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Amine Benabdelkader, Amina Taleb, Jean-Luc Probst, N Belaidi, Anne Probst. Anthropogenic contribution and influencing factors on metal features in fluvial sediments from a semi-arid Mediterranean river basin (Tafna River, Algeria): A multi-indices approach. *Science of the Total Environment*, 2018, 626, pp.899-914. 10.1016/j.scitotenv.2018.01.107 . hal-01713164

**HAL Id: hal-01713164**

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Submitted on 20 Feb 2018

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**To link to this article** : DOI: 10.1016/j.scitotenv.2018.01.107  
URL : <http://dx.doi.org/10.1016/j.scitotenv.2018.01.107>

**To cite this version** : Benabdelkader, Amine<sup>✉</sup> and Taleb, Amina and Probst, Jean-Luc<sup>✉</sup> and Belaidi, N and Probst, Anne<sup>✉</sup> *Anthropogenic contribution and influencing factors on metal features in fluvial sediments from a semi-arid Mediterranean river basin (Tafna River, Algeria): A multi-indices approach.* (2018) Science of The Total Environment, vol. 626. pp. 899-914. ISSN 0048-9697

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# Anthropogenic contribution and influencing factors on metal features in fluvial sediments from a semi-arid Mediterranean river basin (Tafna River, Algeria): A multi-indices approach

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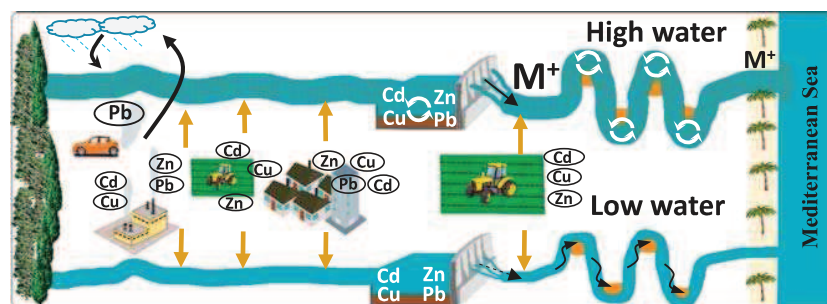
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## HIGHLIGHTS

- Metals contamination of sediments was highlighted up to downstream the Tafna basin.
- Geochemical and isotopes indices deciphered diffuse vs punctual sources of metals.
- Dams and river geomorphology influenced the downstream transfer of particulate metals.
- Storm events washed out the contamination downstream to the Mediterranean sea.
- Metal availability was not strictly linked to the contamination intensity.

## GRAPHICAL ABSTRACT



## ABSTRACT

Metals in river sediments from a semi-arid Mediterranean basin were investigated from upstream to downstream during contrasting hydrological conditions in 2014 and 2015. The level and origin of the contamination were evaluated using several geochemical and isotopic indicators. Elements were grouped by their level of contamination: high ( $Pb > Cd > Zn > Cu$ ) and low (Al, Fe, Cr, Co, Ni). Multiple local sources of contamination were identified (industrial, agricultural and domestic waste), as well as very specific ones (gasoline station) and diffuse pollution from atmospheric deposition (gasoline, ores, aerosols). During storm events, the upstream dams can either be secondary sources of contamination or dilutors through particles derived from natural erosion. The contamination was slowed downstream due to the river geomorphology, but eventually washed into the Mediterranean Sea by intense storm events. Naturally derived elements (Co, Ni, Cr, As) were associated with Al, Fe and Mn oxides or clays, and anthropogenic originated metals with phosphorus (Cd and Zn), sulphur (Cu) and POC (Pb enrichment). Cadmium and Pb were the most available metals upstream and at the outlet, but their availability was not strictly related to their degree of contamination. These conclusions could be drawn thanks to an approach by multiple indicators.

### Keywords:

Trace metals  
River sediments  
Hydrology  
Dam  
Geochemical and isotopic indices  
Available fraction

## 1. Introduction

Trace elements are encountered in varying degrees of concentration in different compartments of the so-called *critical zone*, which is the interface between atmosphere, vegetation, soil and rock (NRC, 2001). The

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sources of metals can be natural from geogenic material and volcanic eruption, or anthropic from industrial emissions, vehicle exhausts, mining, domestic effluents and modern agriculture (fertilisers, pesticides, manures) (Kabata-Pendias and Pendias, 1992).

In aquatic environments draining the critical zone, bed sediments from soil and bedrock erosion are major sinks and carriers for contaminants. Trace elements are transported by rivers from land to the sea mainly by particulate material, especially in high pH conditions (Martin and Whitfield, 1983). Indeed, <1% of contaminants remain dissolved in water, whereas over 99% are stored in sediments because of the affinity of trace elements for the particulate phase (Filgueiras et al., 2004; Ramamoorthy and Rust, 1978; Singh et al., 2005). When environmental conditions change, such as pH, redox potential or the presence of organic chelators, metals can be alternately released in the water column and re-absorbed into the sediment (Casas et al., 2003; Förstner and Wittmann, 1981).

In the past century, trace elements (Pb, Zn, Cd, Cu, Cr, Co, Ni, As) have been discharged into the world's rivers and estuaries as a consequence of rapid industrialisation (Cobelo-Garcia and Prego, 2003; Tam and Wong, 2000), economic development and population growth. Semi-arid basins with limited water resources, are particularly sensitive to such anthropic pressure (Araújo Neto et al., 2017).

