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# Influence of anthropogenic inputs and a high-magnitude flood event on metal contamination pattern in surface bottom sediments from the Deba River urban catchment

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## HIGHLIGHTS

- Untreated wastewaters effluents increased the organic matter content in sediments
- Untreated industrial inputs increased the metal concentration in sediments
- Anthropogenic inputs and high-magnitude floods determined the metal distribution
- Fine sediments gives a better insight into the state of pollution for most metals

## ABSTRACT

The purpose of this study was to assess the influence of anthropogenic factors (infrastructure construction and industrial and wastewater inputs) and hydrological factors (high-magnitude flood events) on metal and organic contamination and on the source variability of sediments taken from the Deba River and its tributaries. The pollution status was evaluated using a sequential extraction procedure (BCR 701), enrichment factor, individual and global contamination factors and a number of statistical analysis methods. Zn, Cu and Cr were found to have significant input from anthropogenic sources, with moderately severe enrichment, together with an extremely high potential risk of contamination. The principal scavenger of Cu and Cr was organic matter, whereas Zn was uniformly distributed among all non-residual fractions. For Fe, the anthropogenic contribution was more obviously detected in bulk sediments (<2 mm) than in fine fractions (<63 µm). Finally, the recent construction of a rail tunnel traversing Wealden Facies evaporites, together with intense rainfalls, was the main reason for the change in the source variability of bottom sediments and metal distribution in headwaters. The occurrence of a high-magnitude flood event resulted in a washout of the river bed and led to a general decrease in fine-grained sediment and metal concentrations in labile fractions of channel-bottom sediments, and a consequent downstream transfer of the pollution.

### Keywords:

Urban catchment  
Metals  
Sediments  
Anthropogenic inputs  
High-magnitude flood

## 1. Introduction

Since the beginning of industrialization and uncontrolled urbanisation in many catchments, rivers have faced several water and sediment quality problems. Metals are considered to be serious inorganic pollutants because of their toxic effects on life in aquatic systems (Zhuang et al., 1994; Yang et al., 2009; Naji et al., 2010). During the 19th and 20th centuries the main sources of metals in aquatic environments were anthropogenic inputs, especially in urban catchments, mainly from industrial or urban effluents (Suthar et al., 2009; Gupta et al.,

2010; Buzier et al., 2011; Maceda-Veiga et al., 2012), mining activities (Elbaz-Poulichet et al., 2001; Salvarredy-Aranguren et al., 2008; Resongles et al., 2014) and atmospheric deposition (Bur et al., 2009). According to Taylor and Owens (2009), many previous anthropogenic sources dominate the contaminant load in urbanised river catchments. Nevertheless, the presence of metals and suspended particulate matter in aquatic environments may also have a natural origin, such as geological weathering, soil erosion and landslides (Roos and Åström, 2005; Göransson et al., 2009; Nystrand et al., 2012). Additionally, sediment sources, which are a direct result of human activities, also include the construction of urban infrastructures such as railway lines, road and channel networks, tunnels, and dams, among others. Some studies have assessed the effect of infrastructure construction on the retention

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and generation of sediments and on the source variability of those sediments (Rijsdijk et al., 2007; Dai et al., 2008; Wu et al., 2012; Velísková and Dulovičová, 2008). In the present study, the effect of tunnel construction on the source variability of sediments on river bed has been investigated.

It has been widely reported that most of the metals in aquatic systems are associated with the particulate phase; over 99% of pollutants are stored in fine-grained sediments and complexed to organic matter and oxides (Carter et al., 2006; Violintzis et al., 2009; Devesa-Rey et al., 2010a; Bartoli et al., 2012), which act as a vector and reservoir of contaminants (Owens and Xu, 2011). Variations in water and sediment physicochemical conditions could therefore play an important role in their mobilisation in the dissolved phase, where they become more bioavailable and disclose toxic chemical forms (Eggleton and Thomas, 2004; Roussiez et al., 2013).

Although sediment-associated metals accumulate in the river during periods of low discharge, they are resuspended and transported downstream during flood events (Ciszewski, 2001), especially during higher-magnitude floods, where the risk of metal mobilisation increases. Great attention should therefore be paid to the hydrological processes and the transport of sediment-associated metals during flood events. These high-magnitude floods are caused by heavy rain episodes, which can episodically flush large amounts of sediments into the river, particularly when there is important runoff (Old et al., 2003; Zabaleta et al., 2007).

The estuary of the Deba River and its impact on the Bay of Biscay have been investigated for nutrients (Borja et al., 2006), sediment-associated metals (Legorburu et al., 2013) and dissolved metals in marine waters (Tueros et al., 2008); however, no study has addressed the occurrence and distribution of metals in the bottom surface sediments of the Deba River catchment, which is one of the most polluted rivers in the province of Gipuzkoa (Basque Country). This is affected by various factors.

- Deba River is characterised by heavy industrial development and a population increase along it and its tributaries over recent decades. Surface waters receive untreated wastewater inputs from the municipality of Ermua, treated effluents from three wastewater treatment plants and partially treated effluents from several sewers that end up in the Bay of Biscay (Table 1).
- About 6773 m<sup>3</sup> y<sup>-1</sup> of untreated industrial effluents are discharged into the Deba River and its tributaries. According to data provided by Gipuzkoa Provincial Council around 19 t y<sup>-1</sup> of suspended sediments (SS), 1.4 t y<sup>-1</sup> of iron, and 687, 104, 56 and 5 kg y<sup>-1</sup> of zinc, nickel, chromium and copper, respectively, are discharged with these industrial effluents (Table 1).
- As part of the project for a new high-speed rail line, work on the construction of the 4.7 km Albertia tunnel mobilised large amounts of sediments. Sections with the presence of sulphated facies (anhydrites and gypsum) were detected during the top heading excavation of this tunnel (Peña and Rodenas, 2011) and sediments of different lithological origin and chemical composition were consequently exposed to being washed-off during rain episodes.

In this context, this paper aims to: *i*) determine the sites with the highest potential of risk from sediment-associated metals and identify their source of contamination; *ii*) assess the impact of natural or anthropogenic disturbances such as the occurrence of a high-intensity flood and construction of a high-speed rail on source variability and change in metal composition in river-bottom sediments.

## 2. Study area

This study was conducted in the Deba River Catchment (538 km<sup>2</sup>), from headwaters to the Altzola gauging station, in the province of Gipuzkoa (NE of Spain, Fig. 1). The station was considered as the outlet of the catchment because the lower part of this catchment is influenced

**Table 1**

Data of physicochemical characteristics of anthropogenic inputs were analysed and reported by Gipuzkoa Water Consortium (A) and Gipuzkoa Provincial Council (B); A) data of treated (TE) and partially treated (PTE) effluents from wastewater plants and sewers; B) data of untreated industrial effluents (UIE). EC (electrical conductivity), SSC (suspended sediment concentration) and SS (suspended sediment load), COD (chemical oxygen demand). The detection limits (<d.l.) are 5 mg L<sup>-1</sup> for SSC, 1 mg L<sup>-1</sup> for Fe and 0.5 mg L<sup>-1</sup> for the rest of the dissolved metals.

A)													
Sewers or wastewaters plants	Sampling period	Degree of treatment	pH	EC (µS/cm)	SSC (mg L <sup>-1</sup> )	COD (mg O <sub>2</sub> L <sup>-1</sup> )	Fe (mg L <sup>-1</sup> )	Mn (mg L <sup>-1</sup> )	Zn (mg L <sup>-1</sup> )	Cu (mg L <sup>-1</sup> )	Cr (mg L <sup>-1</sup> )	Ni (mg L <sup>-1</sup> )	Pb (mg L <sup>-1</sup> )
Apraitz	Jan 2011–Dec 2012	T.E.	6.4–7.2	353–775	<d.l. – 33	22–83	<d.l. – 2.31	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
Mekolalde	Feb 2011–Dec 2012	T.E.	7.3–7.9	361–730	<d.l. – 30	20–102	<d.l. – 1.2	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
Epele	May–Dec 2012	T.E.	7.2–7.7	520–876	6–34	21–968	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
Arrasate sewer	Jan–Sep 2011	P.T.E.	8.0–8.3	945–1157	213–791	559–914	<d.l. – 11.3	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
Oñati sewer	Jan–Sep 2011	P.T.E.	7.0–7.7	611–1169	165–728	621–1552	<d.l. – 1.12	<d.l.	<d.l. – 0.56	<d.l.	<d.l.	<d.l.	<d.l.
B)													
Location	River	Degree of treatment	Main industrial activities			Discharge (m <sup>3</sup> y <sup>-1</sup> )	COD (kg O <sub>2</sub> y <sup>-1</sup> )	SS (kg y <sup>-1</sup> )	Fe (kg y <sup>-1</sup> )	Cr (kg y <sup>-1</sup> )	Zn (kg y <sup>-1</sup> )	Ni (kg y <sup>-1</sup> )	Cu (kg y <sup>-1</sup> )
Eskoriatza	Deba River	U.I.E.	Smelting factories and automotive industries			90	514	1167	178	4.0	1.0	10	–
Aretxabaleta	Deba River	U.I.E.	Metallurgical factories			648	114	59	1.0	–	1.0	–	–
Arrasate	Deba River	U.I.E.	Metallurgical and electrical appliance factories			1052	1741	2032	63	21	14	53	1.0
Bergara	Deba River	U.I.E.	Galvanising factories, steel industries, machines construction			336	2934	3724	539	22	544	8.0	1.0
Soraluze	Deba River	U.I.E.	Galvanising factories			1780	2947	2133	6.0	–	58	18	–
Elgoibar	Deba River	U.I.E.	Construction of machinery			75	2075	2217	13.0	–	–	–	–
Oñati	Oñati stream	U.I.E.	Steel industries, metallurgical and automotive industries			1262	3365	4905	487	1.0	61	5.0	3.0
Eibar	Ego stream	U.I.E.	Metallurgical and smelting factories			1530	2346	2779	78	8.0	8.0	10	–
Total						6773	16,035	19,017	1365	56	687	104	5

