; July 2016 event = 69–90. Each sample was analyzed for: biochemical oxygen demand (BOD), chemical oxygen demand (COD), total phosphorus (TP), total dissolved phosphorus (TDP), dissolved reactive phosphorus (DRP), total nitrogen (TN), total dissolved nitrogen (TDN), nitrate (N-NO₃) and ammonium (N-NH₄), total suspended solids (TSS) and the surrogate parameter caffeine. These allowed definition of a comprehensive picture of the river water quality, as discussed in a subsequent section, with special attention to nutrient concentrations.

Samples were filtered through 1.2 µm GF/C filters to estimate TSS by gravimetric method (APHA 2000). TP and TN were determined by molecular absorption according to Valderrama (1981), after persulphate oxidation at 120 °C. Concentration of N-NO₃ was determined by spectrophotometric reading with Hach-Lange kit (LCK-340). N-NH₄ was analyzed by colorimetric method (Fresenius *et al.* 1988). BOD₅ was determined according to APHA (2000), using a BOD System (Velp Scientifica) and COD by spectrophotometric reading (Hach-Lange kit, LCK 314, after digestion in HL-LT200 dry thermostat). Caffeine was determined by ultra-high performance liquid chromatography/triple quadrupole tandem mass spectrometry (TSQ Quantum Access MAX, Thermo Fisher Scientific Inc., USA). Isotopic dilution with a stable isotope-labelled internal standard compound (SIL-IS) was applied in order to compensate for the matrix effects of samples with high organic matter contents, and an on-line solid phase extraction step was coupled to the analytical system in order to guarantee high sample throughput (Viglino *et al.* 2008).

In the two latter campaigns, screening of trace metals (Ni, Cr, Pb and Cd) and polybromodiphenylethers (PBDEs) in suspended particulate matter was also carried out. In order to reduce the analytical effort without losing excessive information, analyses were conducted on six integrated samples (INT1-INT6), obtained by mixing hourly samples with similar physico-chemical features (in particular turbidity and electrical conductivity).

Suspended particulate matter in water samples was collected for metal determination after filtration onto 0.45 µm filters, which were freeze-dried prior to analysis; for PBDEs determination, water samples were filtered onto GF/C glass microfiber filters. Trace element concentrations were measured using AAS (GF-AAS, with Perkin Elmer

AAAnalyst 600 with Zeeman correction), equipped with a graphite atomization system, after microwave-assisted digestion (Preekem Scientific Instruments Co., EU Excel 2000) of dried samples (minimum 0.05 mg d.w.) with 6 mL of concentrated HNO₃ acid (VWR, Suprapur) and 2 mL ultrapure water. Procedural blanks were regularly run to check for ambient or reagent contamination. For each sample, analyses were run in duplicate, with precision generally better than 5%. Recovery accuracy was between 94% and 104% for all elements except total Cr (55%), estimated using reference materials GBW07305 (Stream sediment powder from National Standard Centre of China).

For PBDEs analysis, the GF/C filters were dehydrated at room temperature in a silica gel-filled dryer, and subsequently extracted with hot Soxhlet apparatus (Büchi, Switzerland) using an n-hexane/acetone (3:1, 234 v/v) mixture, previously spiked with an internal standard solution containing the labeled compounds (BDE-28, -47, -99, -100, -153, -154, -183, -209; Wellington Laboratories, Inc., Canada). The clean-up procedure was performed on a multi-layer column packed with acidified silica gel (30% w/w sulphuric acid, Sigma-Aldrich, Germany) and Florisil® (100–200 mesh, Sigma-Aldrich, Germany). GC analysis was performed using a Thermo Electron Trace GC 2000 coupled with a PolarisQ Ion Trap (ThermoElectron, Austin, TX, USA) mass spectrometer, equipped with a PTV injector and an AS-3000 auto sampler. The system was managed by Thermo Finnigan Xcalibur software version 1.4.1., as reported in Guzzella *et al.* (2016). The performance for PBDEs analysis was evaluated using the candidate certified sediment BROCC-2 CRM (Netherlands Institute of Fisheries Research). Using a signal-to-noise ratio of 3:1, calculated by Xcalibur 1.4.1 software during instrument calibration, limits of detection (LODs) were estimated as 0.05 ng g⁻¹ d.w. for each compound. A procedural blank was also analyzed every eight samples to check laboratory contaminations. The results of procedural blanks were always lower than the LOD value.

Statistical analysis

The normality of data was tested by the Shapiro-Wilk test (Shapiro & Wilk 1965; Hervé 2017). Data were also tested for homogeneity of variance with Levene's test (Fox &

Weisberg 2010). Principal component analysis (PCA) was performed including all physical and chemical variables (except for micropollutant concentrations), in order to obtain information on the relationships among data, and to summarize the relationship found by correlation analysis (Salerno *et al.* 2014b; Salerno *et al.* 2016). The degree of correlation among data was verified by Pearson correlation coefficient (r) after testing that the quantile-quantile plot of model residues (not shown) followed a normal distribution (Venables & Ripley 2002). All tests were implemented in R software (R Development Core Team 2010) with significance level at $p < 0.05$.

To better evidentiare relationships between physical and chemical data (expressed as mean values in each integrated sample) and micropollutant concentrations (trace elements and PBDEs, expressed as concentrations in suspended particulate matter), an additional PCA was run using the year 2016 dataset. Data were log-transformed prior to analysis. To reduce the number of variables (a total of 12 cases were included), a preliminary Pearson correlation analysis was run, which allowed the grouping of correlated variables.

