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Transport of sediment borne contaminants in a Mediterranean river during a high flow event

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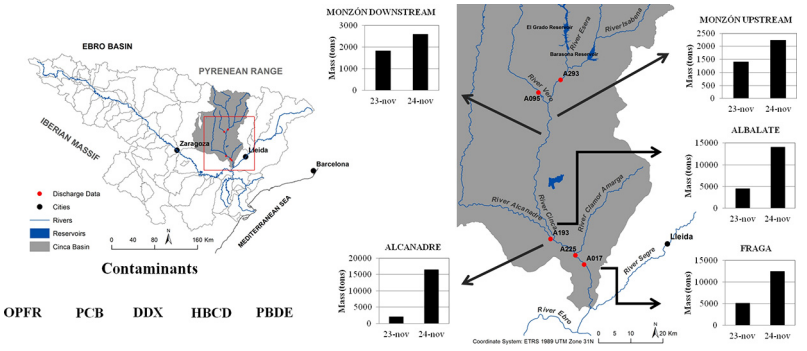
HIGHLIGHTS

- An analysis was performed during a flood event to study the dynamics of sediment borne contaminants in the River Cinca
- Focus was set on substances traditionally used in chemical industries of the area and identified in previous studies
- Sediment transport showed a clockwise hysteresis during the flood event
- The flood mobilized high amounts of PCBs and PFRs
- There is apparently a re-location of the focus of contaminated sediment from the middle to the low reaches of the river

GRAPHICAL ABSTRACT



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ABSTRACT

Pollutants' dynamics in rivers flowing through industrial areas is linked to the entrainment and transport of contaminants attached to solid particles. The transport of sediment is mainly associated to high discharges and flood episodes, and these events constitute one of the main factors causing fluxes of buried pollutants in rivers. We performed a field study in the lower River Cinca (Ebro basin, Northeast Spain) to quantify the mobilization and transfer of several contaminants present in the river bed sediments. We focused on contaminants previously identified (PCBs, DDXs, PBDEs, HBCDs and PFRs) to occur in the river. River bed sediment samples were collected during low flows and a subsequent sampling campaign was used to capture sediment borne contaminants during a flood event. Water samples were taken at the same locations as the static sediment samples and used to determine the suspended sediment concentrations and the contaminants content (i.e. mass of contaminant per sediment mass unit) during the event. We estimated mass fluxes for both sediment and pollutants, and determined that sediment transport followed a clockwise hysteresis. This is typically observed in high flow events after dry summer periods. With sediments there was a large mobilization of PFRs (36 kg in 48 h in one of the main tributaries) and PCBs not previously observed in the static sediment. Observed contaminant load ranges during the two-day sampling campaign were: PCB (34–152 g), DDT (12–213 g), PBDE (50–1740 g), HBCD (0–2.2 g) and PFR (2410–35,895 g). An environmental risk assessment was carried out by comparing the pollutant concentrations found in the sediments with the Canadian quality guidelines (ISQC), showing a significant noncompliance

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for PCBs in dynamic sediments. Our results point out to the need of a regular assessment of the downstream transfer of the sediment-borne pollutants in drainage basins historically affected by intense industrial activities and associated contamination.

1. Introduction

Urban and industrial areas act as focus of contaminants to the river beds. Contaminants are transported with the water flow either dissolved or bound to suspended solids (Quesada et al., 2014; Nasrabadi et al., 2018). Understanding the dynamics and fate of these contaminants is fundamental to water quality assessment. Transport of pollutants is often linked to sediment dynamics, especially for those substances with chemical properties that enhance their capability to attach to a particle surface. This causes contaminants to accumulate in river areas where deposition is favoured, such as lowlands, reservoirs, estuaries and deltas (Herrero et al., 2013). Mobilization of pollutants is linked to flood events, when river bed sediments are set into transport (Rügner et al., 2013, 2014; Schwientek et al., 2013), and ultimately may reach the marine environment (Gómez-Gutiérrez et al., 2006). Flood events are expected to accentuate according to the predictions on climate change (IPCC, Lehner et al., 2006) especially in the Mediterranean area, where climate is already characterized by extreme rainfall events that are followed by long drought periods (e.g. Ceballos-Barbancho et al., 2008; González-Hidalgo et al., 2010; López-Moreno et al., 2010).

Previous studies have analysed the presence of contaminants in the Ebro catchment. These studies determined the occurrence of polycyclic aromatic hydrocarbons (PAHs; Lacorte et al., 2006, Quesada et al., 2014), organochlorine compounds (OCs) (such as dichlorodiphenyltrichloroethane and its degradation products, DDXs; polychlorinated biphenyl, PCBs; hexachlorobenzene, HCB; and hexachlorocyclohexane, HCHs; Fernández et al., 1999, Gómez-Gutiérrez et al., 2006, Lacorte et al., 2006, Quesada et al., 2014), polybrominated diphenyl ethers (PBDEs; Lacorte et al., 2006) and polar pesticides (Gómez-Gutiérrez et al., 2006). There was not any clear conclusion concerning contaminants concentration. While some studies suggested an increase in the downstream direction (Fernández et al., 1999) and the influence of industrial hot spots (Navarro-Ortega et al., 2010; Quesada et al., 2014), others did not detect a particular trend and suggested a low-level diffuse pollution (Lacorte et al., 2006). Most of the studies were focused on steady sediments (i.e. sediments resting in the river bed and channel banks) whereas only a few explored the dynamics of pollutants associated with transported sediments (Gómez-Gutiérrez et al., 2006; Quesada et al., 2014). The origin of the pollutants is also diverse. OCs have been observed associated to flood periods, either in natural conditions (Gómez-Gutiérrez et al., 2006) or associated with flushing flows in heavily polluted industrial sites (Quesada et al., 2014). But others such as the PAHs seem to be related to diffuse pollution (Quesada et al., 2014), while more water soluble pollutants such as agrochemicals present changing concentrations as a consequence of seasonal use (Gómez-Gutiérrez et al., 2006). Studies in other catchments show similar results and stress the increase in sediment loads under increasing levels of urbanization (Liu et al., 2012).

Flame retardants (FR) encompass many of the pollutant substances found in the Cinca basin. Flame retardants are incorporated into polymers in order to prevent combustion and to delay the spread of fire after ignition. However, the usage patterns of FRs are changing in light of environmental hazard and exposure data and new regulations. Following the phase-out of PBDEs, the PFRs have been proposed as replacement. Thanks to their excellent physicochemical properties, technical characteristics and low cost, these compounds are used as FRs, but also as plasticizers and anti-foaming agents in a variety of consumer products (van de Plassche et al., 2002). Another example of the use of PFRs is in PVC as plasticizers (WHO, 1998; WHO, 2000). A number of other applications to which PFRs are added include furniture, textile coatings, upholstery, electronics, paints, polyurethane foams, lubricants and hydraulic fluids.

This study analyses the dynamics of contaminants associated with sediment transport along a river reach in one of the main tributaries of the Ebro catchment, the River Cinca. We specifically aimed to: 1) identify the main contaminants present in the river bed sediment; 2) analyse the sediment-associated transport of these substances during a flood event and 3) quantify the pollutant mass fluxes and characterize potential areas of deposition or pollution hot spots.