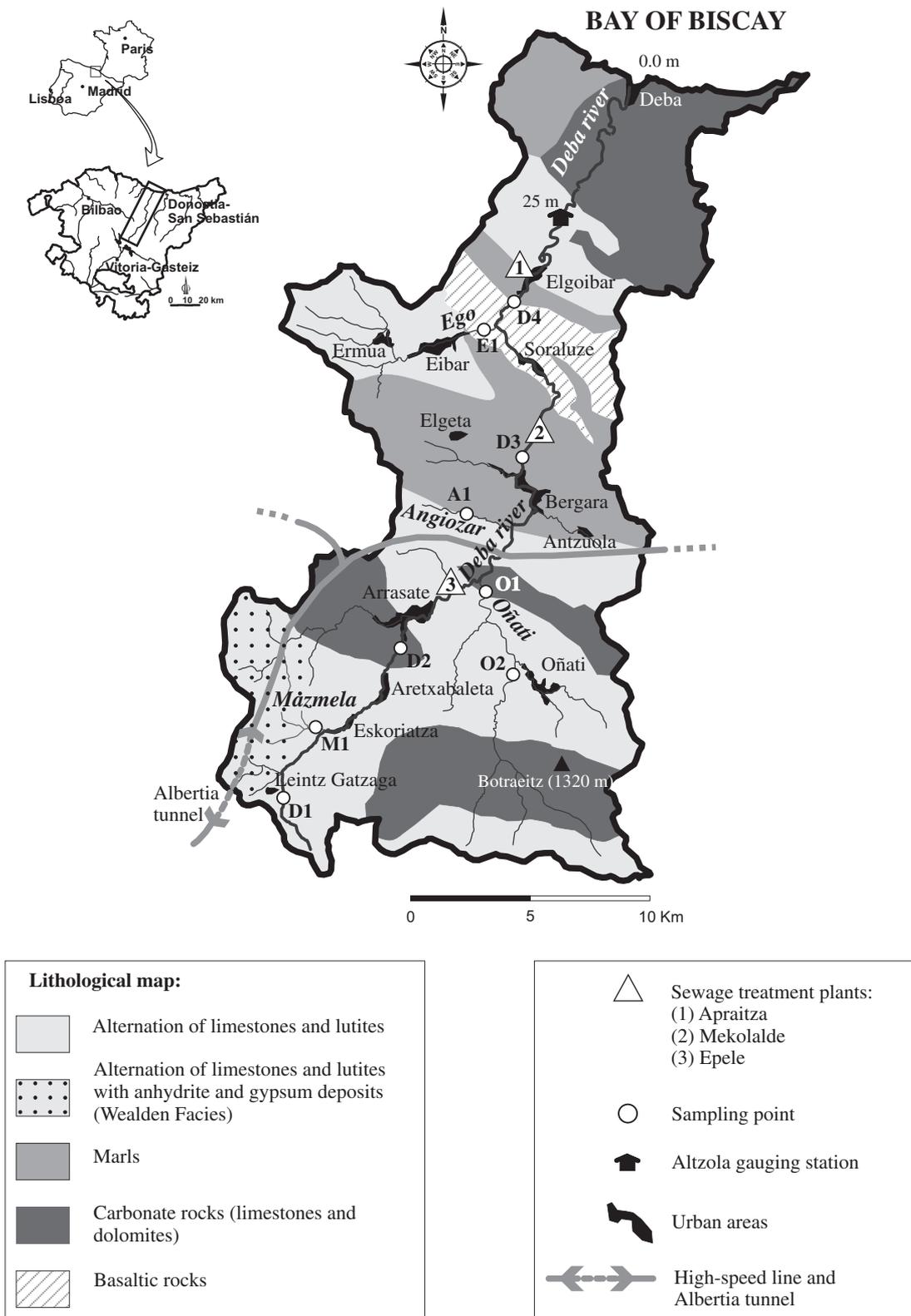


Fig. 1. Lithological map (modified from EVE, 1989). Location of the sampling points, Altzola gauging station, wastewater treatment plants and high-speed line in Deba river catchment.

by seawater when the tide rises. The Deba River, which crosses the catchment from South to North, receives inflows from several tributaries, the most significant being the Ego and the Oñati. The highest point of the catchment lies at 1320 m a.s.l. (the peak of Botraititz) and its lowest is at sea level (0 m a.s.l., Bay of Biscay), while the Altzola gauging station is located at 25 m a.s.l.

The catchment is characterised by a maximum slope of 40% (in headwaters). The main bedrock in the southern part of the catchment is an alternation of limestones and lutites (Fig. 1). In this part, anhydrite and gypsum deposits alternate with silt, mudstone, sandstone and limestones in Wealden Facies evaporites (IGME, 1987; Ábalos et al., 2008; Iribar and Ábalos, 2011). The idea that large volumes of evaporites

occupy the core of major geological structures in this part of the Basque–Cantabrian basin has prevailed during the last decades (Ábalos et al., 2008). Occurrence of gypsum in different rock series (Early Cretaceous Wealden Facies and Triassic Keuper facies) was recognised in several works of the area (tunnel excavation, Peña and Rodenas, 2011; exploration wells). Here evaporitic rocks (mainly gypsum and anhydrite) appear in different ways: diapiric structure (Leintz Gatzaga, Fig. 1), interlayered with the most usual sedimentary rocks, sandstones and mudstones (Supraurgonian Complex, Aptian–Albian), and filling fractures in fault zones. Even though evaporite outcrops are rare in the area, the presence of saline springs supplies an indirect evidence of their occurrence (Iribar and Ábalos, 2011). Saline springs are common in this area, which have a high  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentration with an important presence of dissolved  $\text{H}_2\text{S}$  (Iribar and Ábalos, 2011). The middle part of the catchment consists mainly of marls, and in the north, carbonate rocks dominate (EVE, 1989).

Soils in the catchment are predominantly Cambisols (66%) and Acrisols (25%). This head catchment has been reforested for industrial purposes with *Pinus* spp. (37%); autochthonous forest occupies around 27%, and farmlands and pastures only 11%. However, the primary industries in this catchment are metallurgical, automotive industry, galvanising factories (a layer of zinc is bound to steel in order to protect it against the corrosion), smelting factories and electrical appliance factories, which are concentrated in the urban areas located along the river (Table 1 and Fig. 1).

The Deba catchment is considered to be one of the catchments most polluted by municipal and industrial wastewaters in the province of Gipuzkoa (Borja et al., 2006). The three most important urban areas are Eibar, Arrasate and Ermua, where 50% of all inhabitants live.

In order to avoid contamination of river water with municipal wastewater, three sewage treatment plants have been built in recent years (Fig. 1). Those plants collect urban and industrial effluents, which are previously treated before discharging them into the river water. Before Epele plant was put in continuous operation (May 2012), the rich-organic wastewaters of Arrasate and Oñati towns were discharged into Deba River and Oñati stream by means of two sewers (Table 1). Despite being one of the largest towns in the area, the untreated sewage effluents of Ermua are discharged directly into the Ego stream. In addition to industrial activities and urban impact, as part of construction of a new high-speed rail line, a 4786 m tunnel (the Albertia tunnel) was built between April 2009 and July 2011 (Fig. 1) and large amounts of sediment were consequently extracted and deposited around the tunnel, where there is a slope of 20%.

Hydrological (discharge,  $Q$ ) and meteorological data (precipitation and temperature) have been measured and recorded every 10 min since October 1995 in the Altzola gauging station (Fig. 1) by Gipuzkoa Provincial Council ([www4.gipuzkoa.net/oohh/web/esp/04\\_01.asp](http://www4.gipuzkoa.net/oohh/web/esp/04_01.asp)). Mean annual precipitation and temperature for the last seventeen years (1996–2013) are 1486 mm and 13.6 °C, respectively. The wettest period is from November to January and the driest and hottest months are usually in summer (June–September). During the research period, both hydrological years (2010–2011 and 2011–2012) were unusually dry, 1154 and 1205 mm, respectively. However, 248 mm of rainfall was recorded in November 2011, representing 21% of precipitation for this hydrological year. The mean recorded discharge was 8.25 and 9.34  $\text{m}^3 \text{s}^{-1}$  for the first and second years, respectively. Mean discharge was 10.61  $\text{m}^3 \text{s}^{-1}$  for the 1996–2013 period. Both sampling campaigns, 11th of October 2011 and 17th of October 2012, were carried out in the same hydrological period, low flow period (1.57 and 1.84  $\text{m}^3 \text{s}^{-1}$  respectively) with longer residence time, in an attempt to diminish the influence of hydrological pattern over the physicochemical characteristics of water and sediments.

A 50-year high-intensity flood event occurred in the Deba River from the 5th–9th of November 2011. During this flood event, rainfall was exceptionally high from the 5th–6th of November (213 mm) and a

maximum discharge of 438  $\text{m}^3 \text{s}^{-1}$  was monitored at the Altzola gauging station.

### 3. Materials and methods

#### 3.1. Field methodology

Surface bottom sediment (SBS) samples were collected (Fig. 1) from four sampling points (D1, D2, D3 and D4) along the main river bank and from five sampling points (M1, O1 and O2, A1, and E1) in the Mazmela, Oñati, Angiozar and Ego tributaries, respectively, during the sampling campaign of October 2011. These sampling points were chosen in an attempt to locate the pollution sources in the main river and tributaries from headwaters to the outlet. SBS were again collected in October 2012 at the same sampling sites, except D1, O2 and A1, which were used as background-reference sites because they were not influenced by anthropogenic pollution sources. SBS were collected using a plastic spoon and sealed in clean polyethylene bags.

Water samples were also taken in polyethylene bottles at all sampling points. Electrical conductivity (EC), pH and redox potential (Eh) were measured in situ using a Crison EC-Meter Basic 30+, Crison Micro pH 2000 and Hach ORP/Redox sonde MTC101 with Ag/AgCl electrode, respectively. All water and sediment samples were stored and refrigerated in the dark and transported to the laboratory of Chemical and Environmental Engineering (University of the Basque Country) in the same day.

In addition, precipitation ( $P$ , mm) and discharge ( $Q$ ,  $\text{m}^3 \text{s}^{-1}$ ) were continuously monitored in the Altzola gauging station in order to determine the magnitude of flood events during the study period. This station comprises a crump-profile single-crested weir. Turbidity (TRB, NTU) was also measured in this station using a Solitax infrared backscattering turbidimeter (Dr. Lange devices). Turbidimeters are commonly used to estimate continuous suspended sediment flux (Gippel, 1989; Brasington and Richards, 2000). Several authors (Lewis, 1996; Zabaleta et al., 2007) have satisfactorily used the good relationship between turbidity and suspended particulate matter (SPM) to calculate the continuous time series of SPM from continuous turbidity series. This method was used to calculate the SPM exported during the flood events throughout the entire hydrological year (2011–2012). These three variables ( $P$ ,  $Q$  and TRB) were electronically logged at 10-min intervals.