Owing to their storage capacity, sediments play a major role in determining the pollution pattern of aquatic systems (Casas et al., 2003) and reflecting part of the history of pollutant deposition in aquatic ecosystems (Singh et al., 2005).

Geochemical tracers have long been used to evaluate metal contamination in river sediments (Valette-Silver, 1993) and contamination indices have been regularly applied (Caeiro et al., 2005; Pena-Icart et al., 2017) to predict associated undesirable biological effects, which still present a major challenge. The sediment pollution index (SPI) (Singh et al., 2002) helps assess sediment toxicity, whereas geochemical indices, such as the enrichment factor (EF) (Sinex and Helz, 1981), the index of geoaccumulation (Igeo) (Müller, 1969, 1981), the contamination factor (CF), the degree of contamination (DC) (Hakanson, 1980) and the pollution load index (PLI) (Tomlinson et al., 1980), have commonly been used to assess the extent of contamination. They all compare the total concentrations of metal in the studied sediments with their background concentrations (Pena-Icart et al., 2017). However, the diversity of background conditions from one region to another makes this evaluation difficult (Reimann and De Caritat, 2005). Moreover, depending on the indicator used, various interpretations can be made between the studies on the levels of contamination.

The origins of elements have frequently been investigated and traced using stable isotopes (e.g. Moore, 1977; Court et al., 1981). In the last century, lead contamination was particularly of concern. Industrialisation, mining exploration and the use of leaded hydrocarbons have led to widespread lead contamination in atmospheric particles (Bollhofer and Rosman, 2000; Monna et al., 1997), soil and river sediments (Chow, 1970; Hansmann and Koppel, 2000) and the marine environment (Boyle et al., 2014; Weiss et al., 2003). Lead isotopes have been particularly useful for deciphering natural and anthropic sources in the environment and in top sediments in particular (Chow, 1970; Li and Thornton, 2001; Bur et al., 2009). Although leaded gasoline has been abandoned in most countries in the northern hemisphere, it is still in use in some countries, particularly in northern Africa, which is likely to increase lead pollution in the environment. It therefore remains necessary to be able to determine the source of lead, which is a toxic element, in order to identify solutions to reduce its contamination.

Furthermore, the challenge remains of evaluating the available fraction of metal that can endanger living organisms. The available fraction of metal in sediments has therefore often been estimated using various chemical reagents (Bur et al., 2009; Probst et al., 1999). Trace metals are known to be linked to five main components in the sediments: clays, carbonates, oxides, organic matter and residual fractions (Leleyter and Probst, 1999; Tessier et al., 1979). Clay minerals with their large surface

area affect adsorption of metals (Suresh et al., 2012). Al, Fe and Mn oxides and organic matter play a very important role in the binding of trace metals to and their absorption by sediments (Davis, 1984; Turner et al., 2004).

Hydrological conditions play a key role in metal transfer in rivers. Metals accumulated in sediments during low water can be re-suspended and transported downstream during flooding (Ciszewski, 2001; Martínez-Santos et al., 2015). They also can be mobilised in the dissolved phase, where they become more (bio)available and reveal toxic chemical forms (Eggleton and Thomas, 2004; Roussiez et al., 2013). The Mediterranean climate experiences strong seasonality, with high water conditions that cause severe flooding. Moreover, the presence of an elevated mountain range upstream, the extensive dominance of young rocks, intense human activity and long periods of dryness are agents of very high mechanical erosion rates (Probst and Amiotte-Suchet, 1992; Milliman, 2001). Mediterranean rivers thus transport large quantities of sediment compared to most other regions of the world (Ludwig and Probst, 1998). The hot and dry climate induces extensive low water periods, leading to water shortages in many parts of the Mediterranean drainage basin. Moreover, the intensive exploitation of existing water resources is a widespread phenomenon, which has resulted in more dam construction for water supplies in the last ten years (Ludwig et al., 2003; Sadaoui et al., 2017).

In recent decades, pollution has intensified in the Mediterranean area (Copat et al., 2012), especially by trace metals found in bottom sediments (Palanques et al., 2008) and marine organisms (Copat et al., 2012). Some authors have highlighted the contamination by trace metals in some Mediterranean rivers and their estuaries, for example in France (Radakovitch et al., 2008; Roussiez et al., 2011, 2012; Reoyo-Prats et al., 2017), Spain (Llobregat river, Casas et al., 2003), Greece (Dassenakis et al., 1997) and Tunisia (Ennouri et al., 2010). The Tafna basin is one such river draining semi-arid basins under Mediterranean hydroclimatic conditions with limited resources. Contamination by Pb, Zn and Cd has been discovered in the Tafna estuary sediments (Kouidri et al., 2016). However no other investigations have as yet been carried out on the effect of considerable anthropisation on the contamination of sediments and of the whole basin. As in the other case studies, few have examined the influence of hydrological conditions, erosion processes and dams on the control of the contamination transfer along the river course. Indeed, the extreme hydrological conditions, intense erosion processes and presence of the dams are thought to greatly influence river water quality (Taleb et al., 2004).

This study investigated the sources of some trace metals (for the sake of convenience the metalloid As was also designated as one) in riverbed sediment and their behaviour along the river channels in relation to hydrological conditions. The main objectives of the present study were:

- (i) to quantify and determine the spatial distribution of trace metal contamination in surface sediments and the anthropogenic influence.
- (ii) to identify the intensity of the contamination and the various sources of metals using a collection of indicators.
- (iii) to highlight the role of environmental conditions (dams, hydrology and erosion) on trace metal behaviour and their availability.