Parameters trends in Figure 2 are represented in terms of standardized anomaly, with the exception of precipitation which is in mm, defined as the ratio $(x_i - \bar{x})/\bar{x}$, where x_i is a value of a given series and \bar{x} is the mean value of the series.

RESULTS AND DISCUSSION

Physical variables and nutrients

During the four precipitation events, hourly rainfall (Table 1) ranged between 0 and 29 mm, with maximum value recorded in the Vertemate station during the July 2016 event (Figure 2.4(a)). Average hourly precipitation for Cinisello and Vertemate stations were 1.5 and 1.7 mm, respectively. Discharge was in the range 1.6–41.9 m³ s⁻¹ with a minimum close to the historical average value of the Seveso River (1.8 m³ s⁻¹) and maximum value recorded during the July 2016 event (Figure 2.4(b)). Conductivity range was 202–1,091 μS cm⁻¹ at 25°C, with an average of 439 μS cm⁻¹ at 25°C. The percentage of oxygen saturation ranged between 2% and 123%; values of turbidity, TSS and caffeine were distributed in a rather wide range of

4–767 nephelometric turbidity unit (NTU), 0.4–2,756 mg L⁻¹ and 0.147–7.517 μg L⁻¹, respectively, with the maximum of turbidity and TSS measured during the July 2016 event (Figure 2.4(d)), and the maximum of caffeine measured in the April 2014 event (Figure 3). All nutrients showed very high concentrations with TP and TN in the range of 135–4,267 μg L⁻¹ and 3.1–14.5 mg L⁻¹ respectively. Both TN and TP reached maximum concentrations during the July 2016 event. Dissolved forms of phosphorus (TDP) and nitrogen (TDN) covered on average about 45% and 67% of the respective totals, indicating prevalence of particulate TP and dissolved TN.

Concerning the range of surrogate variables (turbidity, TSS and caffeine) and nutrients (e.g. TP, TN and N-NH₄) concentrations, data collected in this study were always higher than those previously monitored in a nearby urban sub-catchment of the Lake Pusiano basin, located about 30 km north from this study site (Viviano *et al.* 2014). Average caffeine concentrations, for instance, were about 0.4 μg L⁻¹ in the other catchment, and 1.7 μg L⁻¹ in this one, TP concentrations on average about tenfold in this study (1,000 μg L⁻¹ vs. 100 μg L⁻¹, respectively). Thus, data indicate major contributions from point sources (with particular respect to CSOs) in the Seveso River watershed, reflecting a more compromised water quality condition in the watershed addressed by this study.

Each monitored event (Figure 2) was characterized by two principal peaks of precipitation (Figure 2.1(a)–2.4(a)), causing specific responses in both discharge and physico-chemical variables. Discharge peaks (Figure 2.1(b)–2.4(b)) occurred with a delay of about 2–4 h from the corresponding precipitation peaks. Differences in the behavior of the measured physico-chemical parameters can also be noticed: in general, the first parameters group (Figure 2.1(c)–2.4(c)), constituted by caffeine, TN, TP and N-NH₄, mostly dissolved, responds to both precipitation peaks. On the contrary, the second group (Figure 2.1(d)–2.4(d)), consisting of turbidity and TSS, responds more closely to the first precipitation peak than to the second one, behaving as driven by a first-flush phenomenon. Turbidity and TSS trends also appear very similar, in phase with discharge peaks and not aligned with caffeine peaks (Figure 2). Furthermore, the four main caffeine peaks occurred only when precipitation peaks were detected by both weather stations. The first intense