An automatic water sampler (SIGMA 900) was installed in the gauging station and programmed to start pumping 24 water samples of about 800 mL when TRB in the stream rose to 100 NTU, thus ensuring that flood events were monitored. The pumping frequency was 2 h in all flood events (seven in hydrological year 2011–2012). Water samples were taken to the laboratory for determination of SPM and dissolved and particulate organic carbon (DOC and POC).

#### 3.2. Laboratory methodology

SBS were air-dried and ground with a pestle and mortar for homogenization. For texture analysis, sediment samples were sieved through a stainless steel sieve to distinguish the percentage of gravel (>2 mm), sand (63–2000  $\mu\text{m}$ ) and mud (<63  $\mu\text{m}$ ) fractions. However, the percentages of sand (63–2000  $\mu\text{m}$ ) and fine fraction (<63  $\mu\text{m}$ ) were also recalculated taking only the bulk fraction (<2 mm) into account. The moisture content of the sediment samples was determined by heating at  $105 \pm 2$  °C in glass plates at constant weight. All data reported in this paper were calculated on a dry-weight basis.

Chemical analyses were performed on sediment samples in the laboratory of Chemical and Environmental Engineering (University of the Basque Country). Total carbon (TC), nitrogen (TN), and sulphur (TS) were analysed in the fine sediment using a TruSpec CHNS determinator (Leco Corporation). Volatile solids were determined using a muffle furnace as described in Method 2540 E of the Standard Methods (APHA-AWWA-WPCF, 1998). After incineration at 500 °C,

the percentage of weight loss was considered to be representative of total organic carbon (TOC). Total inorganic carbon (TIC) was calculated by the difference between TC and TOC.

Although the fine fraction (<63 µm) has been proven to be the most chemically active sediment phase (Förstner and Salomons, 1980; Ruiz et al., 1991; Ruiz and Romero, 1992; Zhang et al., 2002), it was also considered appropriate to measure the pseudo-total metal content in the bulk fraction (<2 mm) of October 2011. An ETHOS 1, Millestone microwave digestion system was used to digest three replicates of each SBS sample (0.5 g) in Teflon vessels with concentrated HNO<sub>3</sub>:HClO<sub>4</sub> (3:1.5) to determine of pseudo-total content. The digested samples were heated by increasing the temperature to 180 °C for 10 min and kept at that temperature for an additional 25 min (USEPA, 2007). After digestion, all samples were filtered through a 0.45 µm Millipore nitrocellulose filter, and diluted to 100 mL with Milli-Q water. For controlling analytical methods a NBS sediment sample was additionally used (Buffalo River sediment, USA). With this technique, all metals were also measured with mean values close to the certified contents and variation coefficients lower than 8% with the exception of Pb (17% with 0.5 g of sample) (Ruiz et al., 1991).

A sequential extraction method was performed on the fine fraction (<63 µm) of the sediments. Three replicates of each sample point were analysed. This method is based on the procedure used by Tessier et al. (1979) but modified by Baffi et al. (1998), with improvements made in accordance with the European Community Bureau of Reference (BCR 701). This extraction was divided into four operationally defined fractions.

- (1) Exchangeable, water and acid-extractable fraction (F<sub>1</sub>, soluble species, carbonates and exchangeable metals): About 0.5 g of the sample was continuously shaken at 30 rpm for 16 h at 20–22 °C with 20 mL (0.11 M) of acetic acid (CH<sub>3</sub>COOH).
- (2) Reducible fraction (F<sub>2</sub>, Fe/Mn oxyhydroxides): The residue from step 1 was continuously shaken at 30 rpm for 16 h with 20 mL (0.5 M) of hydroxyl-ammonium chloride (NH<sub>2</sub>OH·HCl) adjusted to pH 2 with HNO<sub>3</sub>.
- (3) Oxidisable fraction (F<sub>3</sub>, organic matter and sulphides): The residue from (2) was first oxidised with 10 mL of H<sub>2</sub>O<sub>2</sub> in a water bath at 85 °C till almost dry (about 1 h). This step was repeated again. After cooling, 25 mL of 1 M ammonium acetate (NH<sub>4</sub>CH<sub>3</sub>COO, pH 2 with HNO<sub>3</sub>) was added and shaken for 16 h at 30 rpm.
- (4) Residual fraction (F<sub>4</sub>, remaining, non-silicate bound metals): The residue from (3) was digested in a 15 mL combination of HNO<sub>3</sub>:HClO<sub>4</sub> (3:1.5), as described above in pseudo-total metal digestion.

At the end of each extraction, the extractable fraction was separated by centrifugation at 3000 rpm for 40 min. The supernatant was pipetted and stored in polyethylene bottles in the fridge (4 °C) until analysis.

Finally, the metals under consideration (Fe, Mn, Cu, Cr, Ni, Pb and Zn) in the extracts and pseudo-total digestion were determined by ICP-OES (Perkin Elmer Optima 2000) and by using an Ultrasonic Nebulizer (CETAC, U5000AT+) for those metals with a lower concentration (Cr, Cu, Ni and Pb). The percentage of recovery in each extraction step, taking into account pseudo-total digestion, was also calculated for each metal. For all elements, the recovery ranged between 92% and 117%. The detection limit for these metals was: Pb (1 µg g<sup>-1</sup>), Mn (0.5 µg g<sup>-1</sup>), Fe and Mn (0.4 µg g<sup>-1</sup>) and Cr, Cu and Ni (0.1 µg g<sup>-1</sup>).

Water samples collected at all sampling points were filtered through 0.45 µm filters. One replicate of each sample was acidified to pH < 2 with HNO<sub>3</sub> (65%) for dissolved metals (Fe, Mn, Cu, Zn, Pb, Ni and Cr), base cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>) and silica analysis using ICP-OES, which was connected to an Ultrasonic Nebulizer to reduce the detection limit at 0.1 µg L<sup>-1</sup> for metals. Anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were

measured in the non-acidified replicate using ion chromatography (DIONEX ICS 3000). Alkalinity was determined in the unfiltered sample by titration with HCl (APHA-AWWA-WPCF, 1998). All water samples showed an Ion Balance Error (IBE) between 10% and –10% with the exception of D1 (–14%).

DOC and TOC were respectively analysed in one filtered and one non-filtered replicate of each sample collected during the flood events using a Total Organic Carbon Analyzer (TOC-L Shimadzu). POC was calculated by the difference between TOC and DOC. Additionally, SPM content was also measured using the preweighed 0.45 µm Millipore nitrocellulose filters of the previously filtered samples. Organic carbon data obtained from seven flood events during hydrological years 2011–2012 were used to calculate exportations during floods.

### 3.3. EF, ICF and GCF calculations

The Enrichment Factor (EF) is a useful tool for determining the degree of anthropogenic metal pollution. The enrichment of a given element in sediments relative to a background-reference site is an indication of contribution from anthropogenic sources. The EF concept was developed by Chester and Stoner (1973) and has subsequently been applied by numerous authors to soils (Hernandez et al., 2003), river sediments (Tam and Yao, 1998; N'guessan et al., 2009) and estuary or coastal sediments (Violintzis et al., 2009; Legorburu et al., 2013). The EF for the element M can be calculated in accordance with Eq. (1), where [M]<sub>s</sub> and [R]<sub>s</sub> are the concentrations of the element M and the reference element R in sediment samples, while [M]<sub>rf</sub> and [R]<sub>rf</sub> are the mean concentration obtained from three non-contaminated reference sites (D1, O2 and A1, Fig. 1). As a reference element, Fe was selected because, in this catchment, it is predominately bound to the residual fraction in the fine sediment (as shown below, see Section 4.2.) and it could therefore be considered as a lithogenic component.

The Individual and Global Contamination Factors (ICF and GCF, respectively) of metals integrate all the data obtained by sequential extraction. Determination of these factors is an important aspect, indicating the degree of risk of metal contamination to the environment in relation to retention time in sediments: a high value means a low retention time and, consequently, a higher risk to the environment (Naji et al., 2010). The ICF for the various sampling sites was calculated from the result of the fractionation study, dividing the sum of the first three extractions (F<sub>1</sub>, F<sub>2</sub> and F<sub>3</sub>, constituting the non-residual fraction) by the residual fraction (F<sub>4</sub>) for each site (Eq. (2)). The GCF is equal to the sum of individual factor (Ikem et al., 2003; Naji et al., 2010), as shown in Eq. (3).

$$EF = \frac{([M]_s/[R]_s)}{([M]_{rf}/[R]_{rf})} \quad (1)$$

$$ICF = \frac{C_{non-residual}}{C_{residual}} \quad (2)$$

$$GCF = \sum_{i=1}^n ICF_i \quad (3)$$

### 3.4. Statistical methods

A Shapiro–Wilk test was carried out to check whether variables were normally distributed. Spearman correlation analysis (non-parametric test) and Principal Component Analysis (PCA) were performed to establish relationships and behaviour of the metals and other elements in water and sediments. PCA with an eigenvalue greater than 1 was subjected to an orthogonal varimax rotation. This maximises the variance to obtain a pattern of loadings for each factor that is as diverse as possible, thus lending itself to easier interpretation. A Cluster Analysis using Euclidean squared distance and aggregation Ward's

method was also performed to discriminate metal contents in the fractions isolated using sequential extraction and to identify groups of samples which contain similar contamination levels. The hierarchical method of the cluster analysis used in this study has the advantage that it does not require any prior knowledge of the number of clusters, which is a prerequisite of the non-hierarchical method. Statistical processing of the data was performed using SPSS software 20.0.

## 4. Results

### 4.1. Physicochemical parameters and pseudo-total metals of river waters, sediments and effluents

Some physicochemical parameters were analysed in the different water samples (pH, Eh, EC, ions and dissolved metals, Table 2). In surface sediments, texture data are given as a percentage of gravel (>2 mm), sand (63–2000 µm) and mud (<63 µm) considering all sediment fractions (Table 3). At the same time, sand and mud percentages were also recalculated taking into consideration only the bulk fraction (<2 mm). In the fine sediments (<63 µm), TN, TS, TC, TOC, and TIC and pseudo-total metals were measured and the TOC/TS ratio was calculated. Pseudo-total metals were also determined in the bulk sediment (<2 mm) fraction in 2011 and the ratios of metal concentration in fine fraction versus bulk fraction were calculated (Table 4).