2. Study area

This study was performed in the middle and lower course of the River Cinca (Fig. 1). The basin has forested areas in the headwaters and large agricultural zones in the midlands and lowlands. Forest increased during the second half of the 20th century associated with the abandonment of farmlands (López-Moreno et al., 2008). This process caused a reduction in water yield (Gallart and Llorens, 2004). Though there are not large cities in the basin, there is an important industrial activity, which causes the presence of different pollution sources along the river. Specifically, Monzón is a heavily industrialized town with a very important chemical industry. In this area high levels of contamination of brominated flame retardants (BFRs), PBDEs and hexabromocyclododecane (HBCD), were observed, which are currently banned (Eljarrat et al., 2004a, 2005; UNEP, 2015). Further studies indicated the occurrence of industrial pollution (Eljarrat et al., 2007; Guerra et al., 2009). Industrial activities produce EPS (expandable polystyrene), which are treated with flame retardants, as well as ABS (acrylonitrile-butadiene-styrene) and PVC (polyvinyl chloride). The analysis of static sediments in the river showed that HBCD was not detected 70 km downstream of its source. These former studies also observed the presence of DDT. Although forbidden since 2001, this product has been used as an intermediate in the production of dicofol in one of the industries near Monzón (van de Plassche et al., 2002) and its spill to the Cinca attracted public attention (de la Cal et al., 2008). DDT and its metabolites, DDD and DDE, have been shown to be recalcitrant to degradation. DDT, DDE, and DDD last in the soil/sediment for a very long time, depending on many factors including temperature, type of soil/sediment, etc. It has been estimated that they can potentially last for hundreds of years (ATSDR, 2002). Further details on geographic and climatic characteristics of the study are provided in the supplementary material of the paper.

3. Methods

3.1. Flow discharge

Discharge series used in this analysis were obtained from the Ebro Water Authorities (Confederación Hidrográfica del Ebro, CHE, www.saihebro.com). Fig. 1 shows the location of the stations involved in this study. Discharge at the gauging sites of Fraga (A017) and Alcanadre-Ballobar (A193) was directly obtained from the CHE stations. Discharge at the Albalate site was obtained by subtracting the discharge at stations A225 and A193 from the discharge at station A017. Finally, the discharge at the sites Monzón_{up} and Monzón_{down} was considered the same and evaluated as the addition of the discharges at stations A293 and A095 (see Fig. 1 for location details).

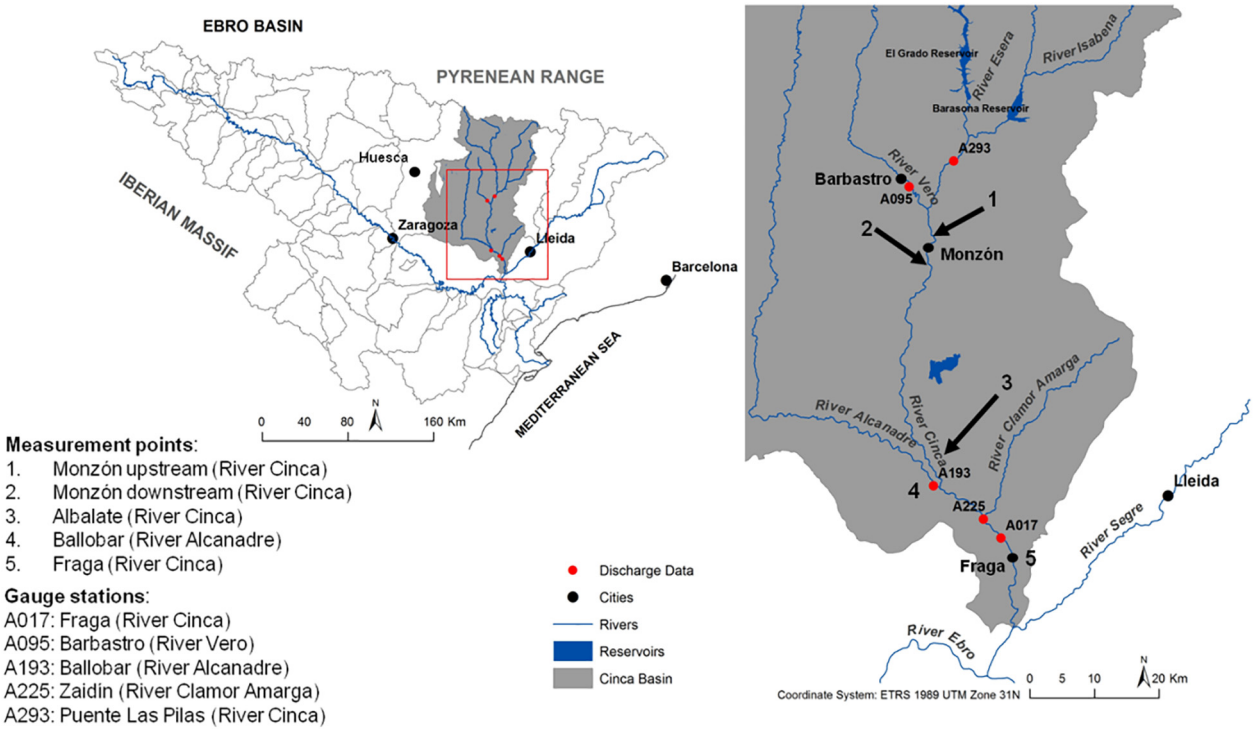

Fig. 1. The River Cinca catchment in the NE of Spain and the Ebro basin. The five monitoring sites of this study are shown (Sites 1, 2, 4 and 5 are located in the mainstem Cinca and site 3 is in the River Alcanadre).

3.2. Sediment sampling

Suspended sediment concentrations (*SSC*) were derived from direct sampling performed from bridges located near to the selected study sections. Suspended sediments were sampled during a flood event (November 23rd and November 24th 2016) by means of a cable-suspended bucket sampler. Due to limitations in the feasible amount of chemical analyses, the sampling campaign was performed during the period with the highest rainfall intensity of the flood event, which lasted from November 22nd to November 30th. Two replicate samples were taken from each site and each day (Table 1). The volume of water from each sample was such that the amount of sediment was enough for the detection of the searched contaminants i.e. 1 g dry weight (dw) approximately. Water was poured into plastic containers, transported and stored in a refrigerated environment (5 °C). The transfer of hydrophobic pollutants from the suspension to the plastic container was not significant. The water samples were afterwards vacuum filtered at the laboratory by means of glass microfiber filters (Diameter: 47 mm, pore size: 0.7 μm). The filters including the collected sediment were covered with aluminium foil in order to preserve samples from chemical alteration. Two plastic containers were filled with de-ionized water and kept in the same environment as the river samples in order to check for the effect of the plastic containers. Additionally, sediment samples were taken from the river bed during low flow conditions (as for suspended sediment, two replicate samples were taken from each site). The sediment taken from the bed was stored in a refrigerated environment (5 °C). These samples were taken during June 2016 (before to the targeted flood event) and are here used for comparison with the suspended sediment. Moreover, data from a turbidimeter placed at Fraga gauge station were available for the whole event. Turbidity data were calibrated based on available samples in order to obtain suspended sediment concentration.

Table 1
Suspended sediment concentrations obtained from the collected samples at the different sampling locations (see Fig. 1 for details).