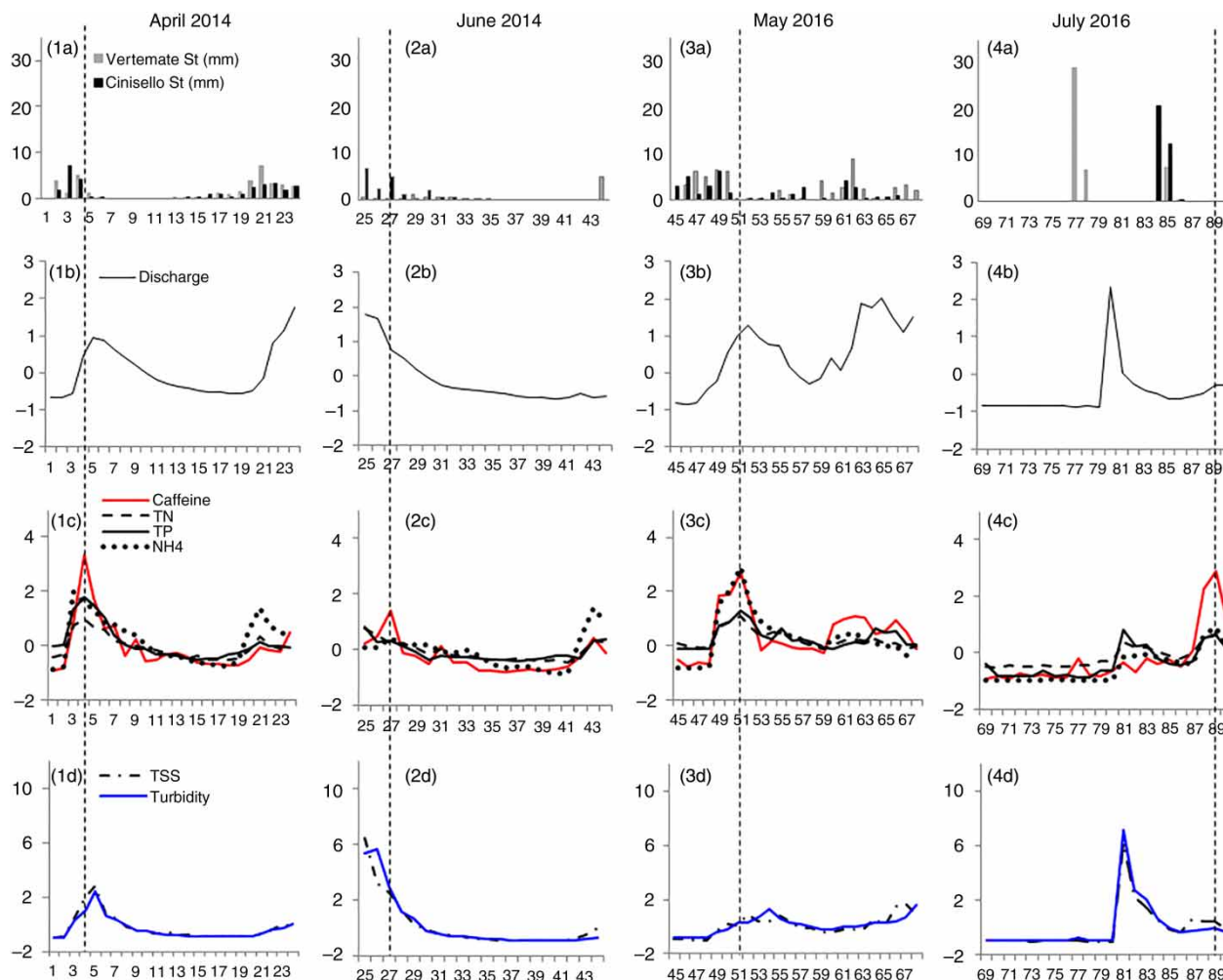


Figure 2 | Precipitation and physico-chemical variables trends during field campaigns: column 1 = April 2014 event; column 2 = June 2014 event; column 3 = May 2016 event; column 4 = July 2016 event. Row (a) Cumulate hourly precipitation (mm) at Vertemate station and Cinisello station; row (b) standardized anomaly of discharge; row (c) standardized anomaly of concentrations of caffeine, TN, TP, N-NH₄; row (d) turbidity and TSS. Vertical dashed lines represent time of maximum caffeine concentration detection.

(28 mm), short precipitation peak of the fourth storm event (Figure 2.4(a)) detected only in the Vertemate station, for instance, was not followed by an observable caffeine peak, indicating that during that event no CSOs were activated.

The relationships among variables was evaluated by correlation analysis, summarized in Figure 3. Conductivity was included in the analysis, resulting, however, not significantly correlated with any other variable, with the exception for discharge ($r = 0.31$), turbidity ($r = 0.28$) and TSS ($r = 0.24$), with a rather weak negative correlation. All other variables were positively correlated with discharge, with values of Pearson's coefficient close to 0.5 ($0.49 < r < 0.52$). Much stronger correlations ($r > 0.7$) were found between turbidity and TSS ($r = 0.95$) and between caffeine and nutrients

($0.77 < r < 0.91$). TP in particular showed a strong and highly significant correlation with caffeine ($r = 0.78$), and a highly significant, although weaker, correlation with turbidity ($r = 0.52$). Similar considerations can be drawn for the relationships TSS-TP ($r = 0.62$) and TSS-caffeine ($r = 0.39$).

To provide a comprehensive overview of the mutual relationships among the variables presented in Figure 2, a PCA was performed (Figure 4) between relevant chemical data and discharge. It can be observed that the first (PC1) and second (PC2) principal components can explain 56% and 24% of the overall variance, respectively. In PC1, all variables have positive loadings, while in PC2 some have positive (turbidity and TSS) and others have negative loadings (TP, TN, caffeine and N-NH₄).

Table 1 | Summary statistics of data collected during storm events. Precipitation data refer to the two weather stations while other variables refer to the river sampling station (shown in Figure 1)

Monitoring		Unit	Median	Mean	Range
Continuous	Rainfall (Cinisello)	mm	0.2	1.5	0.0–23.6
	Rainfall (Vertemate)	mm	0.3	1.7	0.0–29.0
	Discharge	m ³ s ⁻¹	8.0	12.5	1.6–41.9
	Temperature	°C	14.3	18.1	13.5–24.0
	Conductivity	μS cm ⁻¹ at 25 °C	410	439	202–1,019
	pH		7.4	7.6	7.2–8.5
	%O ₂	%	72	56	3–123
	ORP	mV	220	246	113–367
	Turbidity	NTU	58	95	4–767
Grab	TSS	mg L ⁻¹	83.4	169.7	0.4–2,756.0
	Caffeine	μg L ⁻¹	1.294	1.716	0.147–7.517
	TP	μg L ⁻¹	915	1,038	135–4,267
	TDP	μg L ⁻¹	436	477	35–1,036
	P-PO ₄	μg L ⁻¹	399	421	132–951
	TN	mg L ⁻¹	6.6	6.8	3.1–14.5
	TDN	mg L ⁻¹	4.43	4.60	1.0–8.3
	N-NO ₃	mg L ⁻¹	3.16	3.81	1.0–12.0
	N-NH ₄	mg L ⁻¹	1.0	1.0	0.0–4.1
	BOD ₅	mg L ⁻¹	11.2	19.0	0.0–109.9
COD	mg L ⁻¹	18.5	27.7	6.7–170.0	