Surface waters exhibited relatively low concentrations of dissolved metals (Table 2), usually below the detection limit (1 µg L<sup>-1</sup>), while fine fraction (<63 µm) of sediments contributed highly to the pseudo-total metal content in surface bottom sediments, especially Zn (Table 3). On the other hand, untreated industrial effluents (about 6773 m<sup>3</sup> y<sup>-1</sup>) contribute significantly to the total metal content (Fe > Zn > Ni > Cr > Cu), the organic matter load (16,035 kg O<sub>2</sub> y<sup>-1</sup>) and the suspended sediment load (19,017 kg y<sup>-1</sup>) in rivers (Table 1). Concerning treated and partially treated wastewaters discharged into the surface waters they cannot be considered as significant source of metals, usually below 0.5 mg L<sup>-1</sup> for Mn, Zn, Cu, Cr, Ni and Pb, and <1.0–11.32 mg L<sup>-1</sup> for Fe (Table 1). However, partially treated wastewaters from Arrasate and Oñati sewers contributed to increase of the organic matter (559–1552 mg O<sub>2</sub> L<sup>-1</sup>) and suspended sediment concentration (165–791 mg L<sup>-1</sup>) in water from January to September 2011. Apart from that, untreated wastewaters from Ermua town were spilled directly into Ego stream; physicochemical characteristics of those effluents were reflected in E1 sampling point (Tables 2 and 3).

Water samples collected during the high-magnitude flood event were used to calculate exportations of SPM, POC and DOC. This event mobilised 1360 t of SPM, more than 45% of the total amount exported throughout the entire hydrological year (2011–2012) in the Deba catchment. The organic matter shows similar behaviour, with 3.61 t km<sup>-2</sup> of

POC and 1.19 t km<sup>-2</sup> of DOC exported, representing 60% and 29% of the flux of POC and DOC exported during flood events in this year.

#### 4.1.1. Spatial and temporal distribution

The pH in the water for this study period varies between 7.6 (O1) and 8.5 (A1) (Table 2), indicating a weakly alkaline environment but well-buffered surface waters. Redox potential shows positive values (50–263 mV) at most of the water sampling points and negative values in O1 and E1. The most reducing conditions were measured at E1 (–106 mV) during the drier season of October 2011, when discharge at the gauging station was very low (1.57 m<sup>3</sup> s<sup>-1</sup>). The highest values of electric conductivity (1109–2570 µS/cm) and most of the major ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Si, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, Table 2) are found in headwaters (D1, D2 and M1) which could be influenced by groundwater circulation from rocks holding evaporites (Ábalos et al., 2008; Iribar and Ábalos, 2011). Diffuse discharge of groundwater flows from evaporitic deposits, with high content of Na<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, into wetlands has also been observed relatively near from this study area by other authors (Martínez-Santos et al., 2012). On the contrary, the lowest values of dissolved metals are found in headwaters and the highest ones in D3 (560 µg L<sup>-1</sup> of Zn), D4 and E1. There is a general increase of dissolved Fe and Zn in 2012.

The results of texture analysis of all surface sediments are shown in Table 3. The gravel fraction (around 50%) is the major fraction in the sediment samples studied. This is followed by the sand fraction, with a mean mass percentage of 45%, while the mud fraction is the smallest fraction with a percentage of 5%. The sand and mud fractions follow the same pattern in the main river and its tributaries when they are recalculated according to the bulk fraction; however, the mass percentage of both fractions increases (Table 3). Texture data of surface bottom sediments changed in some locations from 2011 to 2012 (Table 3), so that midstream (D3) the percentage of fine fraction increased considerably from 3.2% to 15%, while upstream (D2) this sediment fraction diminished in a similar proportion, from 22.5% to 8.1%. It is worth noting the major decrease of fine fraction (7.8% to 0.9%) from the first to the second campaign in the Oñati stream (O1).

Percentages of TN, TS and total organic and inorganic carbon (TOC and TIC) range from 0.16% to 1.52%, 0.003% to 1.21%, 2.01% to 10.93% and 0.39% to 7.04%, respectively (Table 3). Taking into account the two years of sampling, all these elements are found in higher percentages in the tributaries, especially in E1, which shows the highest contents of TOC (10.9%), TIC (7%), TS (1.21%) and TN (1.52%). In general terms, total sulphur content was markedly increased in some locations in 2012, M1 (0.02% to 1.14%), E1 (0.45% to 1.21%) and D3 (0.12% to 0.67%). On the other hand, the Oñati stream has the greatest temporal variability; while in 2011 it was remarkable for its high contents in all these elements (TOC, TIC, TN and TS), the following year O1 point

**Table 2**

Electrical conductivity (µS cm<sup>-1</sup>), pH, redox potential (Eh, mV), ions (mg L<sup>-1</sup>), total alkalinity (Alk., meq L<sup>-1</sup>) and dissolved metals (µg L<sup>-1</sup>) were measured in water samples taken in both sampling campaigns. D1, O2 and A1 were considered as background-reference sites. The detection limit (d.l.) is below 0.1 µg L<sup>-1</sup> for all dissolved metals.

Year	River	Sites	EC	pH	Eh	Ca	Mg	Na	K	Si	Cl	NO3	SO4	Alk.	Fe	Mn	Cu	Zn	Pb	Ni	Cr	
2011	Deba	D1	1109	8.3	263	86.0	12.9	83.2	1.6	4.8	252	1.0	92.5	3.0	5.4	1.0	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	
		Oñati	304	8.3	183	54.7	2.5	20.8	1.0	1.8	6.2	2.7	14.2	2.6	0.9	1.0	<d.l.	1.8	<d.l.	<d.l.	<d.l.	
		Angiozar	A1	363	8.5	156	57.4	5.9	23.3	1.7	4.3	14.1	4.1	19.1	3.1	2.9	2.0	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
2011	Deba	D2	2570	8.4	190	143	19.8	392	6.8	2.9	570	4.7	271	3.5	7.6	22.8	0.7	10.3	<d.l.	2.2	<d.l.	
		D3	711	8.0	181	77.5	6.6	44.9	5.8	2.9	93.4	2.9	64.4	3.8	75.1	61.1	0.9	16.1	<d.l.	9.1	1.1	
		D4	583	8.1	161	71.6	5.7	36.8	5.6	3.0	59.1	15.9	58.9	3.2	18.2	19.1	0.8	6.0	<d.l.	12.7	3.0	
		Mazmela	M1	1174	8.2	247	138	24.6	70.5	6.4	4.4	119	3.5	297	4.8	2.6	4.5	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
		Oñati	O1	349	7.7	-29	57.6	3.4	22.5	1.7	2.0	10.0	0.8	21.0	3.0	49.5	38.1	0.6	7.6	1.5	1.6	<d.l.
2012	Deba	E1	716	7.7	-106	76.3	3.9	38.6	8.8	3.6	45.0	0.0	70.4	4.4	41.4	84.9	<d.l.	19.8	<d.l.	30.0	13.0	
		D2	1747	8.2	191	133	17.4	183	5.1	2.4	338	2.2	214	3.4	89.1	34.0	1.2	10.6	<d.l.	2.1	0.7	
		D3	535	7.8	50	80.8	5.4	30.8	4.8	2.6	48.5	8.7	52.2	2.9	90.4	34.3	1.4	560	<d.l.	36.5	3.8	
		D4	504	8.1	133	71.2	5.2	26.1	4.7	2.3	39.0	8.4	44.3	2.9	91.6	24.9	1.3	55.7	<d.l.	16.3	3.7	
		Mazmela	M1	1171	8.2	164	157	29.8	69.7	7.2	6.5	77.8	1.7	315	4.7	41.9	12.1	<d.l.	0.7	<d.l.	1.0	<d.l.
		Oñati	O1	317	7.6	-80	59.4	3.0	10.5	1.8	1.5	10.3	2.6	16.3	2.7	88.3	59.7	<d.l.	21.2	<d.l.	2.0	0.5
		Ego	E1	584	7.7	-83	82.8	4.3	22.1	8.3	3.9	29.4	1.7	33.2	4.6	38.4	77.5	0.5	35.3	<d.l.	19.1	2.3

**Table 3** Gravel, sand and mud (%) are calculated for total fraction (>2 mm–<63 µm) and bulk fraction (<2 mm). Total organic and inorganic carbon (TOC and TIC, %), total nitrogen (TN, %), total sulphur (TS, %) and pseudo-total metals (Fe (mg g<sup>-1</sup>); Mn, Cu, Cr, Ni, Pb and Zn (µg g<sup>-1</sup>)) were analysed in fine sediments (<63 µm) of all sampling sites. TOC/TS ratio was calculated. D1, O2 and A1 are considered as background-reference sites.

Year	River	Sites	Total fraction			Bulk		TOC	TIC	TN	TS	TOC/TS	Fe	Mn	Cu	Cr	Ni	Pb	Zn	
			Gravel	Sand	Mud	Sand	Mud													
2011	Deba	D1	64.0	29.6	6.4	82.2	17.8	4.8	1.0	0.45	0.03	167	22.7	470	23.6	32.6	42.8	66.9	215	
		Oñati	O2	48.4	47.6	4.0	92.3	7.7	3.4	0.9	0.31	0.003	1117	29.4	592	28.6	37.1	32.2	57.1	243
		Angiozar	A1	55.7	41.8	2.5	94.4	5.6	3.3	0.4	0.29	0.01	384	27.1	865	33.1	53.0	23.6	27.6	232
2011	Deba	D2	38.0	48.0	14.0	77.5	22.5	2.9	2.6	0.30	0.02	185	26.9	778	83.3	51.4	38.1	17.0	480	
		D3	7.5	89.5	3.0	96.8	3.2	3.8	1.8	0.49	0.12	32.8	34.1	490	201	319	137	63.7	2015	
		D4	68.1	31.2	0.6	98.0	2.0	5.1	3.0	0.79	0.13	40.4	27.9	1117	299	505	177	74.2	3083	
		Mazmela	M1	37.1	56.9	6.1	90.4	9.6	2.2	0.9	0.16	0.02	142	32.9	705	28.3	44.7	37.1	11.5	222
		Oñati	O1	76.5	21.7	1.8	92.2	7.8	5.0	2.2	0.81	0.34	14.7	29.3	478	253	255	73.4	75.0	2507
2012	Deba	Ego	E1	55.0	42.1	2.9	93.5	6.5	10.6	6.7	1.52	0.45	23.5	21.5	491	318	679	230	88.3	5356
		D2	60.7	35.9	3.5	91.9	8.1	3.6	3.5	0.43	0.03	119	27.5	1080	93.0	52.6	35.4	44.7	753	
		D3	19.3	66.5	14.3	85.0	15.0	3.5	1.2	0.37	0.67	5.2	35.0	356	112	493	79.5	62.7	3275	
		D4	56.0	43.6	0.4	99.1	0.9	4.1	2.1	0.64	0.07	58.9	35.3	651	196	272	113	94.7	2417	
		Mazmela	M1	33.9	58.1	8.0	89.2	10.8	2.0	2.8	0.18	1.14	1.8	25.8	423	27.9	28.5	31.0	33.0	117
		Oñati	O1	89.2	10.7	0.1	99.1	0.9	2.0	1.1	0.16	0.22	9.3	38.1	559	391	282	91.9	94.0	3169
		Ego	E1	53.4	45.3	1.3	97.3	2.7	10.9	7.0	1.30	1.21	9.0	29.9	502	308	435	171	111	5564

presented the lowest concentrations of TIC (1.1%), TOC (2.0%) and TN (0.16%). The total sulphur content still remained quite high (0.22%).