## 2. Materials and methods

### 2.1. Description of the study area

The Tafna basin is located in the north-western part of Algeria in the region of Tlemcen. The Tafna is the main river draining this area of 7245 km<sup>2</sup>, whose elevation ranges from sea level to 1900 m a.s.l. After a 170 km course, it reaches the Mediterranean Sea. Of its many tributaries, the Isser wadi is the most important, but the amount of water it delivers to the Tafna has been markedly reduced since the construction of three



dams (including the Sikkak Dam (DamS)). During the rainy season they hold most of the water for irrigation and drinking water supplies in the hot season. Upstream, the most important tributary is the polluted Mouillah wadi (Taleb et al., 2004), which drains the Maghnia region and its one main industrial centre. It receives untreated domestic sewage and industrial effluents in the upper part, mainly from the Moroccan town of Oujda, but is also polluted by effluents from the Ouerdeffou and El Abbes wadis (secondary tributaries) (Fig. 1). Several anthropogenic activities, including the region's four main industrial sites (Sebdou, Tlemcen, Maghnia, Oujda), may have an impact on water quality along the river. The middle stream of the Tafna basin is impacted by anthropic inputs caused by emissions from four industrial units: ENOF (bentonite:  $600 \text{ m}^3 \cdot \text{day}^{-1}$ ), ENCG (fats:  $528 \text{ m}^3 \cdot \text{day}^{-1}$ ) ERIAD (corn mill  $1600 \text{ m}^3 \cdot \text{day}^{-1}$ ) and CERTAF (ceramics:  $130 \text{ m}^3 \cdot \text{day}^{-1}$ ) (A.E.B., Tidjani et al., 2006). In this basin, several main dams were constructed, including the Boughrara Dam (DamB), the largest in the basin with a capacity of the 177 million  $\text{m}^3$ , Beni Bahdel (DamE) with 66 million  $\text{m}^3$  and DamS with 27 million  $\text{m}^3$  (Dahmani et al., 2002). In the upstream part of the Tafna basin there is a textile plant and the five main dams (including DamB and DamS), ensuring water supplies along the river course. After becoming full, from time to time these dams are emptied during high water flow periods, leading to the downstream transfer of stored sediments.

The climate is of a Mediterranean type with a sub-arid tendency: average precipitation ranges between 350 and 450 mm and the mean annual temperature is  $16^\circ\text{C}$  (period 1997–2006) Daily temperatures can reach up to  $47^\circ\text{C}$  (2009), which increases the rate of evapotranspiration. The hydrological regime is Mediterranean with alternating heavy storm events and severe drought periods: the mean annual flow in the last fifteen years has varied between  $0.11 \text{ m}^3 \cdot \text{s}^{-1}$  (2008) and

$10.95 \text{ m}^3 \cdot \text{s}^{-1}$  (2014) at the downstream station (National Agency of Hydrologic Resources, ANRH, 2016) ([www.anrh.dz/contact.htm](http://www.anrh.dz/contact.htm)).

With regard to bedrock types, the Tafna basin is divided into two zones: the upstream part where the river runs in a canyon through Jurassic rocks rich in limestone and dolomite, and the downstream part where it drains a tertiary basin characterised by Miocene marls covered by recent alluvium belonging to the quaternary (Taleb et al., 2004).

Salt soils are encountered in the middle course of the Tafna Wadi. Some forests, sparse vegetation and pasture mainly occupy the upper basin, with irrigated crops occupying the rest (Bouanani, 2000). The land use is composed of cereal covering  $1699 \text{ km}^2$  (23.6% of the total area), horticulture  $342 \text{ km}^2$  (4.75% of the total area) and arboriculture  $263 \text{ km}^2$  (3.65% of the total area) (Algerian Ministry of Agriculture, 2011) (<http://www.minagri.dz/>). In the whole Tafna basin, the slope ranges from <5% to >30%. In the Mouillah sub-catchment, the slope is estimated to be <5% with an erosion rate of  $400 \text{ t} \cdot \text{km}^{-2} \cdot \text{yr}^{-1}$ . In the upstream Tafna basin, the slope is >25% and exceeds 30% in the Isser sub-catchment, with an erosion rate of  $1000 \text{ t} \cdot \text{km}^{-2} \cdot \text{yr}^{-1}$  (Tidjani et al., 2006).

## 2.2. Sampling strategy

### 2.2.1. Location of the stations

In the Tafna basin, samples were taken from ten stations along the water course (T1, T3, T5, MG, M2, T6, T7, S2, I5, T8) and from two dams (DamB and DamS). Based on previous preliminary survey results, these stations were chosen in order to characterise the impacts of the various anthropic sources of metal contamination and hydraulic structures on water quality and the transfer of matter downstream to the Mediterranean Sea (Fig. 1). The stations are located as follows:

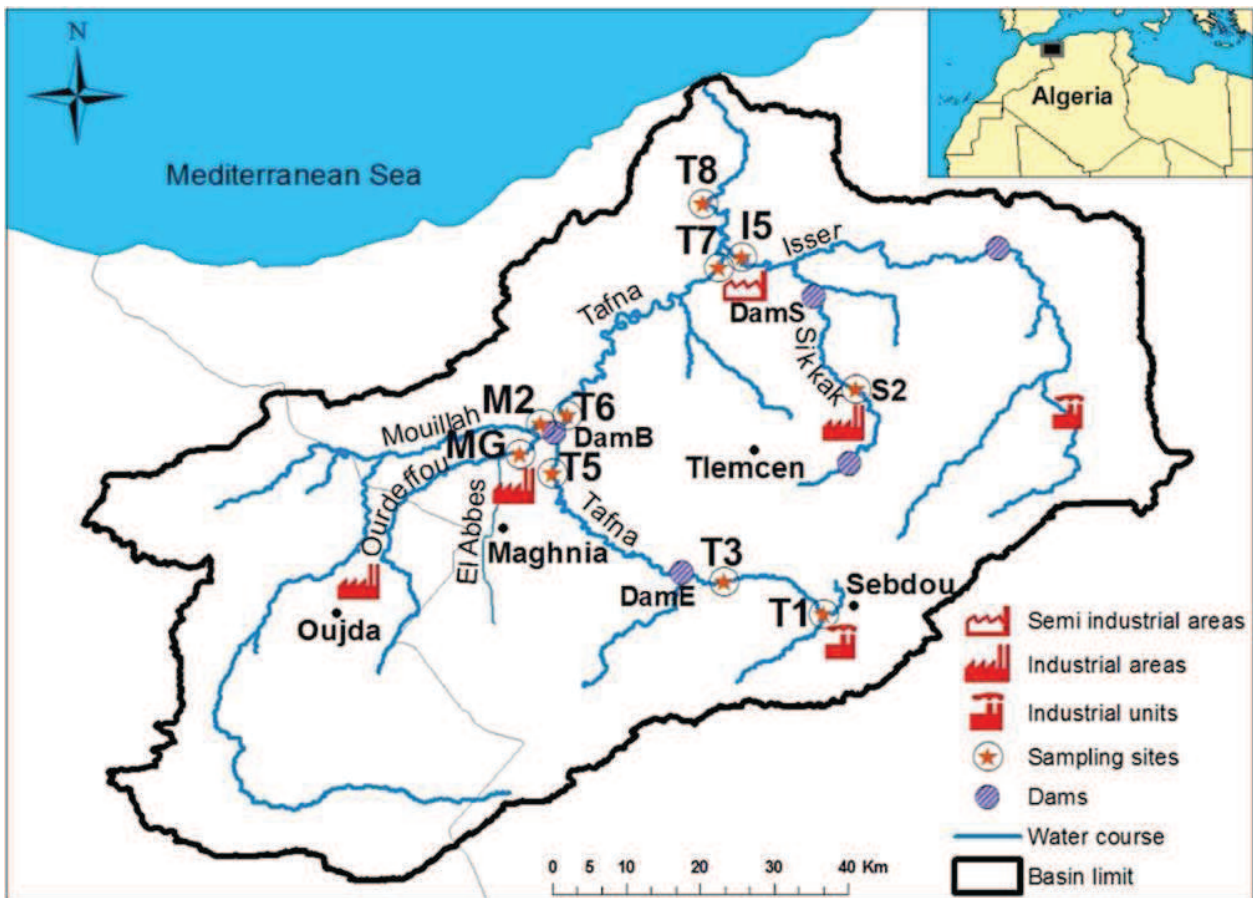


Fig. 1. Study area and sediment sampling sites in the Tafna River (north-western Algeria).

downstream an urban area with industrial units (T1, MG and S2) in addition to a public dump (S2), upstream (M2 and T5) and downstream (T6) of DamB, upstream (T6) and downstream (T7) of a large flat agricultural area with a number of river meanders, at the outlet of the main downstream tributary the Isser wadi (I5), and finally at the outlet of the whole Tafna basin (T8) before any seawater influence.

### 2.2.2. Sampling protocol and preparation

Samples of surface sediments (the top 3 cm) were collected using polyethylene containers during four sampling campaigns: June 2014 (low water flow), October 2014 (medium water flow), February 2015 (high water flow) and August 2015 (low water flow) at each sampling site. Samples of bedrock at each station were taken from outcropping sites supposed to be representative of the dominant drainage bedrocks. Bottom sediment in dams was taken from the surface in the central part using an Ekman grab.

Once in the laboratory, the samples were air dried, carefully homogenised with an agate mortar (without crushing) and quartered, then sieved (with a nylon sieve) to obtain three fractions (a fine fraction <63 µm, a coarse fraction (63 µm–2 mm), and finally a fraction >2 mm). Each fraction was weighed. Mineralisation was performed on the <63 µm fraction owing to its dominance and its affinity for metals (Probst et al., 1999).

### 2.3. Chemical treatments and analysis

For the analysis of total trace metals and major elements, each sediment sample was digested by a chemical mixture HF/HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> following a well calibrated multi-step procedure (Marin, 1998; N'Guessan et al., 2009). In the EcoLab clean room, 100 mg of sediment was first digested in a Teflon cup with 0.6 ml HNO<sub>3</sub> (suprapure) and 0.5 ml HF at 90 °C for 17 h, then a further 0.6 ml HNO<sub>3</sub> was added, the solution left overnight at 85 °C and finally the solution was evaporated. In a second step, to remove the organic matter, H<sub>2</sub>O<sub>2</sub> (0.5 ml) was added three times, interspersed by 15 min in an ultrasonic bath (Branson 1510), until the effervescence had disappeared when the solution was stirred. Finally, after complete evaporation, the residue was recovered by 2 ml HNO<sub>3</sub> 2%. Blanks and standard sediments SUD-1, WQB-1, STSD-3 followed the same digestion procedure.