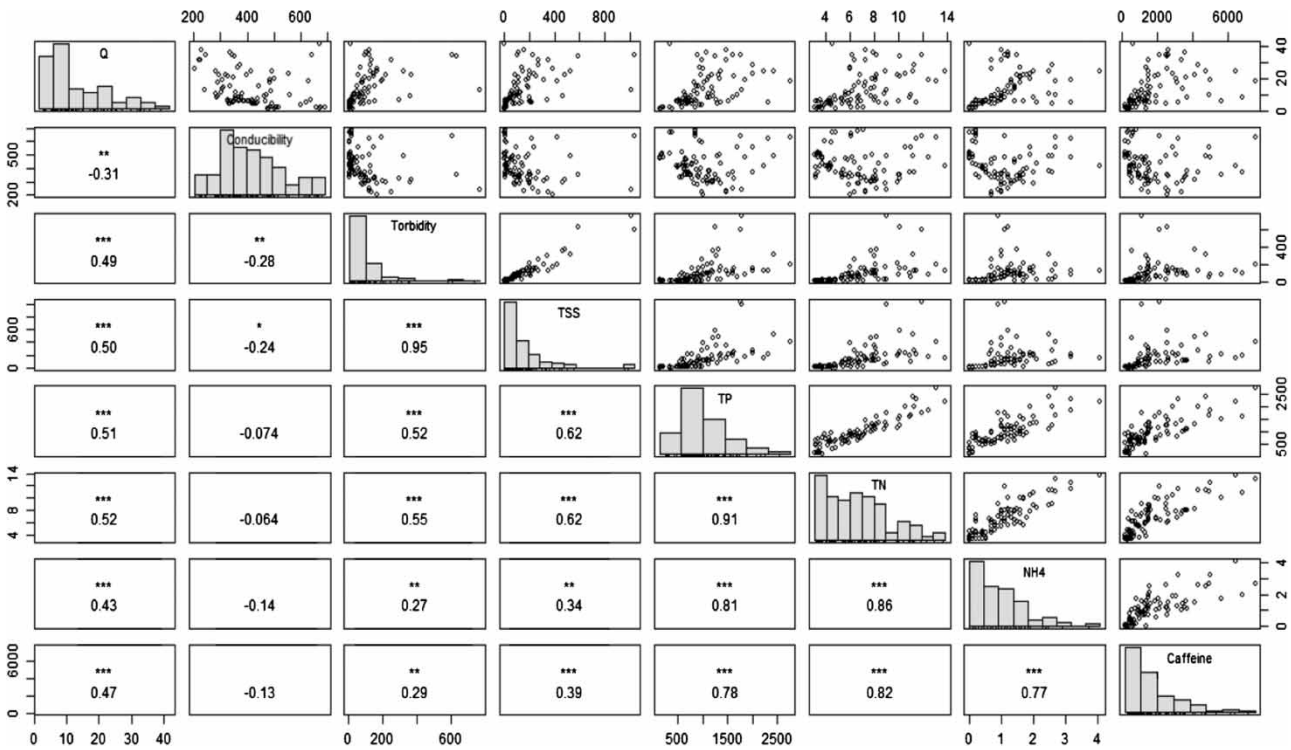


Figure 3 | Correlation matrix of selected variables: discharge, conductivity, turbidity, TSS, TP, TN, N-NH₄, caffeine. The asterisks indicate the level of significance of Pearson's correlation matrix (*** $p < 0.001$; ** $p < 0.01$; * $p < 0.05$).

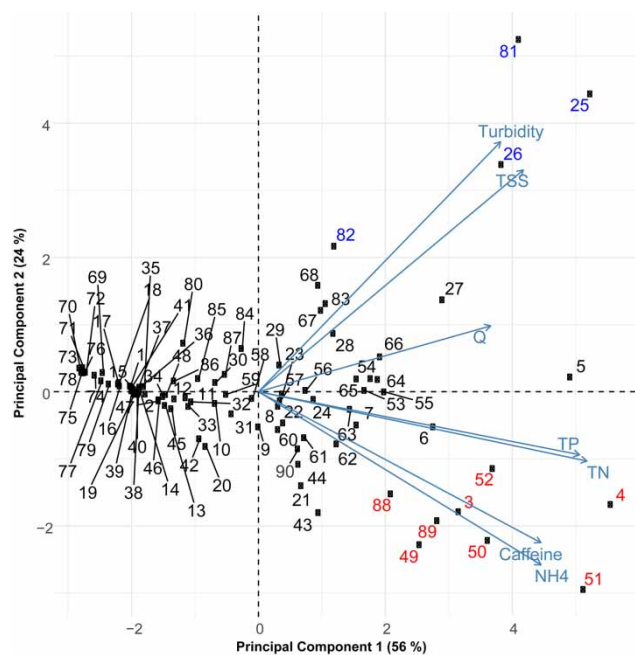


Figure 4 | PCA between nutrients and discharge data. Dots represent the water samples, while the numbers represent the temporal position of hourly water while numbers represent temporal position of hourly water samples. Numbers 25, 26, 81, 82 indicate samples more influenced by non-point sources; numbers 3, 4, 49–52, 88 and 89 indicate samples more influenced by point sources. Please refer to the online version of this paper to see this figure in color: <http://dx.doi.org/10.2166/ws.2018.146>.