Site	Sampling time	Q (m^3/s)[1]	C (g/l)[2]	SL (kg/s)[3]
Cinca - Fraga	Nov 23rd 1:20 pm	130.4	0.55	71.7
Alcanadre - Ballobar	Nov 23rd 2:10 pm	33.9	0.49	16.6
Cinca – Albalate	Nov 23rd 3:10 pm	93.4	0.56	52.3
Cinca – $Monzón_{down}$	Nov 23rd 4:10 pm	38.5	0.55	21.2
Cinca – $Monzón_{up}$	Nov 23rd 5:00 pm	36.8	0.42	15.5
Cinca - Fraga	Nov 24th 2:30 pm	265.5	0.81	215.1
Alcanadre - Ballobar	Nov 24th 3:10 pm	120.8	1.42	171.6
Cinca – Albalate	Nov 24th 4:20 pm	148.2	1.09	161.5
Cinca – $Monzón_{down}$	Nov 24th 4:55 pm	65.4	0.46	30.1
Cinca – $Monzón_{up}$	Nov 24th 5:45 pm	63.7	0.40	25.5

[1] Flow discharge.
[2] Suspended sediment concentration.
[3] Sediment load.

3.3. Chemical analysis

Different families of organic pollutants including some legislated and some emerging were included in this study. OCs, PCBs, PBDEs, and HBCD are amongst the currently banned compounds, whereas decabromodiphenylethane (DBDPE) and organophosphorus flame retardants (PFRs) belong to the group of emerging pollutants and are widely used today. Table S1 shows the complete list of analytes as well as their physicochemical properties. All the legislated compounds and DBDPE have high octanol/water partition coefficient (log K_{OW}) values, ranging between 5.07 and 11.2; while PFRs constitute a family with a wide range of log K_{OW} values ranging from 1.44 to 9.49. Generally, high log K_{OW} values enhance the capacity of chemicals to be adsorbed to the sediments. However, particle borne transport predominates if the distribution or partitioning coefficient (K_d) is larger than the water-to-solid ratio. The latter here is around 1000 l/kg and thus only compounds with $K_d \geq 1000$ kg/l are affected. Assuming an organic matter content (f_{oc}) of approx. 1%, and considering that $K_d \approx K_{OW} \cdot f_{oc}$ only

compounds with log $K_{OW} > 5$ are predominantly transported by particles.

3.4. Sample preparation

The extraction of OCs, PCBs, PBDEs and HBCD from sediments was performed by selective pressurized liquid extraction (SPLE) (de la Cal et al., 2003). Freeze-dried sediment (1 g dw) was spiked with labeled internal standards, d_8-4.4′-DDT, d_8-4.4′-DDE, ^{13}C-PCBs, ^{13}C-PBDEs, and d_{18}-HBCD. The sample was grown with alumina and copper (1:2:2) and loaded into an extraction cell previously filled with alumina (6 g). SPLE was used using hexane:dichloromethane (1:1) as solvent extraction. Extracts were reconstituted in 40 μl of toluene for the instrumental analysis. The extraction of PFRs was carried out by PLE (Giulivo et al., 2016). Freeze-dried sample (1 g dw) was extracted with hexane:acetone (1:1). Purification was performed on-line at the beginning of the instrumental analysis. Labeled PFRs standards were added prior to analysis by turbulent flow chromatography (TFC) coupled to LC-MS-MS, correcting the possible fluctuations of the analytical instrument.

3.5. Instrumental analysis

OCs, PCBs, and PBDEs were analysed with an Agilent 7890A gas chromatograph coupled to an Agilent 7000B triple quadrupole mass spectrometer. Chromatographic separation was carried out by gas chromatography (GC) with a DB-5 ms column (15 m × 0.25 mm × 0.1 μm of film thickness). Tandem mass spectrometric determination (MS-MS) was carried out using electron ionization (EI) at 300 °C. The instrumental conditions were based on a previous work (Barón et al., 2014a). Due to the low sensibility of GC-EI-MS-MS for decabrominated compounds, BDE-209 and DBDPE were analysed by GC-MS with the same chromatographic conditions in an Agilent 5975A mass spectrometer, using negative chemical ionization (NCI) at 250 °C (Eljarrat et al., 2004b). On the other hand, HBCD was analysed by liquid chromatography coupled to tandem mass spectrometry (LC-MS-MS) with a hybrid triple quadrupole linear ion trap Applied Biosystem MSD Sciex 4000QTRAP instrument (Applied Biosystems, Foster City, CA, USA) equipped with an electrospray (ESI) Turbospray interface. Chromatographic separation was carried out with a Symmetry C_{18} column (2.1 mm × 150 mm, 5 μm) preceded by a C_{18} guard column (2.1 × 10 mm). Experiments were carried out in negative ionization mode using H_2O: methanol (3:1 v/v) at a flow rate of 0.25 ml/min (Guerra et al., 2008).

For PFRs, online sample purification and LC-MS-MS analysis were performed with a Thermo Scientific TurboFlow™ system according to previous work (Giulivo et al., 2016). CycloneTM-P (0.5 × 50 mm) and C18-XL (0.5 × 50 mm) columns were used in combination for purification. Chromatographic separation was achieved with an analytical column Purosphere Star RP-18 (125 mm × 0.2 mm). Mobile phase was a gradient of water (0.1% formic acid) and methanol (0.1% formic acid) at 0.75 ml/ min. Mass spectrometric analysis was performed with a triple quadrupole with a heated-electrospray ionization source. LC flow rate was 5 μl min^{-1}, ion transfer tube temperature was 320 °C and vaporizer temperature was 50 °C. The Selective Reaction Monitoring (SRM) mode was used for all the chemical analyses, with two transitions monitored, the most intense one for quantification and the second one for confirmation. Quantification was carried out by isotopic dilution method based on the use of labeled standards. Table S2 shows the quality parameters of the different analytical methods used, such as recoveries, reproducibility (RSD), method limits of detection (mLODs) and method limits of quantification (mLOQs) of all the analysed compounds. Recoveries ranged from 55 to 120%, being always within the range established as acceptable by isotopic dilution methods (40–120%). In addition, reproducibility was also good, below 20% in all case (i.e. from 1 to 15.7%).

4. Results

4.1. Discharge

Fig. 2 shows flow hydrographs at the different study sites during the monitored event. Water flow data were used to evaluate the *Q* at the sites where sediment samples were taken for the subsequent analysis of contaminants. The gauging station of Puente Las Pilas directly measures the flows released from the Grado Dam, and displayed a very low flow for most of the study event. However, a short and sharp peak (70 m^3/s; November 24th 11 am) occurred associated with the opening of Grado gates to alleviate a large incoming discharge.

Further downstream, the hydrograph shape of the River Alcanadre in Ballobar (near the confluence with the Cinca) was notably similar to the one observed in the lowermost section of Fraga, suggesting the major contribution of this tributary to the overall flood event. A peak *Q* of 252 m^3/s was measured shortly before the peak in Fraga (November 25th 2 am). The River Vero had a less significant but still remarkable contribution to the overall flood event. The hydrograph in Barbastro (near the confluence with the Cinca) showed a characteristic two-peak shape and a largest *Q* of 103 m^3/s (November 24th 5 am). The Alcanadre and the Vero are non-dammed rivers where the hydrological response directly follows the rainfall input from the upstream basin. Finally the lowermost gauge station of Fraga showed an initial *Q* phase with a constant base flow of around 40 m^3/s followed by a progressive increase that occurred from November 22nd (10 am) until November 25th (5 am). The peak discharge attained 416 m^3/s and it was followed by a falling limb more abrupt than the rising limb. The flood receded at around 125 m^3/s (November 26th 2 pm) and the subsequent descent was more progressive. As a reference, measured *Q* in Fraga and Ballobar corresponded to a return period of ca. 1 and 2 years, respectively.