After the dilution process, the major elements Ca, Al, Fe, S, P and Mn were initially analysed on an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES Thermo IRIS Intrepid II XDL) at EcoLab (Toulouse, France), and then trace elements Zn, Pb, Cr, Ni, Cu, Co, As and Cd were analysed on an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS Perkin-Elmer ELAN 6000) at OMP (Observatory Midi-Pyrénées analytical platform Toulouse, France). The yielded recovery rates for the standard SUD-1, WQB-1 and STSD-3 were between 85% and 110%, while the blank samples used to check solvent contamination were below detection limits. The detection limits (DL) for the elements are around 0.5 µg l<sup>-1</sup> for ICP-OES, and between 10<sup>-3</sup> and 10<sup>-2</sup> µg l<sup>-1</sup> for ICP-MS as follows: Cd < Co = Cs = Pb < Cu < As < Ni. For Cr, Sc and Zn, DL are 0.049, 0.167 and 0.187 µg l<sup>-1</sup> respectively.

The isotopic ratios for lead <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb, <sup>208</sup>Pb/<sup>204</sup>Pb, <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>208</sup>Pb/<sup>207</sup>Pb were performed on sediment samples from two main campaigns (during low water flow, all samples in August 2015, and in addition T5 in June 2014; during high water flow, some samples (T1, T6, MG, S2) in February 2015) using the ICP-MS (Elan 6000, Perkin-Elmer) in Toulouse. The standard reference material (SRM981) was used for correction of stability and mass bias effects by bracketing technique (Aries et al., 2001). The concentrations were adjusted to 10 µg·l<sup>-1</sup> in order to guarantee the work on the same pulls of the detector, and each sample analysed three times. The <sup>206</sup>Pb/<sup>207</sup>Pb mean value of the NIST-SRM-981 was 1.0947 as compared to the reference value of 1.0933 (National Institute of Standards and Technology, 1991).

Major and trace elements and lead isotopes in bedrocks were analysed with ICP-MS at the Service d'Analyse des Roches et des Minéraux (SARM) of the Centre for Petrographic and Geochemical Research (CRPG, Nancy, France) (2017) (<http://helium.crpq.cnrs-nancy.fr/SARM/indexanglais.html>) after the alkaline fusion method with lithium metaborate (Garzanti et al., 2010; Govindaraju and Mevelle, 1987). The same quality guarantee as for sediment analysis was ensured.

A simple chemical extraction was used to determine the available fraction of trace elements in the sediment: one gram of sediment was leached with 10 ml of 0.05 mol l<sup>-1</sup> EDTA at ambient temperature and filtered using a 0.22 µm porosity filter (Ghestem and Bermond, 1998). After dilution, the solution obtained was analysed in the same way as the total digestion of sediment.

Particulate organic carbon (POC) was analysed using a Flash 2000 ThermoFisher. Samples were first exposed to concentrated HCl (2 N) until disappearance of effervescence and left on the hot plate at 60 °C overnight to remove all inorganic carbon.

### 2.4. Data treatment

#### 2.4.1. Contamination indices

**2.4.1.1. Enrichment factor.** The enrichment factor (EF) has commonly been used to assess the degree of anthropogenic metal pollution at various sites (Chester and Stoner, 1973). The enrichment of a given element in sediments relative to a background reference is an indication of the contribution from anthropogenic sources.

The major concerns with this index are the choice of the reference element, called a normaliser (N'Guessan et al., 2009; Roussiez et al., 2005), and of the background reference material (Duce et al., 1975; N'Guessan et al., 2009), which has often been a subject of discussion (Reimann and De Caritat, 2005). Several normaliser elements were tested in accordance with other studies: Fe (Sinex and Wright, 1988), Li (Loring, 1990), Cs (Roussiez et al., 2005), and Sc (Grousset et al., 1995; Hernandez et al., 2003; Hissler and Probst, 2006). Aluminium was chosen as the normaliser element in the present case study because it is a fairly conservative element and a major constituent of clay minerals, and has also been used successfully in various studies (Hirst, 1962; Windom et al., 1989).

The reference materials most frequently used are the UCC (Upper Continental Crust, Wedepohl, 1995) and the PAAS (Post-Archean Australian Shale; Taylor and McLennan, 1985) since they are universal and allow a relative comparison between sites. However, it has also clearly been shown that they may lead to an overestimation of the degree of contamination (Hernandez et al., 2003; N'Guessan et al., 2009). In this study, UCC and the local bedrock were used as references for comparison purposes.

The enrichment factor (Chester and Stoner, 1973) is expressed as follows:

$$EF = (C_x/Al)_{Sample} / (C_x/Al)_{Reference\ material} \quad (1)$$

where C<sub>x</sub> is the concentration of a given element and Al is the normaliser element.

The reference material is either UCC or the local bedrock.

**2.4.1.2. Geoaccumulation index (I<sub>geo</sub>).** The intensity of metal contamination can be evaluated using the geoaccumulation index (Müller, 1969):

$$I_{geo} = \log_2(C_n/1.5B_n) \quad (2)$$

where C<sub>n</sub> is the measured concentration of the considered metal (n) in the sediment and B<sub>n</sub> is the geochemical background concentration of the metal (n). Factor 1.5 is the background matrix correction factor due to lithogenic effects.