Therefore, three main groups of water samples can be graphically identified. The first group (numbers in blue) is constituted by samples 25–26 and 81–82, all characterized by high values of both turbidity and TSS and relatively low values of caffeine; the second group (numbers in red) is constituted by samples 3–4, 49–52 and 88–89 characterized by high concentrations of TP, TN, N-NH₄ and caffeine, but relatively low turbidity and TSS. Samples of the first group correspond to the major peaks of turbidity and TSS, while samples of the second group are generally related to the caffeine peaks (Figure 2). The third and largest group (black numbers) is constituted by the remaining samples. The pattern of samples in the present PCA, thus, is rather different from that described by Viviano et al. (2014), in which samples were clearly divided in just two distinct groups: the first, characterized by high values of turbidity and TSS, associated to the catchment natural runoff, and the second characterized by high values of caffeine and thus to domestic wastewater contamination. In this study, instead, the degree of separation among samples is rather less marked, a fact

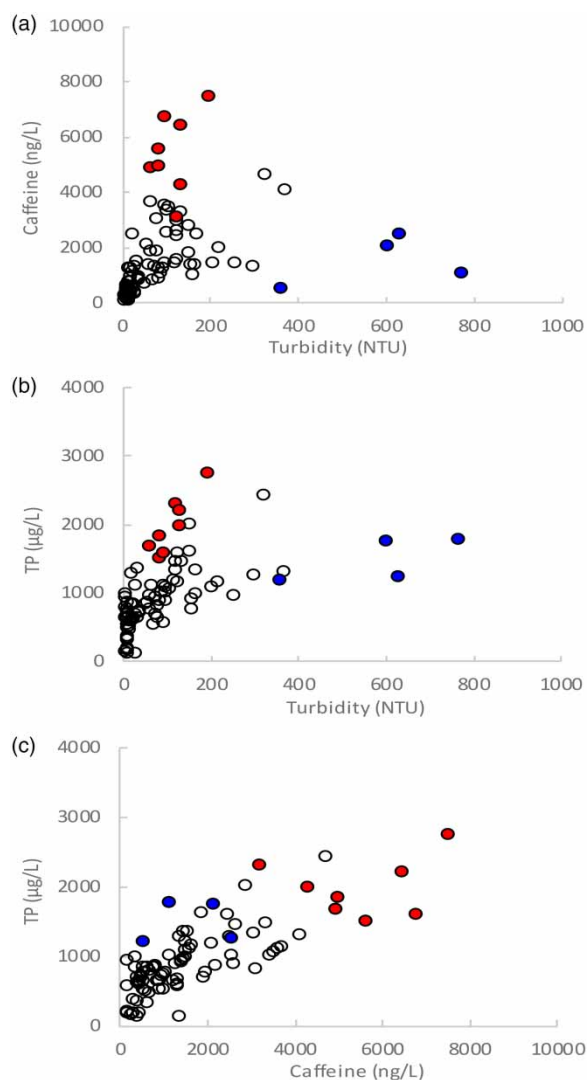


Figure 5 | The relationship between turbidity and TP in samples collected during intensive field campaigns. Dark grey dots indicate samples more influenced by non-point sources, light grey dots indicate those more influenced by point sources. Please refer to the online version of this paper to see this figure in color: <http://dx.doi.org/10.2166/ws.2018.146>.

most likely due to the diverse nature of the two catchments: mountainous and less populated, the urban sub-catchment of Lake Pusiano basin, and flat and more influenced by domestic activities, the Seveso River catchment. In the latter, thus, a broad prevalence of point sources (with particular respect to CSOs) can be observed, as indicated also by the high concentrations of caffeine and nutrients detected in all examined storm events (Table 1).

Figure 5(a)–5(c) show the scatter plots of turbidity-caffeine, turbidity-TP and caffeine-TP data points corresponding to

the three principal group of variables identified by the PCA. The greater degree of differentiation is obtained considering the relation turbidity-caffeine, where a group of samples (Figure 5(a), blue dots) with turbidity > 350 NTU and caffeine < 2.5 $\mu\text{g L}^{-1}$ is well separated by the group characterized by turbidity > 350 NTU and caffeine > 2.5 $\mu\text{g L}^{-1}$ (red dots). The first group is the one most influenced by urban runoff, and thus by diffuse sources, while the second one is more influenced by the discharge of CSOs, and thus by point sources. A similar pattern is underlined by the turbidity-TP scatterplot (Figure 5(b)) with the first group characterized by relatively high turbidity and relatively low TP and vice versa for the second group. The caffeine-TP scatter plot (Figure 5(c)), in contrast, does not show any separation among samples, underlying a much more linear relationship among the two variables, confirming broad contamination mostly from point sources (CSOs) with presence of caffeine even at relatively low concentrations of TP.