The Ego stream shows the highest concentrations of pseudo-metals except for Fe, Mn and Cu in the fine fraction of sediments, Cr (679 µg g<sup>-1</sup>), Ni (230 µg g<sup>-1</sup>), Pb (111 µg g<sup>-1</sup>) and Zn (5564 µg g<sup>-1</sup>). The lowest pseudo-metal concentrations in fine sediments were measured in the headwaters of the Deba River (D1) and tributaries (M1, O2 and A1), followed by D2 (Table 3). Therefore, O1 and D3 present intermediate concentrations between downstream (E1 and D4) and upstream sampling points. There is no difference in the spatial distribution of Fe; its concentration is similar in the fine sediments of the main river and of the tributaries. Finally, the same metal concentration pattern was repeated for the two years in fine sediments from the Deba catchment, so that Fe is the dominant metal followed by Zn > Mn > Cr > Cu > Ni > Pb, except at the upstream sites where Mn > Zn.

Ratios of metal concentration in fine fraction (<63 µm) versus bulk sediment (<2 mm) at each sampling point are shown in Table 4. The values of this ratio vary between locations but, focusing on the mean value, we can see that Fe alone has values of <1 at all sampling points with the exception of E1, indicating lower concentrations in the fine sediment than in the bulk; Mn has almost the same mean value in both fractions with a ratio of about one; however, five metals (Cu, Ni, Cr, Pb and Zn) have mean values of >1, indicative of higher concentrations in the fine fraction. Comparing the mean values of this ratio in the Deba River to its tributaries (Table 4), the fine fraction has higher metal concentrations in the main river. On the other hand, apart from

**Table 4** Ratio of metal concentration in fine fraction (f, <63 µm) versus bulk fraction (b, <2 mm) were calculated in each sampling site in October 2011. The relationship (r<sup>2</sup>) between metal concentration in fine sediments and bulk sediments was also calculated. N is the number of samples considered.

River	Sites	Fe f/b	Mn f/b	Cu f/b	Ni f/b	Cr f/b	Pb f/b	Zn f/b
Deba	D1	0.82	1.12	1.10	1.30	1.42	3.87	1.36
Deba	D2	0.48	1.01	1.30	0.95	1.35	0.86	1.15
Deba	D3	0.48	1.00	2.64	1.58	3.15	1.51	2.70
Deba	D4	0.54	1.05	1.35	1.76	3.27	1.28	2.39
Mazmela	M1	0.87	1.20	1.75	1.52	2.14	0.78	1.45
Oñati	O1	0.69	0.89	1.46	1.34	1.53	1.89	1.48
Oñati	O2	0.52	0.89	1.33	1.11	1.61	2.28	1.25
Angiozar	A1	0.49	0.78	1.06	0.78	1.29	0.96	0.99
Ego	E1	1.15	1.11	1.31	1.17	1.24	1.61	1.03
	r <sup>2</sup> (N = 9)	0.49	0.84	0.93	0.92	0.78	0.79	0.87

Fe (r<sup>2</sup> = 0.49, Table 4), metal concentrations in both fractions are well correlated, suggesting that most of the metals followed the same trend in both fractions of all sampling points.

TOC/TS refers to the ratio of total organic carbon (TOC) to total sulphur (TS) percentages in sediment. Sulphate reduction below an oxygenated water column typically has TOC/TS ratios in the range of 1.5 to 5.0. Except at M1, O1 and E1 where these values were close in 2012, this ratio is much higher in all the sampling points. A dramatic temporal decrease in the TOC/TS ratio was observed at M1 (142 to 1.8) and D3 (32.8 to 5.2) from October 2011 to 2012 (Table 3). This decrease was mainly caused by the increase in TS, whereas TOC content remained fairly stable. This suggests that sediments might be deposited under periodic anoxia, although the redox potential measured in water indicates oxygenated conditions.

#### 4.2. Metal distribution in the fine fraction of the sediments

Table 5 shows the mean Fe, Mn, Cr, Cu, Ni, Pb and Zn concentrations and percentages (in parentheses) of the four fractions discriminated by sequential extraction in the fine fraction of sediment for all sampling stations and the two sampling periods. A Cluster Analysis using Euclidean distance and aggregation Ward's method was also carried out to identify different groups of metals according to their distribution in those four fractions for each sampling year. The results of the Cluster Analysis show the same pattern metal groups for the two years (Fig. 2), so that two main groups can be distinguished.

- (i) One group includes Cu, Cr and Pb, which are found predominantly in the potentially most mobile fractions (F<sub>1,2,3</sub>). These metals are predominantly extracted in F<sub>3</sub> (38.4–71.1%, Table 5), indicating that organic matter and/or sulphides are the major sinks for these metals, followed by residual fraction (24–39.2%). Less than 9% of Cu and Cr are represented in the other non-residual phases (F<sub>1,2</sub>). Copper presents a pronounced tendency for complexation with sediment organic matter due to its high affinity to humic substances (Jain et al., 2007; Pacifico et al., 2007; Davutluoglu et al., 2011a), while Pb is likely to form stable organic complexes and/or to be bound to sulphides (Tüzen, 2003). Chromium presents similar high concentrations and fractionation profiles to Cu (Fig. 3 and Table 5), suggesting that both metals originate from the same anthropogenic source.

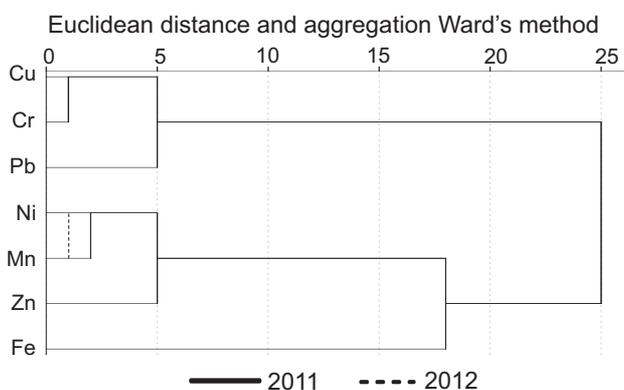
**Table 5**

Total metal content and distribution in fine sediments for all sampling sites (N = 6) of each year. The mean and standard deviation ( $\pm$ SD) data are presented in  $\mu\text{g g}^{-1}$  dry weight (dw) for all metals, except for Fe ( $\text{mg g}^{-1}$ ). The values in parentheses show percentage of elemental concentration, where the highest percentage for each metal is shown in bold. Sum:  $F_1 + F_2 + F_3 + F_4$ ; the total was determined by microwave assisted acid digestion; recovery:  $(\text{Sum}/\text{Total}) \times 100$ .

Year	Metal	F <sub>1</sub> : exch/carbonates	F <sub>2</sub> : reducible	F <sub>3</sub> : oxidizable/sulphides	F <sub>4</sub> : residual	Sum	Total	%Recovery
2011	Fe	0.89 $\pm$ 0.93 (2.8)	3.0 $\pm$ 2.4 (9.8)	2.7 $\pm$ 0.4 (9.2)	23.2 $\pm$ 4.1 ( <b>78.2</b> )	29.7	28.8	103
	Mn	339 $\pm$ 278 ( <b>46.8</b> )	181 $\pm$ 239 (19.7)	53.7 $\pm$ 38.5 (9.9)	125 $\pm$ 43.0 (23.6)	699	678	103
	Cr	6.8 $\pm$ 7.5 (1.8)	33.0 $\pm$ 42.0 (6.6)	246.6 $\pm$ 233 ( <b>59.0</b> )	49.9 $\pm$ 27.3 (32.6)	336	309	109
	Cu	0.51 $\pm$ 0.63 (1.3)	6.5 $\pm$ 12.9 (5.1)	146.2 $\pm$ 115 ( <b>68.1</b> )	28.7 $\pm$ 13.3 (25.6)	182	197	92
	Ni	52.6 $\pm$ 54.6 (34.4)	17.5 $\pm$ 16.8 (12.4)	15.7 $\pm$ 6.5 (18.1)	26.9 $\pm$ 8.1 ( <b>35.1</b> )	113	116	98
	Pb	2.3 $\pm$ 2.4 (2.1)	13.8 $\pm$ 12.5 (16.8)	55.7 $\pm$ 74.4 ( <b>42.8</b> )	36.5 $\pm$ 26.5 (38.2)	108	103	106
	Zn	903 $\pm$ 827 ( <b>30.7</b> )	983 $\pm$ 1095 (29.8)	576 $\pm$ 692 (26.1)	108 $\pm$ 68.2 (13.4)	2569	2277	113
2012	Fe	0.74 $\pm$ 0.89 (2.3)	2.7 $\pm$ 2.3 (9.0)	3.8 $\pm$ 3.0 (13.9)	23.9 $\pm$ 9.0 ( <b>74.8</b> )	31.2	31.9	98
	Mn	213 $\pm$ 88.0 ( <b>40.1</b> )	144 $\pm$ 186 (20.6)	61.2 $\pm$ 39.0 (10.1)	171 $\pm$ 148 (29.2)	590	595	99
	Cr	6.4 $\pm$ 6.1 (1.9)	27.5 $\pm$ 35.7 (6.6)	190.3 $\pm$ 185.7 ( <b>54.3</b> )	75.6 $\pm$ 74.9 (37.2)	300	261	115
	Cu	0.30 $\pm$ 0.34 (0.6)	4.6 $\pm$ 9.2 (4.4)	112 $\pm$ 112 ( <b>71.1</b> )	20.2 $\pm$ 8.8 (24.0)	137	128	106
	Ni	31.0 $\pm$ 33.1 (26.5)	12.4 $\pm$ 11.2 (12.5)	14.4 $\pm$ 1.6 (22.1)	31.7 $\pm$ 21.9 ( <b>38.9</b> )	89.5	86.9	103
	Pb	1.8 $\pm$ 1.6 (2.1)	17.0 $\pm$ 21.9 (20.4)	31.4 $\pm$ 20.7 (38.4)	28.5 $\pm$ 13.8 ( <b>39.2</b> )	78.8	67.4	117
	Zn	720 $\pm$ 638 (25.6)	952 $\pm$ 1033 ( <b>31.8</b> )	579 $\pm$ 650 (27.8)	259 $\pm$ 424 (14.8)	2511	2549	98