There are seven classes:  $I_{geo} \leq 0$ : unpolluted,  $0 < I_{geo} < 1$ : unpolluted to moderately polluted,  $1 < I_{geo} < 2$ : moderately polluted,  $2 < I_{geo} < 3$ : moderately polluted to strongly polluted,  $3 < I_{geo} < 4$ : strongly polluted,  $4 < I_{geo} < 5$ : strongly polluted to extremely polluted and  $I_{geo} \geq 5$ : extremely polluted (Müller, 1981).

**2.4.1.3. Contamination degree (CD).** Unlike the other indices, the contamination degree (Hakanson, 1980) allows the estimation of a polymetallic contamination for each sampling site:

$$CD = \sum CF \quad (3)$$

where the contamination factor (CF) is the metal concentration in the sediment/background value of the metal. The background value for this study was taken as the mean bedrock concentration for the Tafna basin.

According to Hakanson (1980), this index is associated with four quality classes:  $CD < 6$  (low contamination),  $6 \leq CD < 12$  (moderate contamination),  $12 \leq CD < 24$  (considerable contamination) and  $CD \geq 24$  (very high contamination).

**2.4.1.4. Sediment pollution index (SPI).** The sediment pollution index (Singh et al., 2002) allows the degree of toxicity in the sediments to be evaluated, in contrast to the geoaccumulation index and the enrichment factor, which only quantify the degree of contamination and do not take into consideration toxicity for living organisms.

SPI is defined as a linear sum of the metal enrichment factors weighed by the toxicity of a given metal. It is believed that metal concentrations in unpolluted sediments should not exceed the values of average shale. A weight of 1 was assigned to Cr and Zn, the less toxic metals. The calculated weight was 2 for Ni and Cu, 5 for Pb and 300 for Cd (Singh et al., 2002):

$$SPI = \frac{\sum(CF_x * W_x)}{\sum W_x} \quad (4)$$

where  $W$  is the toxicity weight of metal  $x$  and  $CF$  is the contamination factor defined as the ratio between the metal concentration in the sediment and in the mean bedrock for the Tafna basin (see Eq. (3)).

SPI is associated with five quality classes:  $0 \leq SPI < 2$  (healthy sediment),  $2 \leq SPI < 5$  (poorly polluted sediment),  $5 \leq SPI < 10$  (medially polluted sediment),  $10 \leq SPI < 20$  (highly polluted) and  $\geq 20$  (hazardous sediment).

**2.4.1.5. Pollution level index (PLI).** The pollution load index assesses the level of metal contamination. PLI has been defined as the  $n^{\text{th}}$  root of the product of the metal concentration; a PLI value  $> 1$  implies the existence of contamination and  $PLI < 1$  indicates no pollution (Tomlinson et al., 1980):

$$PLI = \sqrt[n]{CF_1 * CF_2 * CF_3 * CF_n} \quad (5)$$

where  $CF$  is the metal concentration in the sediment/background value of the metal. The background value for this study was taken as the mean bedrock concentration for the Tafna basin.  $n$  is the number of metallic elements.

#### 2.4.2. Lead isotope ratio

Of the four lead isotopes,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$  are produced by the radioactive decay of the long-lived radioactive parents  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$  respectively, while  $^{204}\text{Pb}$  is not radiogenic. As commonly described in the literature, several authors have used lead isotopic composition to identify different Pb sources to determine their respective contributions, particularly those of anthropogenic sources (Agnan et al., 2015; Bur et al., 2009; Hansmann and Koppel, 2000; Hernandez et al., 2003; Komárek et al., 2008; Roussiez et al., 2005).

#### 2.4.3. Statistical analysis

The statistical investigation was carried out using STATISTICA software version 8.0.306.0 (2007) and Excel (2010). Spearman correlation analysis was used to determine the relationships between different elements since the normality test of data distribution failed. A log-ratio data transformation (using R software version 3.3.1, rgr package) was used for principal component analysis (PCA) to identify parameters that could influence the distribution of trace elements and the link with other environmental variables.

### 3. Results

#### 3.1. Trace and major element concentrations in sediments

The average concentration of studied trace metals in sediments were in the following order of abundance:  $\text{Zn} > \text{Pb} > \text{Cr} > \text{Cu} > \text{Ni} > \text{Co} > \text{As} > \text{Cd}$  (Table 1).

Trace metal concentrations in the Tafna sediments can be compared with other rivers flowing into the Mediterranean Sea (Table 1). The concentrations were lower (except for lead) in the Tafna watershed than in a contaminated watershed in south-east Spain (Llobregat basin, Casas et al., 2003), but they were higher for Zn, Pb, Cu, Cd than those of the Rhône river (Ferrand et al., 2012). Concentrations for Zn, Pb and Cr were much higher than in sediments from the lower Moulouya watershed in Morocco, near the Tafna basin (Tovar-Sanchez et al., 2016), but lower for Ni, Cu, Co and As (Table 1). In contrast, in the upper Moulouya basin Pb and As concentrations were one to three orders of magnitude higher than in the Tafna River at between 97 and 11,200  $\mu\text{g}\cdot\text{g}^{-1}$  and 110–160  $\mu\text{g}\cdot\text{g}^{-1}$  respectively (El Azhari et al., 2016).