Micropollutants: trace metals and PBDEs in suspended particulate matter

Trace elements and PBDE concentrations in suspended particulate matter showed strong variations across individual storm events (Table 2, Figure 6). In particular, Cd, Ni, Pb and Cu showed maximum values 2–5 times higher than the minima, while Cr concentrations increased more than 20 times. PBDEs revealed the widest range, with maximum

Table 2 | Summary statistics of trace metals and PBDEs data collected at the Seveso River station. Concentrations of trace metals are related only to suspended solids, while concentration of PBDEs are related to both suspended solids and water. Σ PBDEs indicates the sum of all the PBDE congeners

Micropollutant	Unit	Median	Mean	Range
Cr	mg kg ⁻¹ d.w.	34.7	48.3	6.2–132.3
Cd	mg kg ⁻¹ d.w.	0.47	0.61	0.35–1.91
Ni	mg kg ⁻¹ d.w.	91.3	92.3	38.4–171.3
Pb	mg kg ⁻¹ d.w.	55.2	51.7	38.4–89.9
Cu	mg kg ⁻¹ d.w.	262.0	300.6	155.2–645.5
Σ BDEs	$\mu\text{g g}^{-1}$ d.w.	1.9	3.7	0.01–21.2
BDE – 209	$\mu\text{g g}^{-1}$ d.w.	1.9	3.6	0.01–21.2
Σ PBDEs	ng L ⁻¹	240.2	390.0	6.2–1,256
BDE – 209	ng L ⁻¹	226.8	375.9	6.2–1,196.8

values three orders of magnitude higher than the lower ones. Chemical analysis showed that BDE-209 was the main congener, accounting for $\geq 92\%$ of the total PBDEs (Table 2). Concentrations of Cu, Pb, Cd and Cr were positively correlated ($0.64 < r < 0.94$, $p < 0.05$), showing a common behavior and/or origin, and Pb was positively correlated to SST ($r = 0.60$, $p < 0.05$). Thus, these elements were mainly found in the particulate phase. Ni was positively correlated to water temperature and pH ($r = 0.68$ and 0.65 , respectively, $p < 0.05$) and negatively to N-NH₄, ORP and caffeine ($r = -0.65$, -0.65 and -0.77 , respectively, $p < 0.05$), showing a higher affinity for the dissolved phase. PBDEs were inversely correlated to turbidity and COD ($r = -0.68$ and -0.61 , respectively, $p < 0.05$).

Concentration trends of both trace elements and PBDEs, as well as of precipitation, turbidity and conductivity during the 2016 storm events are reported in Figure 6. In the first event (May 2016), conductivity decreased in integrated samples INT3 and INT5 following rainfall, and turbidity showed two peaks in samples INT4 and INT6 after rainfall peaks. Ni, Cu and Cr showed the highest values in INT2, when turbidity and conductivity were still not affected, then they showed an abrupt decrease with the first rainfall peak in INT3, and then an increasing trend up to a second peak in INT5, as well as Cd, corresponding to the new rainfall peak. On the contrary, PBDEs showed the maximum values in INT3 and INT5, Pb in INT3 and INT6.

The second event (July 2016) was different, with two short and intense rainfalls in INT1 and INT6, respectively. Conductivity increased in INT2 and INT3 and decreased in INT4. Turbidity reached a strong peak in INT4. Pb, Cu and Ni showed the highest values in INT1, corresponding to the first rainfall and in INT5, as well as Cr and Cd, after the turbidity peak. On the contrary, PBDEs showed the maximum values in INT2, after the strongest rainfall. Both events showed that Ni, Cu, Cr, and Cd concentrations showed peaks at the beginning of precipitation, probably as an effect of first flush, and after turbidity peaks, as an effect of remobilization of river sediments. PBDEs showed a common behavior in the first event, with the highest values before turbidity peaks, due to activation of CSOs. Pb followed PBDEs in the first event, while in the second one the trend was in agreement with the other metals.