4.2. Sediment transport

Table 1 shows the results of *SSC*. Concentrations during November 23rd were similar across the different measurement sites and lower than those obtained in November 24th, in parallel with a rise in *Q* on that date. An exception occurred in Monzón, where *Q* increased the second day but concentrations remained constant or slightly lower. The rate of increase of *SSC* varied amongst the different sites, and was the highest in the River Alcanadre. Sediment mass flux associated with

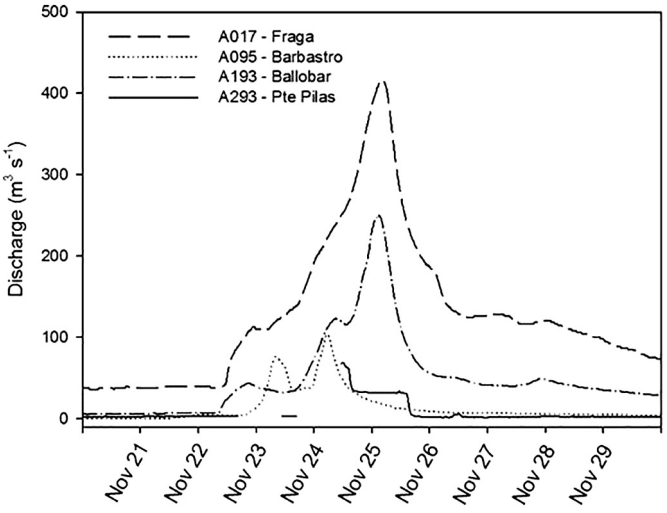

Fig. 2. Flood hydrographs during the November 23rd and 24th 2016 flood event at the different gauging stations in the River Cinca basin (see Fig. 1 for location details). A017: Fraga (River Cinca); A095: Barbastro (River Vero); A193: Ballobar (River Alcanadre); A293: Puente Las Pilas (River Cinca).

the suspended sediment transport was calculated as the product of *Q* and *SSC* (Table 1). The mass flux was higher during November 24th.

Turbidity data available in the Fraga gauge station (Fig. 3a) were used to quantify the suspended sediment transport at this point during the whole event (November 20th until November 30th). Fig. 3b shows the relationship between *Q* and *SSC*, highlighting a clockwise hysteresis cycle. The peak in suspended sediment concentration occurred slightly before the peak in *Q* and concentrations during the rising limb were 30 to 50% higher than during the falling limb. Divergence between rising and falling limbs started at a *Q* of ca. 250 m^3/s. Below this value the curve *SSC* - *Q* was similar for both stages, and could be adjusted using a power law relationship (Leopold and Maddock, 1953) which in our case was $SSC = 0.246 \cdot Q^{0.171}$ ($R^2 = 0.795$). Based on *Q* and *SSC* data, we computed the mass of sediment transported through Fraga gauge station from November 20th until November 30th (Fig. 4). The total mass mobilized was slightly above 85,000 tons. November 25th was the day with the highest mass flux (30%, ca. 25,000 tons) and the period from November 23rd to November 26th concentrates 72% (59,970 tons) of the total mass.

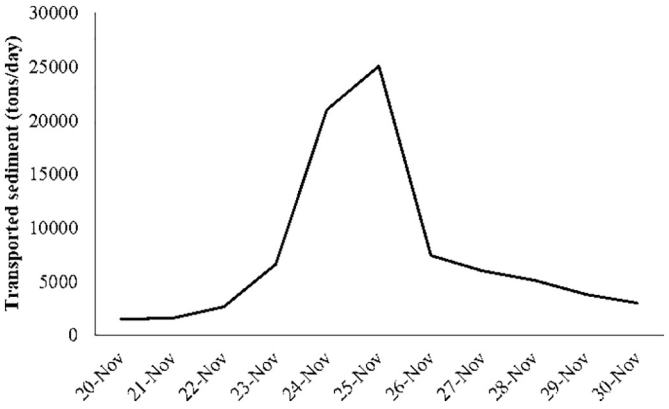

Fig. 4. Total mass of sediment transported in Fraga based on turbidity data.

4.3. Contaminants dynamics

The static sediment samples were used to identify the contaminants present in the sediments of the River Cinca (See Fig. 5). Previous studies carried out in this area were also taken as a reference to estimate potential contaminant concentrations (Eljarrat et al., 2004a; Eljarrat et al., 2005). We therefore focused our analyses on PCBs, DDXs, PBDEs, HBCDs, emerging BFRs, such as DBDPE, and PFRs. Results are presented in Table 2 (for individual analytical results see Supporting Information, Table S3).

Relatively constant and moderate concentrations of PBDEs were found in all the static sediment samples, being slightly higher in Albalate (ca. 10 ng g^{-1}, on average). In contrast, concentrations of HBCDs were variable, with very low concentrations in the lower area of study and a sharp peak in $Monzón_{down}$, which contrasts with the non-detectable values in $Monzón_{up}$. A high concentration of DBDPE was found in the Cinca-Ballobar site, whereas in the rest of the stations were generally moderate. PCBs were not detected in the static sediments. The obtained values for DDXs concentrations were moderate (lower than 12 ng g^{-1}), being the highest the ones of Cinca-Ballobar. Finally, high values in concentrations of PFRs were found in the lowermost site (Fraga) and Alcanadre, being moderate in the upstream sites of the Cinca.

Table 3 and Fig. 5 show the contaminant concentrations on the suspended sediment samples collected during the high flow event (for individual analytical results see Supporting Information, Table S4). PBDEs concentrations are consistent with those observed in the static sediment (Fig. 6). The highest concentrations were measured in the samples of $Monzón_{up}$ and $Monzón_{down}$, especially in November 23rd, when results were slightly higher and the samples of Cinca-Ballobar slightly lower. Concentrations were generally higher during November 23rd, except for those obtained in $Monzón_{down}$. The vast majority of the PBDEs content is in the form of BDE-209 (Table S3 and Table S4, see supplementary material), both in the static sediment and in the suspended sediment.

The HBCDs in the suspended sediment samples differed from those in the static sediment (Fig. 6), and concentrations were very low. HBCDs were not detected at the mouth of the Alcanadre (Ballobar site). The peaks observed in $Monzón_{down}$ for the static sediment were not detected in the suspended sediment. There were no systematic or significant differences between the results of November 23rd and November 24th. HBCD presence was in the form of α-HBCD and γ-HBCD, both in the static and the suspended sediment.

DBDPE concentrations in the suspended sediment were generally higher than in the static sediment, except in Albalate. This substance mobilized along the investigated river reach. Especially remarkable are the values in the two stations of Monzón (UP and DOWN), significantly higher than those obtained in the static sediment. Concentrations were generally higher during the second day of measurements, except for $Monzón_{down}$, where they were lower.

PCBs were not detected in the static sediment but achieved high concentrations in the suspended sediment in Fraga, Alcanadre, and $Monzón_{up}$ sites. These values were observed especially during the first day, and decreased in the second, particularly in Fraga where they were very low. PCBs were mainly dominated by PCB-118.