In the Tafna sediments, the highest concentrations for Zn were found at stations T6, MG, S2 and for Pb at T5, MG, T6 (Table 1). Cadmium concentrations were highest at stations MG, T7 and T6, whereas Cu was higher at MG and S2 and M2, and As at M2, T6 and T7. Concentrations of the metals Ni, Co and Cr were fairly homogenous between the stations, except for a higher Cr concentration at I5. All the elements except Ca exhibited much higher concentrations in sediments from DamB compared with the river (two to three times higher except for Zn and Pb), whereas those of DamS were comparable (Table 1). Lead concentration was highly variable, as reflected by the standard deviation of the mean, the mean value being exceeded in particular at stations T1 and T5. Except for As and Ca, the metal concentrations of the Tafna bedrocks were lower than those of UCC (Upper Continental Crust) (Wedepohl, 1995).

Among the major elements, Ca exhibited the highest concentration at all stations, but particularly at stations in the upper part of the basin, which is in agreement with the carbonate content of the bedrocks of the Tafna basin.

As also shown in Table 1, the organic carbon content (POC %) steadily decreased in sediments in the main Tafna channel from the upstream station (3.6%, T1) to downstream station (1.15%, T8), and similarly for the Isser tributary from the upstream station M2 (2.9%) to downstream station I5 (1.4%).

#### 3.2. Relationships between the different elements and with the POC

Basic relationships between each of the considered elements and POC were evaluated using Spearman  $\rho$  coefficients (Table 2) to explore converging behaviour and/or sources of metals in the Tafna basin. All the significant correlations were positive. A large number of elements were significantly correlated, such as Al, Fe, Ni, Cr and Co ( $0.85 \leq \rho \leq 0.97$ ,  $p < .01$ ). The strongest relationship for As was found with Fe, Co, Ni and Al, but As was also linked to Mn, as were Cd, Ni, Cr and Co. Cadmium and Cu were well related with P and Zn, and with Pb. Finally, Cd, Cu, Zn were significantly linked with P and S, whereas Ca was the only element significantly linked with POC.



**Table 1**  
Mean ( $\bar{x}$ ), standard deviation ( $\sigma$ ), min. and max. concentrations of trace metals and major elements in sediments collected during the four sampling periods ( $n = 40$ , except dams only once) at each sampling station of the Tafna River (TR). Are also indicated UCC composition (Wedepohl, 1995), Mean ( $\bar{x}$ ) and standard deviation ( $\sigma$ ) for TR bedrocks and TR sediments of the whole basin (Dams not included). Sediment composition from two contributing rivers to the Mediterranean Sea, the Llobregat basin (Sed Llobregat, Spain, Casas et al., 2003) and the Rhône basin (Sed Rhône, France, Ferrand et al., 2012), are given. (—): not determined.