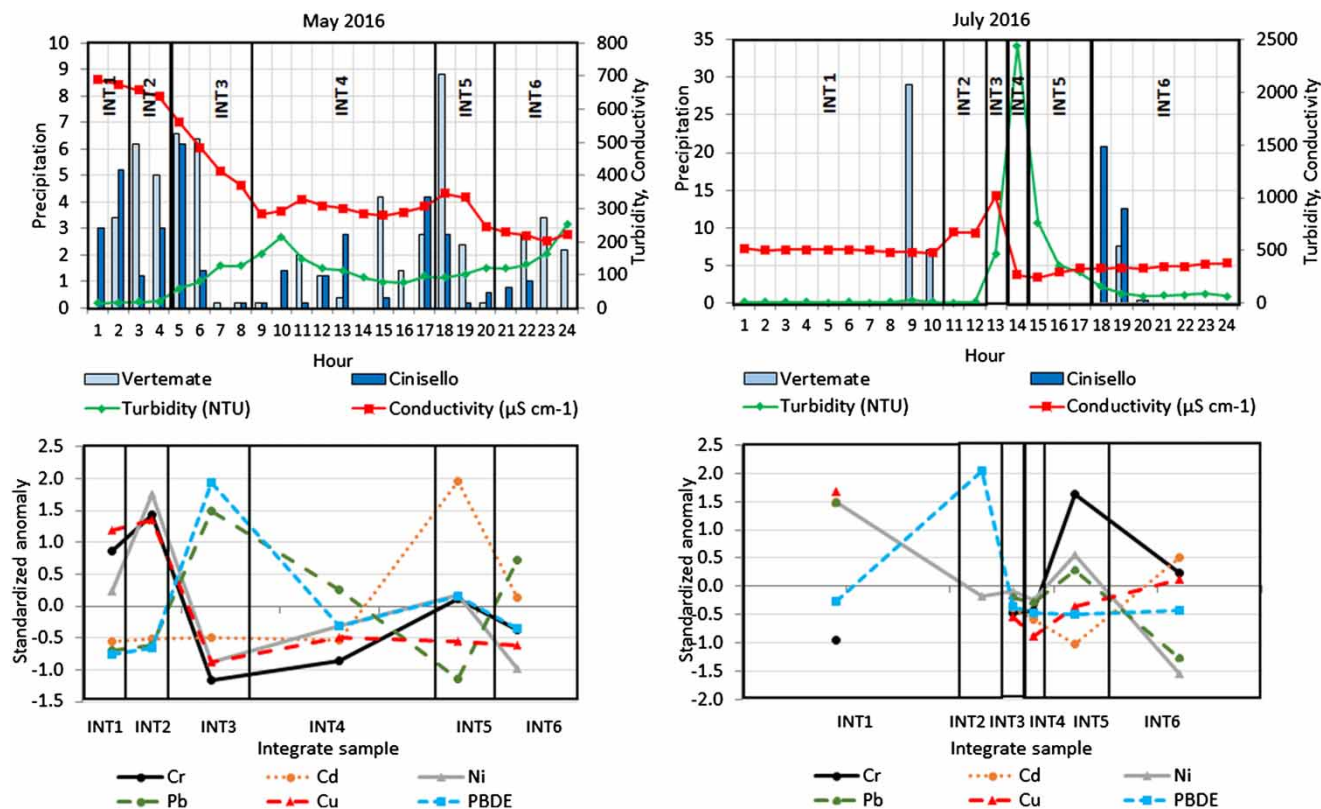


Figure 6 | Trends of precipitation (columns, mm), turbidity (mg L^{-1}) and conductivity ($\mu\text{S cm}^{-1}$) registered for 24 h during the storm events of May 2016 and July 2016 (top panels). These variables were used to group samples of suspended particulate matter into integrated samples (INT1-INT6). Standardized anomaly of micropollutant concentrations in suspended solids collected during both events are also reported (bottom panels).

A second PCA analysis was carried out with the aim of clarifying the relations between micropollutant concentrations and the other physical and chemical variables (Figure 7). To reduce the number of variables, a preliminary Pearson correlation analysis was run and allowed to include correlated variables as follows:

- (1) discharge was not correlated to the other variables and thus was included in PCA;
- (2) conductivity was included as representative of caffeine concentrations ($r = -0.72$, $p < 0.05$): these variables showed dilution during rainfall events;
- (3) turbidity was included as representative also of SST, TP, TN, N-NH_4 and COD ($r = 0.96$, 0.90 , 0.68 , 0.84 and -0.71 , respectively, $p < 0.05$): these variables could represent remobilization of river bottom sediments;
- (4) TDP was included as representative also of P-PO_4 , TDN, N-NO_3 , ORP, BOD₅, water temperature and

percentage of dissolved oxygen saturation ($r = 0.99$, 0.88 , 0.62 , 0.76 , -0.80 , -0.67 and -0.76 , respectively, $p < 0.05$): these variables could indicate inflow of sewage water due to CSOs activation;

- (5) Cu was included as representative also of Cr, Cd and Pb ($r = 0.78$, 0.99 and 0.94 , respectively, $p < 0.05$);
- (6) Ni and PBDEs were not correlated with the other micropollutants and thus were both included in PCA.

The first PCA axis (Figure 7, left panel) accounts for 36% of the total variance, and correlated positively to turbidity and negatively to conductivity, TDP and rainfall. Cu, Cr, Cd and Pb concentrations were positively correlated to this axis, while PBDEs were negatively correlated. The second axis accounted for 27% of total variance, relating positively to Ni, and negatively to discharge.

As expected, trace metal concentrations (Cu, Cr, Cd and Pb) were related to turbidity (which was also correlated to

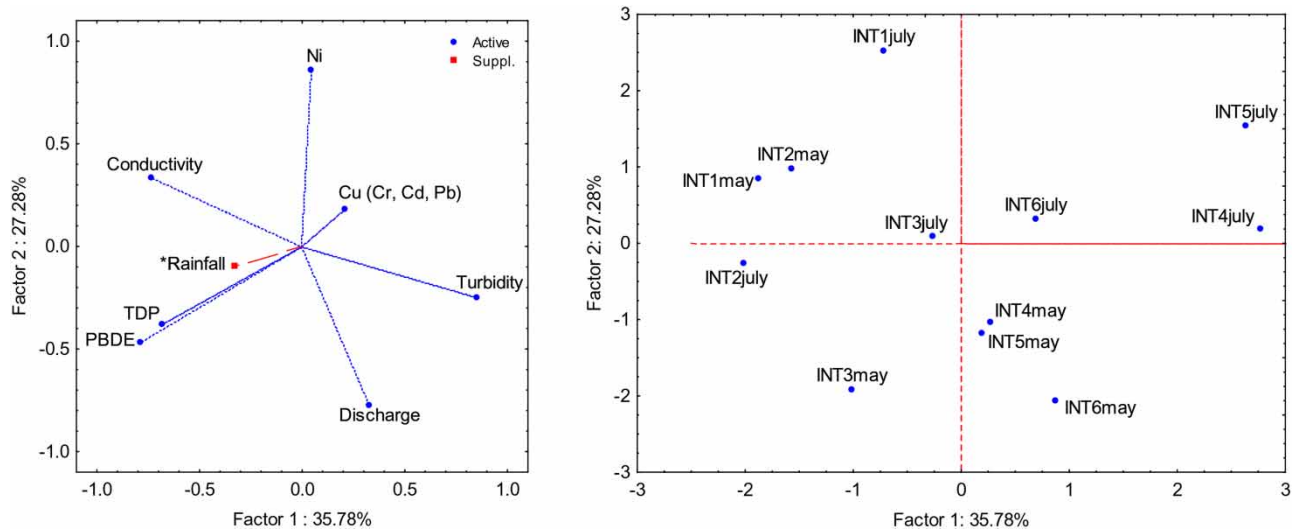


Figure 7 | PCA results considering micropollutant concentrations and the other physical and chemical data as variables, according to PCA axes 1 and 2 (left panel). Rainfall was plotted as supplementary variable. Factor scores of the integrated samples of the two storm events (May 2016 = may and July 2016 = july) are also plotted (right panel).