There was a high correlation between DDXs concentrations in steady and suspended sediments. DDXs were found in moderate concentrations, the highest values being recorded in Albalate and $Monzón_{up}$. The highest contributions to DDXs concentrations were in the form of

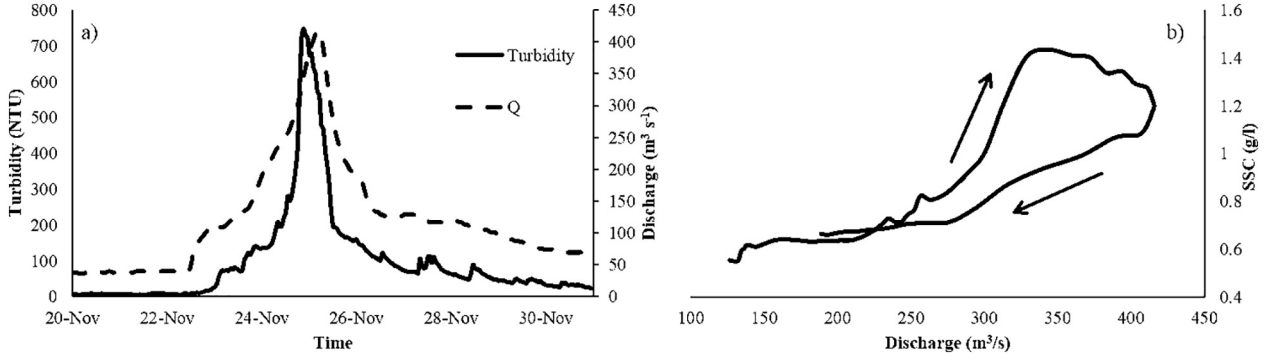

Fig. 3. a) Time series of turbidity and *Q* (m^3/s) in the River Cinca at the Fraga gauging station. b) Suspended sediment concentration vs *Q* at the Fraga gauging station. Arrows indicate the clockwise hysteretic followed by the sediment concentrations, suggesting a deficit of sediment supply during the flood event.

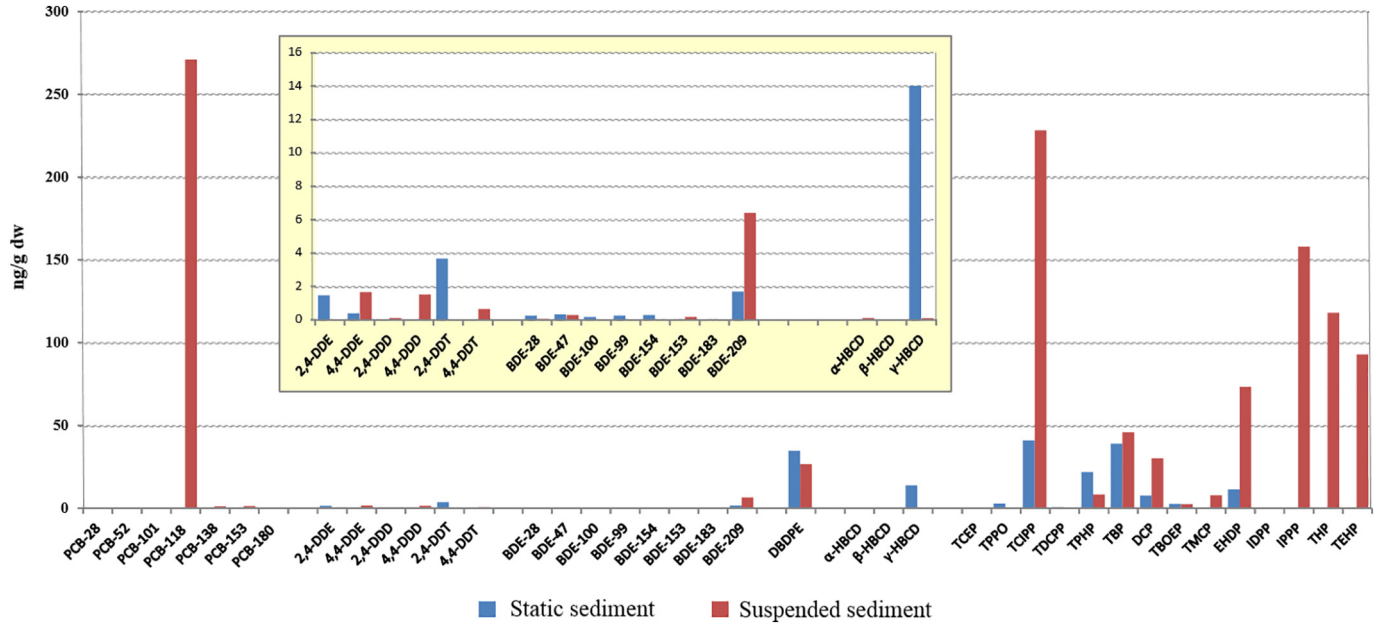

Fig. 5. Comparison between profiles of contaminants in static and suspended sediments collected in the Fraga measuring station (Data correspond to mean values obtained from both replicates).

4.4 – DDD, indicating an old contamination since, in the environment, DDT degrades to DDE and DDD (e.g. Metcalf, 1973).

The PFRs concentrations in the suspended sediment samples were high in all the stations. Concentrations were also high in the static sediment, indicating their large mobilization from both the Alcanadre and the Cinca during the event. Several specific compounds contributed to the total concentration of PFRs, being the most important *tris* (chloroisopropyl)-phosphate (TCIPP), 2-ethylhexyldiphenyl phosphate (EHDP), isopropyl phenyl phosphate (IPPP), trihexyl phosphate (THP) and *tris*(2-ethylhexyl) phosphate (TEHP).

Contaminant mass fluxes (g s^{-1}) were obtained from the product of the measurements of contaminant content in the sediment, the *SSC* and mean *Q* (Fig. 6). Fluxes of PBDEs in the Cinca were higher than in the Alcanadre, although most of them remain in the order of 1 mg s^{-1} or less. Even lower were the fluxes of HBCDs, just above the limit of detection. PCBs fluxes were high during the first day, specifically in Fraga (around 18 mg s^{-1}), but values above 1 mg s^{-1} were also obtained in Alcanadre and in $Monzón_{up}$. Concerning DDXs, mass fluxes were from low to moderate (Albalate and Fraga). Above all, the mass fluxes of PFRs reached up to 402 mg s^{-1} in the Alcanadre, and high values were also obtained in Fraga and in Albalate.

We calculated the mass of contaminant transported during the sampling campaign based on the above results (See Table 4). Moreover, sediment transport data derived from the turbidity data in Fraga were used to estimate the mass of contaminant mobilized during the whole event (November 20th–November 30th) at this point. The estimated transported mass of contaminant of PCBs and PFRs was above 50 kg. The transport of the other contaminants was much lower. These results should be taken as approximate, given the average contaminant content of the sampling campaign might not be representative of the whole event (Fig. 3).

5. Discussion

The analysis we performed highlights an important mobilization of contaminants in the River Cinca. Substances detected in the static sediment were mostly present in the suspended sediment transported during the event: only PCBs were detected in the dynamic (i.e. transported) sediment but had not been previously found in the static samples, indicating for the presence of other sources of polluted sediments, likely in the reach between Monzón and Albalate (Fig. 1). This study confirms

Table 2
Concentration levels, expressed in ng g^{-1} dw, in static sediments (results correspond to the average of the two replicates) (see Fig. 1 for location details).