(ii) The second group is composed of Mn, Ni, Zn and Fe. This cluster could be separated into two sub-clusters:

- The first sub-group is composed of Mn, Ni and Zn. These metals are distributed, to a greater or lesser extent, among all four fractions (Table 5). The greatest proportion of Mn is mainly associated with F<sub>1</sub> (up to 46.8%), followed by residual (F<sub>4</sub>), reducible (F<sub>2</sub>) and oxidizable (F<sub>3</sub>) fractions (up to 29.2, 20.6 and 10.1%, respectively). Manganese tends to be present in less thermodynamically stable phases in the sediments (Tessier et al., 1979; Sakan et al., 2009). The relative predominance of Mn in the exchangeable fraction is due to this element being reduced in bottom sediments. Although Ni is mostly bound to the residual fraction (F<sub>4</sub>), especially in October 2012 (38.9%), it is closely associated to the exchangeable/carbonate fraction, F<sub>1</sub> (up to 34.4%). More than 30% of Ni is bound to F<sub>2,3</sub> (Table 5). The distribution of Zn in non-residual fractions (F<sub>1,2,3</sub>) is similar (between 25.6% and 31.8%) and the lowest proportion is found in the mineral lattice of the sediment (F<sub>4</sub> < 15%). A relative Zn uniformity among fractions was also found by Pacifico et al. (2007) and Devesa-Rey et al. (2010a).
- The second sub-group is exclusively composed of Fe. In contrast, the largest proportion of Fe is associated with residual fraction (F<sub>4</sub> > 74.8%), so that this metal is strongly retained in the lattice of mineral in the fine sediment fraction and consequently this metal cannot be remobilized under normal conditions encountered in nature. This result accords with data reported by other investigators, who found that 67–90% of the total Fe was in the residual fraction (Tüzen, 2003; Jain et al., 2007; Yuan et al., 2004).



**Fig. 2.** Cluster analysis of metals according to their distribution in the four fractions for each sampling year.

Regarding spatial-temporal changes in the metal distribution (Fig. 3), two sampling points in particular (M1 and O1) show a strong temporal variation in metal content in the different phases. In the case of M1, a general relative increase of Fe, Cu, Ni and Zn concentration was observed in the F<sub>3</sub> fraction in the second sampling year. At O1, indeed, the proportion of all metals diminishes in the mobile fractions (F<sub>1,2,3</sub>) and increases in the residual phase (F<sub>4</sub>) in 2012, whereas the previous year most metals (Cr, Cu, Pb and Zn) were mainly bound to F<sub>3</sub>. The temporal variation of metal distribution, from F<sub>3</sub> to F<sub>4</sub>, might be linked to a decrease in organic matter content, 5% and 2% in October 2011 and October 2012 respectively (Table 3).

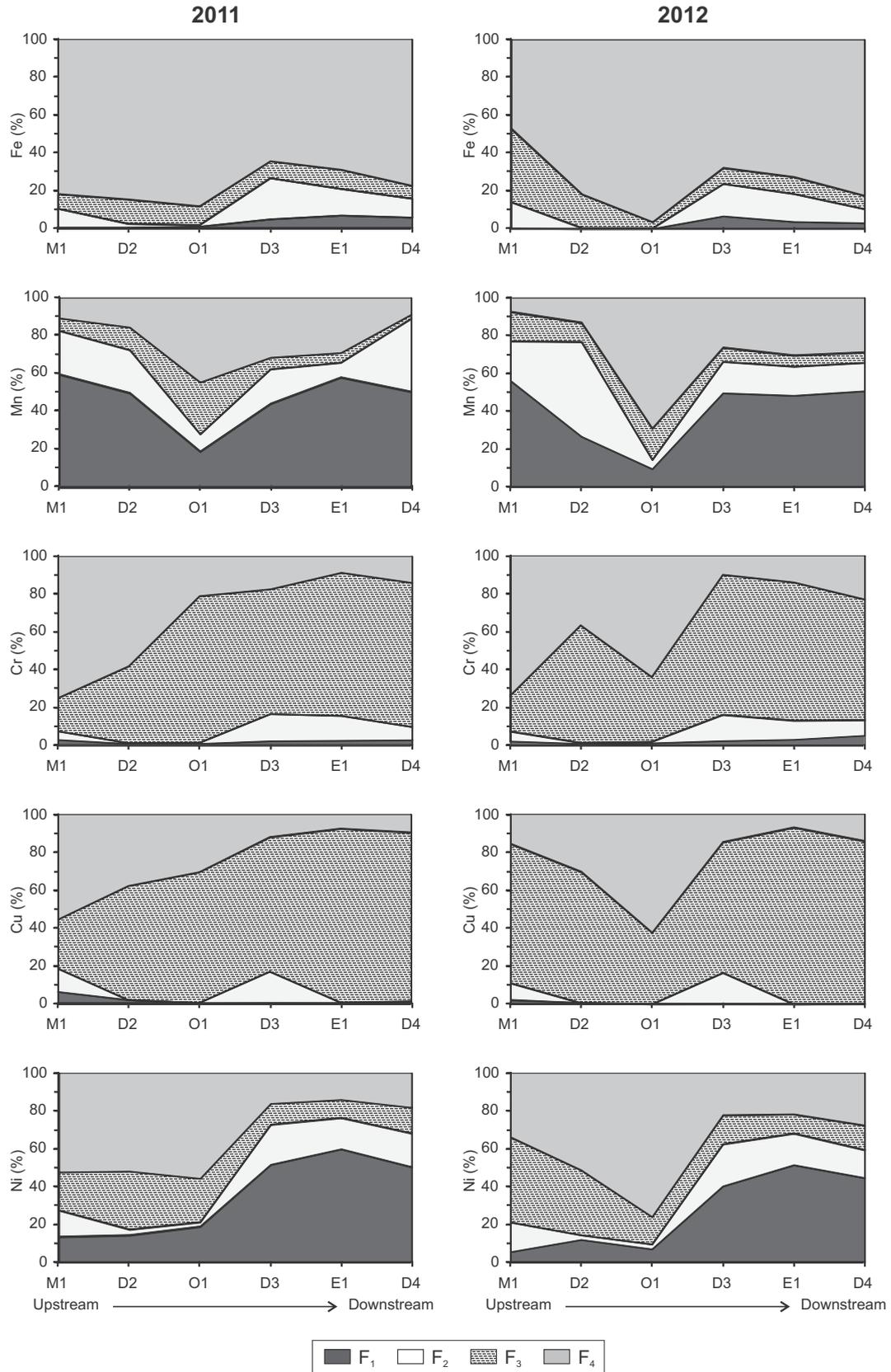
At sampling points E1, D3 and D4, there are slight temporal variations in the percentage of metals and their distribution among the four fractions between the two years (Fig. 3). Nevertheless, the mid-(D3) and downstream (E1 and D4) sampling points show the highest proportions in the mobile fractions of Cu, Cr and Pb (first group of previous classification) and Mn, Ni and Zn (first sub-group).

#### 4.3. Spearman's correlation and principal component analysis (PCA)

In order to determine affinities between physicochemical water, sediment parameters and metal distribution and thus improve our understanding of their origin and behaviour in the Deba River catchment, Spearman's correlation matrix were performed, as shown in Table 6. This non-parametric test was carried out after the results of non-normally distributed data given by Shapiro–Wilks test. Dissolved metals were not included in this analysis since many values were below the detection limit (Table 2).

Some elements ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , alkalinity and, to a lesser extent,  $\text{K}^+$  and Si) present a significant positive correlation to one another and to EC in water (Table 6a). Nevertheless, they all show negative correlations, mostly statistically insignificant, with pseudo-total metals (Cu, Ni, Cr, Pb, Zn and Fe) in fine sediments. Most of the pseudo-total metals (Ni, Pb, Cu, Cr, and Zn), in turn, display a strong negative correlation with the pH and Eh of the water, but a positive correlation with TOC, TN and TS in fine sediments (Table 6a). A very significant correlation ( $r = 0.97$ ) between TOC and TN indicates that the main origin of nitrogen is the mineralisation of organic matter. To a lesser extent, TIC is also positively correlated with TOC, TN and TS.

A significant positive correlation between Fe<sub>2</sub> and Cu<sub>2</sub>, Ni<sub>2</sub>, Pb<sub>2</sub>, and Cr<sub>2</sub> metals ( $0.71 < r < 0.76$ ) implies that these elements are bound to Fe oxides/hydroxides, which could play an important role in complexation of these metals (Table 6b). The absence of a good correlation between these metals and Mn<sub>2</sub> suggests that the Mn oxides/hydroxides do not play a dominant role in sorption of these metals; indeed, Mn is



**Fig. 3.** Metal distribution in the four fractions considered by BCR 701 (F1, exchangeable/carbonates; F2, reducible; F3, oxidizable/sulphides; F4, residual) for both sampling campaigns and all sites.