TSS), showing that these elements (Figure 7) were mainly found in the particulate/solid phase: this behavior is frequent for these elements in freshwater ecosystems (Salomons & Förstner 1984) and it was confirmed in studies concerning metal contamination deriving from runoff waters (e.g. Hergren *et al.* 2005). Therefore, the peaks observed during storm events were mainly associated with increased discharge and TSSs, i.e. fine sediments from the river bottom resuspended by increased water velocity and/or by more intense surface runoff become, and CSOs activation (Bertrand-Krajewski *et al.* 1998). This conclusion is supported by the corresponding low conductivity values, showing dilution corresponding to sudden discharge increase (INT4 and INT5 of July 2016, Figure 7 right panel).

Ni showed a different behavior, being related to high conductivity and low discharge and turbidity (Figure 7): the highest peaks of this metal were associated with the very first rainfall hours, when conductivity and turbidity were still not affected (INT1 of both events, INT2 May 2016). Therefore, high Ni values may be related to the first flush phenomenon, i.e. the earliest runoff from surrounding urban and industrialized soils, carrying high concentrations of micropollutants. This metal generally shows high mobility in freshwater ecosystems, being more often found in dissolved forms; however, concerning the runoff component, some studies showed that metals may behave differently

(particulate vs. dissolved) according to local land use (industrial, residential or commercial) (Hergren *et al.* 2005; Soller *et al.* 2005). A first flush effect can be observed also for Cu and Cr in INT1 (May 2016) and for Cu and Pb in INT1 (July 2016) (Figure 6). In the following rainfall phases, high concentrations in the first flush were diluted by surface runoff. Concentration curves of these elements are typical of particular first flush events observed also by other authors (e.g. Lee & Bang 2000; Lee *et al.* 2002): a pollutant concentration peak occurring before peak flow is caused by early runoff, accumulating pollutants from the streets and sewers before the main runoff peak arrives to the river (Soller *et al.* 2005). Diffuse pollution resulting from stormwater runoff has been identified as one of the major causes of quality deterioration in receiving waters (Hergren *et al.* 2005).

Lastly, PBDEs concentrations were positively related to TDP (which was in turn correlated to nutrients such as P-PO₄, TDN, N-NO₃) (Figure 7): this result shows that the main source of these compounds may be sewage water, contributed by the activation of CSOs. In fact, the highest values were found in INT2 July 2016 and INT3 May 2016 (Figure 7, right panel). WWTPs are known as important sources of PBDEs deriving from a variety of sources including urban and agricultural runoff, domestic wastewater, industrial point source discharges, wet and dry deposition of

atmosphere (Gevao et al. 2008). Due to their chemical physical properties, PBDEs, and in particular deca-PBDE, such as BDE-209, are strongly bound to solid particles and accumulate in sewage sludge (Cincinelli et al. 2012). In fact, in this study BDE-209 dominated the congener profile. This also evidences present diffuse use of this technical formulation by industrial activities in the River Seveso watershed areas from where wastewater is originated (e.g. electrical device productions, textile industrial effluents, etc.). In fact, after the introduction of severe restrictions in the use and marketing of octa and penta PBDE mixtures, higher brominated BDE congeners such as BDE-209 have shown an increased industrial demand, mirrored by increasing environmental concentrations (Cincinelli et al. 2012).

CONCLUSIONS

The Seveso River is an emblematic case of highly anthropized and strongly polluted urban river, and the results herein presented point out that a marked deterioration of water quality clearly occurs, during strong precipitation/discharge events. Urban water pollution is dominant in the basin, as evidenced by high dissolved concentrations of caffeine, used as anthropogenic tracer, even during storm events. Basinwide correlation between specific parameters (i.e. caffeine and PBDEs) and other typically urban pollutants shows evidence of a prevailing contribution of CSOs to in-stream water quality degradation. Concentrations of caffeine measured during the study are also accompanied by high nutrient concentrations, in particular TP, also indicating strong point source contamination, linked to CSOs contribution. Concentrations of trace metals measured in the solid and particulate phases generally follow the observed trends of turbidity and TSS; however, events of advanced first flush may be observed at the onset of each storm event, when discharge and conductivity are still unaffected by it, representing important sources of diffuse pollution.

Results presented in this study suggest that both caffeine and PBDEs can be considered suitable tracers of domestic sewage discharges. In particular, caffeine, as also indicated by other studies, is mostly found in dissolved phase, while PBDEs (congener BDE-209, in particular) are mainly

bound to suspended particulate matter. As a general conclusion, the study underlines the importance of using surrogate variables, possibly measured in continuous fashion, to identify different active sources of pollution. In these situations it is important to determine with a good degree of accuracy the source of contaminants entering a stream during high flow events. Replication of the approach described in this study to other watersheds could provide similarly important information with reduced monitoring effort. This approach could also be introduced in the control procedures adopted by basin management authorities.

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