Site	ΣPCBs[3]	ΣDDXs[3]	ΣPBDEs[3]	DBDPE[3]	ΣHBCDs[3]	ΣPFRs[3]
Cinca – $Monzón_{up}$	nq[1]	1.80	5.68	7.81	nd[2]	39.9
Cinca – $Monzón_{down}$	nq[1]	3.27	7.91	9.97	189	18.8
Cinca - Alcanadre	nq[1]	7.69	1.91	17.8	nd[2]	112
Cinca - Ballobar	nq[1]	11.9	11.2	121	9.52	105
Cinca - Fraga	nq[1]	5.58	3.06	34.8	14.0	127

[1] nq: not quantifiable.
[2] nd: not detected.
[3] PCBs: polychlorinated biphenyls; DDXs: dichlorodiphenyltrichloroethane; PBDEs: polybrominated diphenyl ether; DBDPE: decabromodiphenyl ethane; HBCDs: hexabromocyclododecane; and PFRs: organophosphorus flame retardants.

Table 3
Contaminant content, expressed in ng g-1 dw, in dynamic sediments (results corresponded to the average of two replicates).

	ΣPCBs[2]	ΣDDXs[2]	ΣPBDEs[2]	ΣHBCDs[2]	ΣPFRs[2]
$Monzón_{up}$ 23/11	105	1.73	16.2	0.31	1478
$Monzón_{up}$ 24/11	17.9	8.94	5.07	0.19	210
$Monzón_{down}$ 23/11	1.29	8.27	8.89	0.26	763
$Monzón_{down}$ 24/11	34.2	6.80	10.7	0.17	732
Albalate 23/11	21.6	11.2	6.56	0.46	805
Albalate 24/11	3.27	11.6	6.21	0.05	790
Ballobar 23/11	138	11.5	3.13	nd[1]	1200
Ballobar 24/11	1.17	0.23	0.92	nd[1]	2341
Fraga 23/11	277	2.60	8.35	nd[1]	1022
Fraga 24/11	0.95	3.85	5.09	0.22	316
ISQC[3]	34.1	5.3[4]	19[5]	1600	–

[1] nd: not detected.
[2] PCBs: polychlorinated biphenyls; DDXs: dichlorodiphenyltrichloroethane; PBDEs: polybrominated diphenyl ether; DBDPE: decabromodiphenyl ethane; HBCDs: hexabromocyclododecane; and PFRs: organophosphorus flame retardants.
[3] ISQC: Interim Sediment Quality Guidelines. Interim Sediment Quality Guidelines. Canadian Environmental Quality Guidelines Canadian Council of Ministers of the Environment. Results exceeding the corresponding reference value are highlighted in bold.
[4] Limit given for ΣDDX is derived from the respective limits for ΣDDE = 1.42; ΣDDD = 3.54 and ΣDDX = 1.19.
[5] Limit set for BDE-209, which is the major constituent of the mixture.

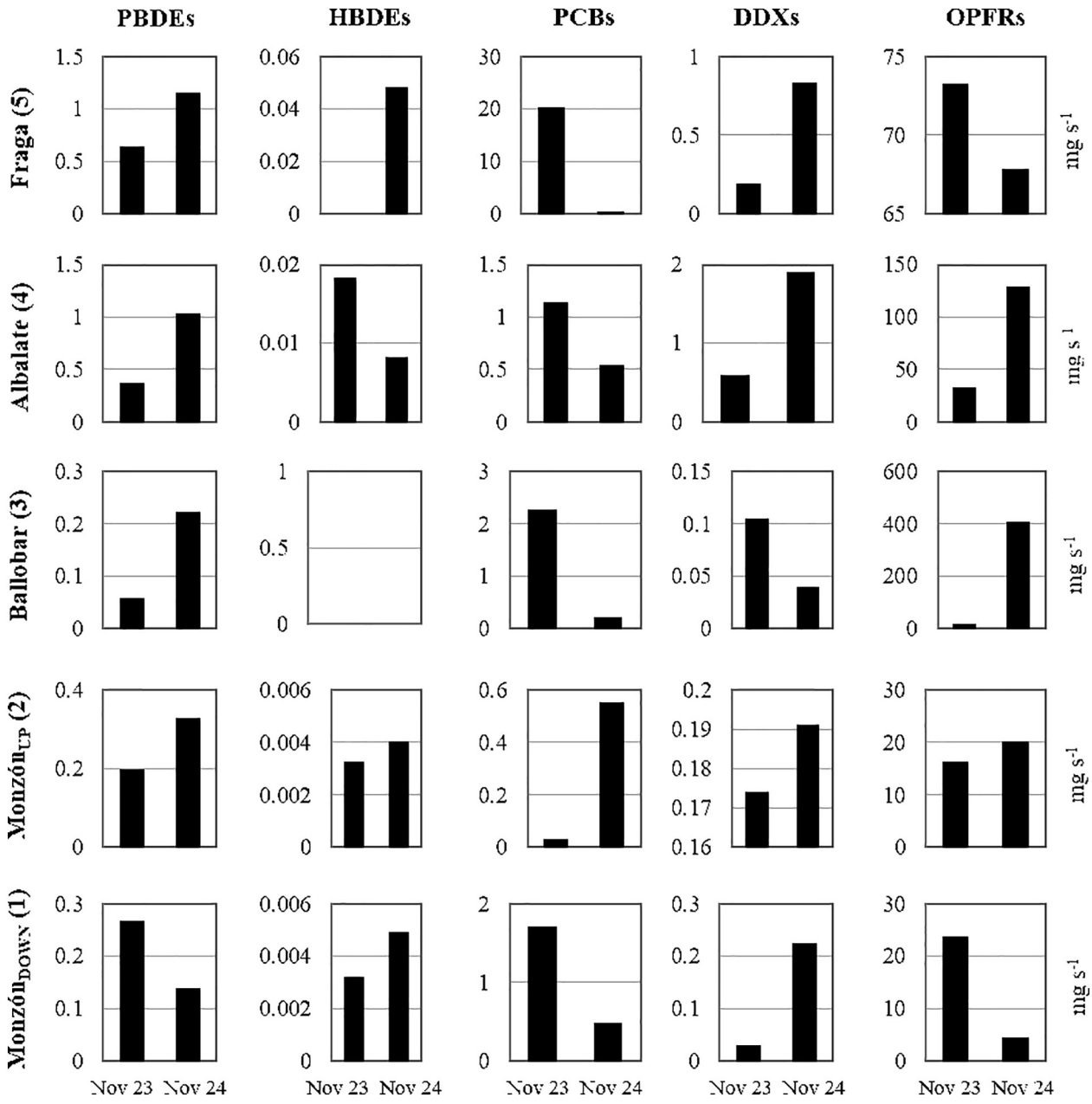

Fig. 6. Contaminant mass flux (mg s^{-1}) at the different measurement sites and for each type of contaminants. Results are based on the chemical analysis of suspended sediment samples taken during the sampling campaign.

Table 4
Mass of transported contaminant for each of the substances analysed. The first row corresponds to the estimated transported mass in Fraga during the whole event (November 20th – November 30th) based on the sediment transport calculated from the turbidity data. The rest of data correspond to the mass of contaminant transported during the sampling campaign (November 23rd – November 24th). PCB: polychlorinated biphenyl; DDX: dichlorodiphenyltrichloroethane and its degradation products; PBDE: polybrominated diphenyl ethers; HBCD: hexabromocyclododecane; PFR: phosphate flame retardants.