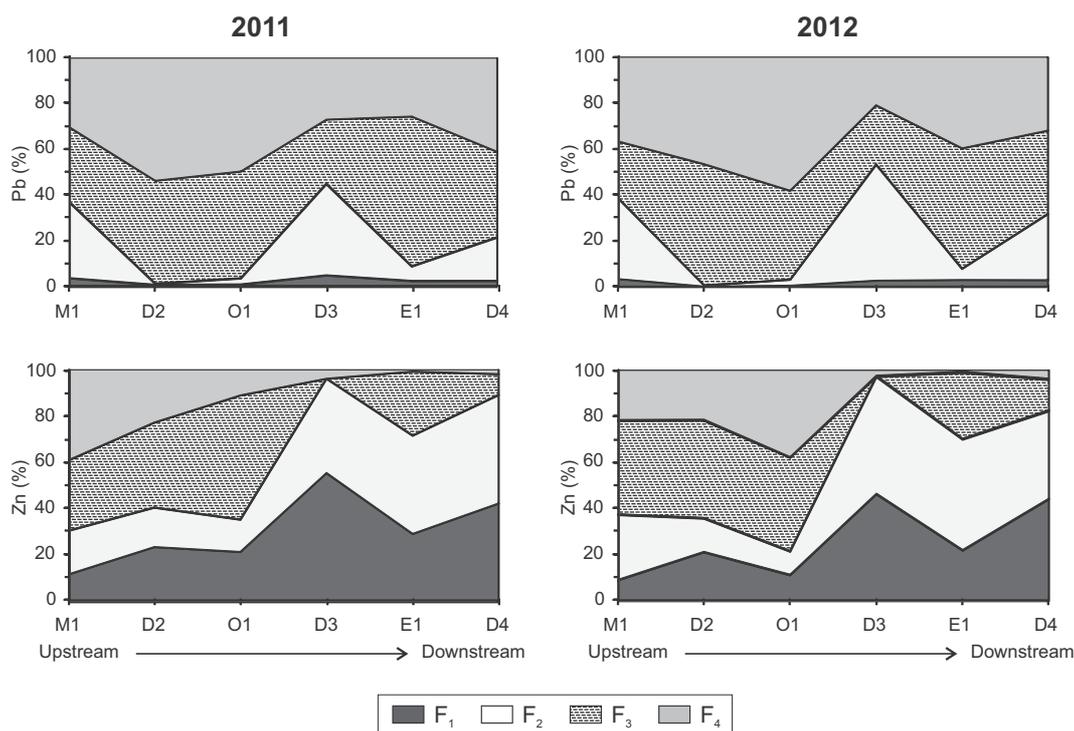


Fig. 3 (continued).

predominantly bound to  $F_1$  (Table 5). The positive correlation of  $Mn_1$  and  $Mn_2$  with the pH and Eh of water ( $r > 0.77$ ) could be explained by continuous changes in the potential redox which favour solubilisation of Mn compounds and favour the adsorption of this metal to the  $F_1$  fraction (Devesa-Rey et al., 2010a). On the other hand,  $Cu_3$ ,  $Ni_3$ ,  $Pb_3$ , and  $Cr_3$  also show a strong positive correlation with TOC ( $0.73 < r < 0.95$ ), thus suggesting selective adsorption of these metals into the organic matter. Finally, the positive correlation between the residual fraction of some metals ( $Ni_4$ – $Mn_4$ ,  $Ni_4$ – $Cr_4$ ,  $Fe_4$ – $Zn_4$ , and  $Fe_4$ – $Mn_4$ ,  $0.58 < r < 0.74$ ) is likely to be the consequence of a common origin in rock minerals.

A Principal Component Analysis (PCA) was performed with the results of metal fractions (Table 5), all data included in Table 3, except texture data and total metal concentrations, and pH and Eh of water (Table 2). However, instead of considering all metal fractions individually, the sum of non-residual fractions was taken into account in the PCA. The non-residual fractions considered can be summarised as:  $F_{12}$  ( $F_1$ , exchangeable-carbonates, plus  $F_2$ , bound to Fe and Mn oxides/hydroxides) and  $F_{123}$  ( $F_2$  plus  $F_3$ , bound to organic matter and sulphides). The residual fraction ( $F_4$ ) is also included, but individually.

The factorial planes I–II (Fig. 4a) reflect the most important information, with Factor I (43% of the variance) characterised by TIC, TOC, and TN, and the non-residual fractions ( $Cu_{123}$ ,  $Ni_{12}$ ,  $Ni_{123}$ ,  $Cr_{12}$ ,  $Cr_{123}$ ,  $Pb_{123}$ ,  $Zn_{12}$  and  $Zn_{123}$ ) and residual fraction of  $Pb_4$ , and Factor II (23%) positively characterised by almost all residual fractions ( $Ni_4$ ,  $Cr_4$ ,  $Fe_4$ ,  $Zn_4$  and  $Mn_4$ ) and negatively by Eh and pH. Factor I therefore represents the sorption of Cu, Ni, Cr, Pb and Zn by mutual substrates, such as carbonates, oxides/hydroxides, and organic matter/sulphides, and Factor II represents the elements that are retained in the crystal lattices of minerals and, consequently, have low mobility. It can clearly be seen that the sediment samples with higher organic matter and labile metal fractions are distributed towards the positive side of Factor I. These sediment samples are progressively followed, in decreasing order of organic matter and labile forms, by E1, D4, O1, D3, D2 and M1. Content of organic matter and non-residual metal forms diminishes in E1, D4 and O1 sediments from the second year (2012). On the other hand, only one sediment sample (O1) from the 2012 sampling stands on the

positive side of Factor II. The O1 site shows a strong temporal change in chemical composition from 2011 to 2012, suggesting that most metals were bound to mobile fractions in 2011 and to non-mobile fraction ( $F_4$ ) in 2012.

On the factorial planes II–III (Fig. 4b), Factor III (13%) is characterised by the association of  $Cu_{12}$ ,  $Pb_{12}$ ,  $Fe_{12}$  and  $Fe_{123}$  with TS (oxidisable and/or reducible fractions of S). Sediments collected at M1 and D3 show a significant increase in these elements in 2012 along this axis, which means that they are principally associated with the carbonate and Fe/Mn oxide fractions but, in the case of Fe, also with the organic/sulphide fraction. As mentioned above, Factor II is characterised by the residual fractions. Thus, Ni, Cr, Zn, Mn and Fe are predominantly bound to the structure of minerals at O1 and, to a lesser extent, at D4 in 2012, with a relative loss of non-residual fractions.

#### 4.4. Contamination assessment

Fig. 5 shows the results of metal enrichment factors (EFs) for all locations considered in the two years. There is no general consensus concerning threshold of natural variability but some authors (Hernandez et al., 2003; Roussiez et al., 2013) have suggested that  $EF > 2$  is indicative of a probable anthropogenic influence. Taking this threshold as a reference, it can clearly be seen from these plots that median EF values of Pb ( $< 1.2$ ) and Mn ( $< 0.9$ ) are below this limit. The median Ni value, however, is distributed around the limit of natural variability, especially for the second year of sampling. In contrast, the median EF value for Cu (4–7), Cr (5–6) and Zn (around 8) far exceeds the natural threshold. This range of values is considered by some authors (Acevedo-Figueroa et al., 2006; Sakan et al., 2009; Guo et al., 2014) as a moderately severe enrichment (from 5 to 10). It is worth noting the high EF values of Cr (20) and Zn (28), which are considered by the previous authors as a severe (10–25) and very severe (25–50) anthropogenic enrichment.

Regarding temporal variability, a decrease in anthropogenic influence is observed in all metals except Zn, to a greater (Cu) or lesser (Mn and Pb) extent, between 2011 and 2012 (Table 7). The locations





**Table 7**  
Enrichment factor (EF) and individual and global contamination factors (ICF and GCF) of Cu, Ni, Cr, Pb, Zn, Mn and Fe. Mean and standard deviation (SD) are calculated for each year.

		Cu		Ni		Cr		Pb		Zn		Mn		Fe	GCF
		EF	ICF	EF	ICF	ICF									
2011	D2	2.87	1.64	1.13	0.91	1.23	0.71	0.33	0.85	2.05	3.36	1.19	5.33	0.17	13.0
	D3	5.46	7.31	3.22	5.07	6.02	4.68	0.97	2.67	6.77	23.5	0.59	2.15	0.54	45.9
	D4	9.90	9.45	5.08	4.40	11.6	6.03	1.39	1.42	12.7	46.8	1.65	10.1	0.28	78.5
	M1	0.80	0.79	0.90	0.90	0.88	0.33	0.18	2.25	0.77	1.55	0.89	8.15	0.21	14.2
	O1	7.99	2.27	2.01	0.78	5.59	3.71	1.33	1.00	9.80	7.88	0.67	1.23	0.12	17.0
	E1	13.7	12.2	8.57	5.94	20.3	10.3	2.14	2.86	28.6	100.4	0.94	2.42	0.44	134.6
	Mean	6.8	5.6	3.5	3.0	7.6	4.3	1.1	1.8	10.1	30.6	0.99	4.9	0.29	50.5
SD	4.7	4.7	2.9	2.4	7.4	3.7	0.73	0.87	10.1	38.2	0.39	3.6	0.16	48.4	
2012	D2	3.13	2.31	1.03	0.94	1.23	1.71	0.85	1.14	3.14	3.61	1.62	6.64	0.22	16.6
	D3	2.96	5.83	1.82	3.47	9.08	8.78	0.93	3.73	10.7	35.6	0.42	2.80	0.47	60.7
	D4	5.14	6.07	2.55	2.59	4.96	3.29	1.40	2.11	7.84	23.9	0.76	2.47	0.21	40.7
	M1	1.00	5.44	0.96	1.95	0.71	0.35	0.67	1.71	0.52	3.58	0.67	12.5	1.12	26.7
	O1	9.51	0.61	1.93	0.31	4.83	0.56	1.29	0.72	9.54	1.64	0.61	0.44	0.04	4.32
	E1	9.56	13.3	4.59	3.56	9.38	6.02	1.93	1.51	21.4	103.4	0.69	2.28	0.38	130.5
	Mean	5.2	5.6	2.2	2.1	5.0	3.5	1.2	1.8	8.9	28.6	0.79	4.5	0.41	46.6
SD	3.6	4.4	1.3	1.3	3.7	3.3	0.46	1.05	7.3	39.1	0.42	4.4	0.38	45.5	

Owens, 2009; Yang et al., 2009), the contribution of this fraction in some sites of this catchments (D4 and O1) is very low. Given the lack of uniformity of fine-grained fraction content among the different sampling sites, the representativeness of contamination could be biased. Nevertheless, this fraction has been used by many authors to compare the metal contamination in river sediments and, consequently, it is widely considered as a good way to compare the status of different rivers (N'Guessan et al., 2009; Varol, 2011; Bartoli et al., 2012).