Transported mass (kg)	PCB	DDX	PBDE	HBCD	PFR
Fraga (whole event)	11.6	0.269	0.561	0.018	55.8
Monzón$_{UP}$	0.186	0.022	0.035	$6.97 \cdot 10^{-4}$	2.411
Monzón$_{DOWN}$	0.050	0.032	0.045	$6.24 \cdot 10^{-4}$	3.119
Albalate	0.144	0.214	0.120	$2.27 \cdot 10^{-3}$	13.80
Ballobar	0.212	0.012	0.024	0	35.90
Fraga	1.744	0.087	0.153	$4.15 \cdot 10^{-3}$	12.18

the direct link between contaminant dynamics and sediment transport during periods of high discharge.

5.1. Sediment dynamics

The two days of sampling provide results which may be used to obtain a partial estimate of areas with predominant erosion or deposition. Fig. 7 shows the mass of sediment transported through each of the measurement sites during November 23rd and 24th. Notably, the sediment load upstream and downstream of Monzón is much lower than the one observed in the other sites, probably due to the presence of reservoirs upstream of this area. The difference between sites 2 and 4 reflects the mass of sediment eroded between Monzón and the confluence of the Cinca and the Alcanadre. The sediment load accounts for ca. 3500 and 12,000 tons during November 23rd and November 24th respectively. The comparison of the loads between the confluence of the Cinca and

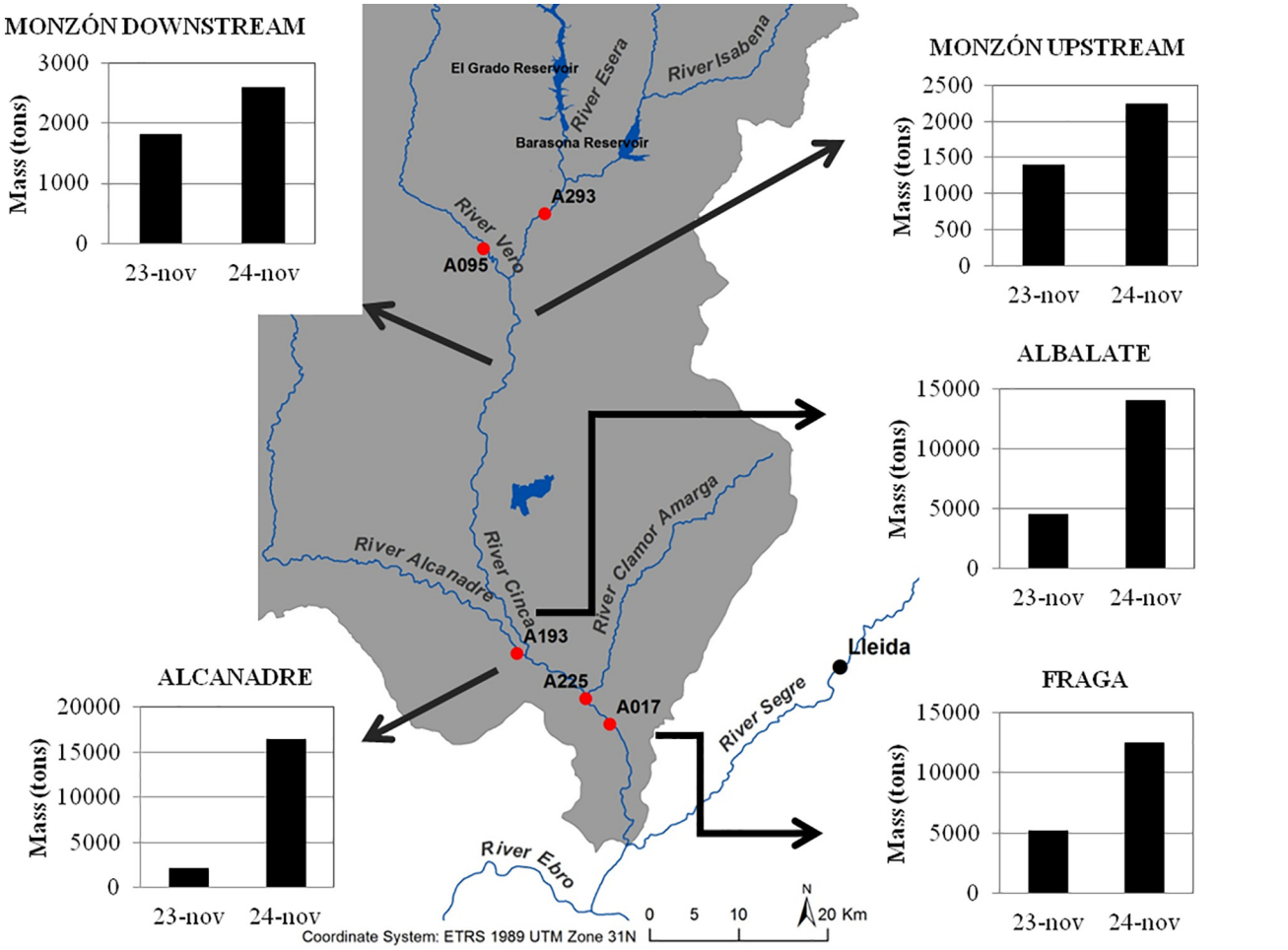

Fig. 7. Mass of sediment transported at each of the measurement sites in the area of study during the November 23rd and November 24th 2016 flood event.

the Alcanadre (sites 3 and 4) and Fraga (site 5), indicates an important deposition of sediment (2000 tons and 18,000 tons during November 23rd and 24th respectively). Deposition of sediment in this section can be interpreted as a consequence of the reduction in the flow transport capacity downstream from the confluence of both rivers, being lower than the sum of the individual transport capacities of each of the rivers.

Turbidity data show a clockwise hysteresis cycle of suspended sediment transport at Fraga gauge station. Even though the relationship between *Q* and suspended sediment concentration (*SSC*) is often assumed to follow a power function (e.g. Church and Gilbert, 1975; Walling, 1977), a large scatter occurs when relating measurements of both variables for a particular site (Gallart et al., 1998; Asselman, 1999; Bača, 2008; Eder et al., 2010; Tena et al., 2011). This variability between flood events accounts for the influence of the amount and intensity of the rainfall (Eder et al., 2010), the soil water content (Olive and Rieger, 1985), land use changes (Klein, 1984) and time of the year (Wood, 1977). This variability in the relationship between *Q* and SSC also exists within a single flood event, and produces complex hysteretic *Q*-SSC cycles. The occurrence of a clockwise hysteresis in sediment transport can be associated with mobilization of sediment in the main channel (Seeger et al., 2004), sediment loads from tributaries near the measurement gauge (Asselman, 1999), sediment depletion (Asselman, 1999; Bača, 2008) and dilution due to base flow contribution during the falling limb of the hydrograph (Wood, 1977). In this case, the pattern observed in the Cinca (Fig. 3) combined with the large mass of sediment transported through the Ballobar and Albalate stations suggests a sediment supply limitation, possibly owing to deposition between the confluence of the Rivers Alcanadre and Cinca, and the Fraga measurement site. The deposited sediment remained available for subsequent high flow events, which could probably show other type of Q-SSC cycles, reflecting the complexity of these hydro-sedimentary processes i.e. such complexity is highlighted in the literature through the occurrence of other types of hysteresis cycles. Anticlockwise hysteresis is observed, when the SSC peak occur after the maximum *Q*. This behaviour is mainly related to sediment sources being far from the measurement site and bank failure at high discharges which puts large amounts of sediment at flow's disposal at late stages of the hydrograph (Asselman, 1999). Anticlockwise hysteresis is also enhanced by a high initial soil water content which favours the contribution of the whole catchment to runoff and sediment mobilization (Seeger et al., 2004). Eight-shaped or even more complex cycles are also observed as a consequence of combinations of the mentioned processes (Eder et al., 2010).

5.2. Contaminants' dispersion

The comparison between results from different sites highlights patterns concerning deposition and mobilization of the analysed contaminants at different parts of the study area. PCBs transported in Fraga are significantly higher than the mass observed at the confluence between rivers Alcanadre and Cinca, suggesting an eventual mobilization from the area upstream of Fraga. DDXs show an opposite behaviour, highlighting mobilization from the area between Monzón and Albalate and deposition after the confluence with River Alcanadre. Concerning PBDEs, mobilization seems relatively homogeneous along the study area, without significant point reaches of erosion or deposition. Results

related to HBCD are very low and difficult to interpret in terms of mass balance at the different reaches. Finally, PFRs show an important focus at the Alcanadre subcatchment and an accumulation at the area between the confluence with the River Cinca and Fraga. It should be noted that these balances refer to the period of the sampling campaign and may show some variations if considered along the whole high flow event.

Furthermore, the results obtained in this study show that contaminant content in both the transported sediment and the static sediment are generally higher in the lower part of the River Cinca. This conclusion is in contrast to previous studies that identified the area of Monzón as an important focus of contaminated sediment as a consequence of the presence of several chemical industries (Eljarrat et al., 2004a, 2004b, 2005). Overall, this study suggests a progressive re-location of the contaminated focus from the middle to the low section of the Cinca basin. The ban of the flame retardants considered in this study in the chemical industries of area has apparently improved the status of river sediments locally but the effects of this industrial activity show a long term inertia that is expected to finish with the accumulation of these pollutants in the reservoirs system of the lower River Ebro.

There was a high spatial and temporal variability in contaminant content in the transported sediments. This variability might be likely due to several factors. One is the irregular spatial distribution of pollutants (in the XYZ directions) throughout the river bed. For example, deep packs of polluted sediments can be only mobilized after the outer layers have been already flushed out. Another is the higher dispersion effects for polluted sediments traveling from long distances than those mobilized closer to the sampling site. A subsequent possibility is that changes in the size of the transported particles may occur, i.e., higher flow velocities can deliver enough energy to mobilize larger sediment particles. Moreover, the distribution of contaminated sediment along the reach upstream of a specific site causes variation of measured contaminant content as sediment transported through that section comes from different origins. This behavior may vary amongst the different compounds, as previous studies have reported i.e. constant PAH loads associated with transported particles (Schwientek et al., 2017). Coping with the aforesaid complexity should require a more comprehensive sampling campaign in terms of space and time coverage, which was not in the scope of this specific study.

In order to have some insight on the environmental relevance of the levels found for the different pollutant families we used the reference values reported in the Canadian Interim Sediment Quality Guidelines (ISQC) (Canadian Council of Ministers of the Environment 2001; Canadian Environmental Protection Act, 2013, and 2016) for DDX, PCBs, PBDE and HBCD which are given in Table 3 and Table S3 (Supplementary Material) for dynamic and static sediments respectively. Reference values for DBDPE and PFRs were not available. Dynamic sediments (Table 3) generally exceeded the reference values for PCBs (ref. value 34 ng g^{-1}) in all the sites monitored by factors up to 7, particularly during the first day of sampling. DDX values were slightly exceeding the reference standards as well, but in the same order of magnitude. PBDEs, which were dominated by BDE-209 (decabromo congener) were equally below the reference limit (19 ng g^{-1}). On the other hand, HBCD was found at levels of 3–4 orders of magnitude below the reference limit (1600 ng g^{-1}). Regarding static sediments (Table S3) the most remarkable difference compared to the dynamic ones refers to PCBs, which were found below the limit of quantification in all the samples analysed. DDX were found at similar levels and close or slightly exceeding the reference values. PBDEs were in general below the reference standards, with the only exception of pentaBDE (BDE-99 and BDE-100) whose limits are more strict (0.4 ng g^{-1}). HBCD levels, though higher than those found in dynamic sediments, are still one order of magnitude below the reference limit.

Finally, results from our study are compared with some of those obtained in related works from the literature published in the last four years (Table 5). Although a large number of published works have reported PBDE levels in river static sediments, there are limited data on emerging PFR. As shown, our PBDE levels were within the concentration ranges obtained in other European locations and slightly lower than the levels found in Asia. Our PFR levels were also within the concentration ranges detected in sediments of rivers from in Europe and Asia.

Table 5
PBDE and PFR concentrations found in static sediments (ng g^{-1} dw) around the world.

Location	Site	ΣPBDEs	ΣPFRs	Reference
Spain	River Ebro	nd - 37.3		Barón et al., 2014b
Spain	River Llobregat	1.50–44.3		Barón et al., 2014b
South Africa	River Gauteng	0.8–44		Olukunle et al., 2014
Netherlands	Western Scheldt estuary	−0.03	<0.1–19.6	Brandsma et al., 2015
North Sea	River Elbe	nd - 0.04		Sühring et al., 2015
China	River Pearlestuary	17.7–43.5		Zhang et al., 2015
North Sea	River Elbe	nd - 0.20		Sühring et al., 2016
Vietnam	Bui Dau	100–350	nq – 4.5	Matsukami et al., 2016
China	River Pearldelta		8.30–470	Tan et al., 2016
Greece	River Evrotas	nd - 4.52	10.5–248	Giulivo et al., 2017
Italy	River Adige	0.26–10.8	11.5–549	Giulivo et al., 2017
Slovenia	River Sava	nq - 16.7	0.31–310	Giulivo et al., 2017

*nd: not detected, nq: not quantifiable.

5.3. Summary and conclusions

This article presents a field study carried out in the River Cinca (NE Spain). The focus was set on the mobilization of different flame retardants (HBCDs, PBDEs, PFRs) and other components associated to suspended sediments during a high flow event. Contaminants are still present in the river bed after chemical industries that were operating in the area (PCBs and DDXs). The combination of sediment mass fluxes and contaminant concentrations measured in the suspended sediments enabled to estimate the load of the different contaminants mobilized during the event surveyed. A total of 84,000 tons of fine sediments in suspension were transported during the monitored event. The main conclusions of the work can be drawn as follows:

1. The profiles found for the various families of contaminants showed significant differences both on space and time. Specifically, there was a large mobilization of PFRs (36 kg in 48 h in one of the main tributaries) and PCBs not previously observed in the static river bed sediments.
2. The high spatial and temporal variability in contaminant content is attributed mainly to the irregular spatial distribution of pollutants in the river bed, together with the higher dispersion effects for polluted sediments traveling from long distances than those mobilized closer to the sampling site.
3. The study suggests the progressive re-location of the contaminated focus from the middle to the lowermost sections of the river. The ban of the flame retardants from the chemical industries may have improved the status of river sediments locally but they still show a long term inertia that will finish with the accumulation of these pollutants in reservoirs of the lower Ebro.

Overall, the research highlights the relevance of flood events on the mobilization of persistent and legacy contaminants associated with suspended sediments, which are particularly important in Mediterranean rivers. Particularly, results from this study show the importance of suspended sediment dynamics on the transport of contaminants in the River Cinca and the influence of the sediment supply sources on the contaminants' dynamics along the basin. An environmental risk assessment of the sediments was carried out by comparing the concentration levels found for some of the pollutants analysed with the Canadian

quality guidelines (ISQC), showing a significant noncompliance for PCBs in dynamic sediments.

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