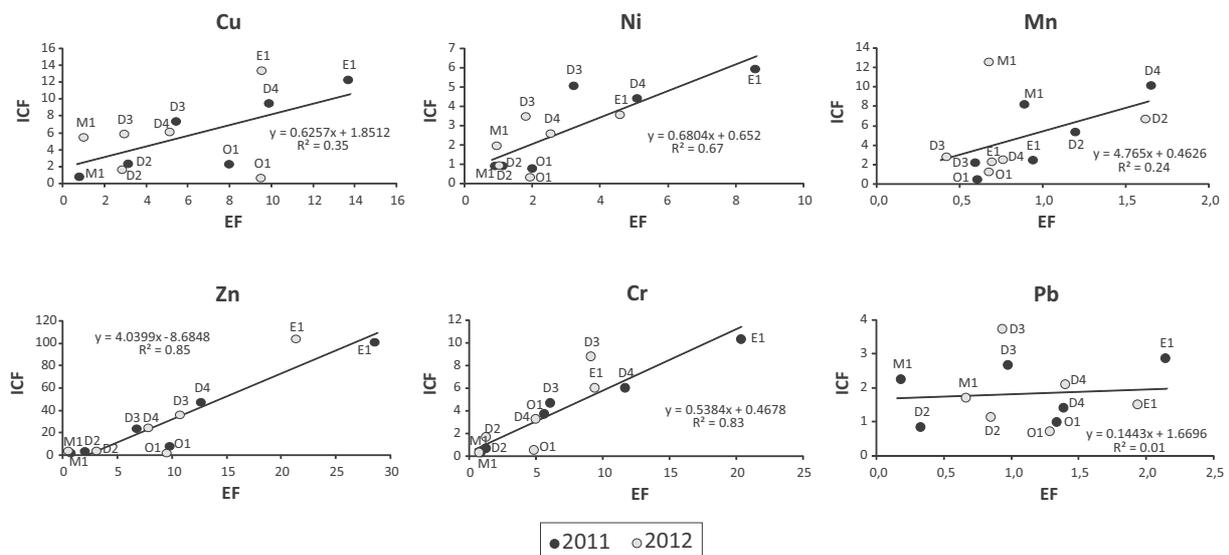
Finally, considering all sources of contamination, it can be concluded that untreated or partially treated wastewaters are the main source of organic contamination in Ego and Oñati streams. Meanwhile, untreated industrial effluents contribute to increase metal concentrations in water and sediments of those streams, but also in the mid- (D3) and low-part (D4) of the Deba River. The polluted nature of the Ego sediments means that contamination tends to be localised in a hotspot near the input (E1) and then dispersed downstream in lower concentrations. Thus, the Deba River (D4) is strongly affected by this stream, although it presents a lower flow rate.

### 5.2. Availability of metals and contamination risks

Organic-rich material from untreated or partially treated wastewater inputs also determines the metal distribution in fine-sediments at

those sampling stations impacted directly (E1 and O1) or indirectly (D3 and D4) by these effluents. A substantial amount of Cu, Cr and Pb (the first group of the dendrogram) was bound to the oxidisable fraction ( $F_3$ ), which means that these metals are favoured to form complexes with humic substances when there is an important organic input. On the other hand, the environmental impact of untreated industrial inputs is also characterised by a higher proportion of Zn, Mn and Ni in the exchangeable/carbonates and reducible fractions ( $F_{1,2}$ ) at the mid- and low-part of this catchment. These elements might be susceptible to re-mobilization if the physicochemical conditions of the river change (Sakan et al., 2009) and, consequently, they could be more available to aquatic biota (Eggleton and Thomas, 2004). Although Fe is the most abundant element in untreated industrial effluents, it appears to be mainly complexed to a coarser fraction, while the origin of this element in fine sediments is exclusively mineral and is consequently immobilised in the mineral lattice of the sediments. Finally, the majority of previously mentioned metals are associated with the residual fraction ( $F_4$ ) at head-water sampling sites, where the impact of the urban and industrial activity is minimum.

Determination of the global contamination factor (GCF) in fine sediments has made it possible to identify the extremely high potential risk for the aquatic environment due to metal pollution in  $E1 > D4 (> O1$  in 2011)  $> D3$ , Zn being the most potentially toxic element for organisms



**Fig. 6.** Relationship between enrichment factor (EF) and individual contamination factor (ICF) for each metal and considering all sampling sites for both years.

in the Deba River catchment, followed by Cu and Cr. Even though the risk of contamination of a water body by Zn is lower in upstream locations, it remains considerably high. As a consequence, this metal can be considered as the most potentially toxic element in the Deba River catchment because in addition to being easily removed or solubilised if physicochemical parameters change (Naji et al., 2010; Morillo et al., 2004; Pérez-Cid et al., 1996), it is also extremely abundant.

### 5.3. Influence of high-speed rail construction and high intensity flood event on the source variability of sediments

Anhydrite and gypsum intercalations with limestone and sandstones (Wealden Facies evaporites) have been reported in the upper-part of the Deba catchment by Ábalos et al. (2008) and Iribar and Ábalos (2011). The recent construction of the Albertia rail tunnel has provided direct evidence of the presence of these sulphated facies in the southwest of this catchment (Peña and Rodenas, 2011) where large quantities of sediments were extracted and deposited around the tunnel. Although hydrochemical data support the ascription of a high content of  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  from groundwater to surface water in headwaters, total S content in surface sediments in October 2011 was very low.

The considerable increase of TS content observed in the Mazmela stream (M1) in October 2012, seems to be the consequence of a high-magnitude flood event preceded and followed by unusually dry years (2010–2011 and 2011–2012 hydrological years). Intense rainfall from the 5th–9th of November 2011 ( $228 \text{ L m}^{-2}$ ) generated a high intensity 50-year flood event ( $438 \text{ m}^3 \text{ s}^{-1}$ ), which may have eroded and mobilised the 45%, 60% and 29% of SPM, POC and DOC, respectively, exported during flood events of this hydrological year. A similar behaviour has also been reported by some authors in other catchments (Webb and Walling, 1982; Ciszewski, 2001; HuiGuo et al., 2007).

This S enrichment in fine sediments of M1 might be attributed to the presence of  $\text{CaSO}_4$  phases in dragged sediments. However, the low value of the TOC/TS ratio suggests that these sediments might have been deposited under periodic anoxia, favouring the process of biological sulphate reduction (Appelo and Postma, 2005) and thus leading hydrogen sulphide gas to react with the iron to form iron sulphides (Raiswell et al., 1987) and with many divalent transition metals to form very insoluble metal sulphides (Fu and Wang, 2011; Ngiam and Lim, 2001). Many of these reactions occur primarily within the region of sediment bounded by oxygenated conditions near the sediment (Relić and Đorđević, 2011). This has been reflected in a temporal change in metal distribution at M1, where the proportion of Fe, Zn, Ni and Cu bound to the sulphide fraction increases with no temporal variation in the content of organic matter. This is indicative of precipitation of Fe-, Zn-, Ni- and Cu-sulphides under anoxic conditions (Du Laing et al., 2009; Violintzis et al., 2009), which might be released if the redox conditions change (sulphide dissolution).

Finally, it can be concluded that intense rainfalls play two different roles. On the one hand, they drag and deposit sediments from soils to the river channel, particularly when runoff is important, as has been observed in the Mazmela stream (M1); on the other hand, rainfalls generate flood events which result in a decrease in metal concentrations in channel bottom sediments, as observed in the 2012 campaign in Ego stream (E1), the mid- and low-part of the Deba River (D3 and D4) and, particularly, in the Oñati stream (O1). A considerable decrease in fine-grained sediments was also detected in D4 and O1 in 2012.

As many authors (Roussiez et al., 2013; Du Laing et al., 2009; Eggleton and Thomas, 2004; Ciszewski, 2001) have reported, more turbulent flow conditions might favour strong metal mobility due to the re-suspension of the sediments and the desorption processes of metals. Therefore, those metals which are not only associated with labile forms but are also abundant in fine sediments should be monitored in this catchment during flood events.

## 6. Conclusions

This study shows the influence of anthropogenic inputs and a high-magnitude flood event on surface bottom sediments and water of the Deba River and its tributaries. There is a clear trend of downstream increase in dissolved metals (Fe, Zn, Mn and Ni) in water and trace metals (Zn, Cr, Cu and Ni) and organic carbon concentration in sediments, which evidence the relatively unpolluted nature of the headwaters (M1, D1, D2 and O2) and the contamination of the river at the mid- (O1 and D3) and low-water courses (E1 and D4) of this catchment.

The presence of most metals (Zn, Mn, Cr, Cu, Ni and Pb) in the mobile fractions of fine sediments signifies the presence of metal-rich inputs at those sites, where Zn is by far the most abundant element. Although iron is the most abundant metal discharged in untreated industrial effluents, it is predominately complexed to a coarser fraction, whereas the origin of this element in fine sediments is exclusively mineral. The untreated industrial effluents from galvanising, steel and metallurgical factories, among others, are responsible for the higher metal content in sediments and water. Meanwhile, wastewater inputs seem to be the main source of organic matter in those sites which still receive (Ego stream) or have received (Oñati stream) untreated or partially treated wastewater effluents for a long time.

The results obtained from the calculation of EF, ICF and GCF in fine sediments show a moderately severe anthropogenic enrichment of Zn, Cr and Cu, being these metals the most potentially toxic elements at the mid- and low-part of the catchment. The extremely polluted sediments of Ego stream reflect how far this stream has been altered from its pristine condition and how these sediments could have a significant impact downstream, at the outlet of the catchment.

The construction of the high-speed rail line traversing Wealden Facies evaporites, together with intense rainfalls, seem to be the main reasons for the change in the source of variability of bottom sediments and metal distribution in the upper-part of the catchment. The S enrichment is attributed to the presence of  $\text{CaSO}_4$  phases in dragged sediments. These sediments were deposited under anoxic conditions, which led to precipitation of Fe-, Zn-, Ni- and Cu-sulphides and to a change in metal distribution in fine sediments over time.

Finally, intense rainfalls play two different roles: dragging and depositing sediments from soils to river channel, particularly when runoff is important and, secondly, generating high-magnitude flood events which result in a decrease in metal concentrations in channel-bottom sediments, as observed in the mid- and low-parts of the Deba River and, especially, in the Oñati stream. A considerable decrease in fine-grained sediments was also detected in D4 and O1.

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