Station	Trace elements ( $\mu\text{g}\cdot\text{g}^{-1}$ )									Major elements ( $\text{mg}\cdot\text{g}^{-1}$ ) except POC (%)							
	Zn	Pb	Cr	Cu	Ni	Co	As	Cd	Ca	Al	Fe	S	P	Mn	POC		
Sediment	T1	$\bar{x}$	39.04	35.45	33.21	12.31	15.48	6.29	3.91	0.11	160.90	27.35	14.84	0.35	0.30	0.30	3.62
		$\sigma$	14.41	36.84	11.79	4.03	5.83	2.09	1.31	0.06	57.26	10.18	5.26	0.13	0.08	0.10	2.86
	T3	$\bar{x}$	42.70	20.00	34.61	13.45	16.16	6.20	3.95	0.11	138.20	28.48	15.49	0.44	0.37	0.30	2.81
		$\sigma$	14.04	9.87	11.11	5.02	5.85	2.40	1.39	0.05	25.77	13.36	5.91	0.07	0.11	0.09	1.94
	T5	$\bar{x}$	43.74	153.62	40.89	12.42	15.90	6.38	4.05	0.11	117.02	31.27	16.31	0.35	0.38	0.30	2.20
		$\sigma$	15.63	255.99	18.41	4.48	6.85	2.59	1.06	0.04	12.32	14.31	6.83	0.07	0.16	0.10	0.80
	MG	$\bar{x}$	126.86	59.00	37.49	33.18	16.32	6.87	5.42	0.21	105.86	30.68	17.61	2.93	1.14	0.25	2.10
		$\sigma$	50.32	26.37	8.30	14.54	4.72	2.99	2.19	0.10	22.22	11.75	6.04	2.08	0.35	0.07	1.01
	M2	$\bar{x}$	54.21	16.23	37.11	17.96	18.83	7.48	6.10	0.06	118.60	33.59	18.72	0.26	0.26	0.41	2.02
		$\sigma$	23.70	3.38	11.21	8.47	7.22	2.78	2.25	0.02	42.34	14.71	6.96	0.07	0.04	0.19	0.90
	T6	$\bar{x}$	135.98	58.08	38.24	16.78	15.73	6.96	6.96	0.55	90.90	28.97	19.87	0.44	0.66	0.53	1.61
		$\sigma$	42.94	34.20	12.47	5.51	5.57	2.52	1.88	0.17	19.70	10.47	6.50	0.15	0.26	0.23	1.24
	T7	$\bar{x}$	68.38	18.26	46.44	14.09	17.39	7.02	5.98	0.24	98.24	33.93	19.27	0.38	0.63	0.38	1.57
		$\sigma$	22.55	8.08	15.02	1.56	4.72	1.74	0.71	0.17	20.00	10.87	3.88	0.04	0.07	0.10	0.41
	S2	$\bar{x}$	112.53	37.47	38.87	28.50	13.92	4.99	4.28	0.18	138.43	25.50	14.89	1.44	1.10	0.24	2.91
		$\sigma$	83.76	18.83	15.49	15.59	6.11	1.69	1.26	0.11	18.80	13.21	5.68	1.05	0.79	0.07	1.12
	I5	$\bar{x}$	60.77	21.80	53.92	12.89	18.62	6.83	5.52	0.13	85.47	34.92	19.53	0.40	0.52	0.29	1.38
		$\sigma$	11.78	9.70	18.03	2.78	4.60	1.44	1.11	0.03	10.92	13.11	5.34	0.07	0.15	0.05	0.95
	T8	$\bar{x}$	58.95	13.75	47.58	13.50	17.91	7.11	5.09	0.16	86.11	32.45	19.78	0.39	0.49	0.35	1.15
		$\sigma$	21.79	2.71	21.28	5.60	7.41	2.87	1.23	0.08	21.08	16.48	8.35	0.05	0.24	0.13	0.48
	Mean TR	$\bar{x}$	74.31	43.37	40.83	17.51	16.63	6.61	5.13	0.19	113.97	30.72	17.63	0.74	0.58	0.33	2.14
		$\sigma$	47.31	83.52	14.42	10.03	5.44	2.18	1.67	0.16	34.96	11.77	5.78	1.04	0.40	0.14	1.41
	Max. TR	$\bar{x}$	237.17	537.50	80.17	51.77	27.41	10.69	9.42	0.79	246.45	53.98	31.00	5.76	2.27	0.87	7.90
		$\sigma$	20.59	9.66	17.05	6.16	6.80	3.05	2.32	0.04	58.07	12.31	8.04	0.16	0.18	0.16	0.55
	DamB	$\bar{x}$	470.00	270.19	82.10	46.49	39.18	16.77	13.57	2.60	92.40	82.97	40.11	1.04	0.82	0.83	1.25
		$\sigma$	69.91	12.58	80.49	16.17	25.62	9.12	7.90	0.12	96.41	52.82	28.54	0.31	0.67	0.35	0.97
	Llobregat	$\bar{x}$	143.10	37.40	51.30	33.90	62.30	—	26.40	0.43	—	—	—	—	—	—	—
		$\sigma$	61.30	14.60	44.60	9.96	25.10	6.30	—	0.08	135.00	44.40	22.40	—	—	0.48	—
Bedrock	Mean TR	$\bar{x}$	22.40	8.60	15.90	10.20	11.80	2.10	6.90	0.10	194.17	16.19	8.29	—	—	0.34	—
		$\sigma$	17.18	12.65	15.42	5.67	6.97	1.58	12.13	0.04	135.00	20.39	7.59	—	—	0.29	—
	UCC	$\bar{x}$	52.00	17.00	35.00	14.30	18.60	11.60	2.00	0.10	29.45	77.44	30.89	—	0.66	0.53	—
		$\sigma$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

### 3.3. Spatial and seasonal variation of trace metals

The mean value of metal concentrations for high and low water flow conditions shown in Fig. 2 was calculated by grouping the different sampling stations according to their positions in the upper (T1, T3, T5), middle (MG, M2, T6, S2), and lower (T7, I5, T8) parts of the Tafna basin. For all trace elements, taking each water flow condition into account, the highest concentrations were observed in the middle part, except for Ni, Co in low water (LW). In the downstream part, the concentrations tended to return to upstream (or slightly higher) values. Whatever the position in the basin, the highest concentrations were found during low water flow conditions for all elements except for Pb, As and Co,

which were equivalent during the two hydrological conditions in the middle part, and for the latter two even stable in the downstream part. It can be seen that the relative increases during low water conditions were significant for Zn and Cd in the middle part.

### 3.4. Estimation of metal contamination intensity

Different indicators of contamination were used to evaluate the metal enrichment in sediment in the Tafna River resulting from anthropogenic activities: the very commonly used enrichment factor (Sinex and Helz, 1981) and various contamination indices: the index of geoaccumulation (Müller, 1969), the sediment pollution index (Singh,

**Table 2**  
Spearman correlation matrix of the elements and POC concentrations in surface sediments from the Tafna River. Bold values: significant correlation, underlined values:  $p < .01$ , others:  $p < .05$  ( $N = 40$ ).

	Pb	As	Cd	Zn	Cu	Ni	Cr	Co	Ca	Fe	Al	Mn	P	S	POC
Pb	—														
As	0.13	—													
Cd	<b>0.31</b>	<b>0.62</b>	—												
Zn	<b>0.47</b>	<b>0.64</b>	<b>0.76</b>	—											
Cu	<b>0.34</b>	<b>0.56</b>	<b>0.44</b>	<b>0.71</b>	—										
Ni	−0.08	<b>0.79</b>	<b>0.40</b>	<b>0.36</b>	<b>0.59</b>	—									
Cr	−0.05	<b>0.69</b>	<b>0.45</b>	<b>0.37</b>	<b>0.50</b>	<b>0.91</b>	—								
Co	0.00	<b>0.81</b>	<b>0.46</b>	<b>0.35</b>	<b>0.55</b>	<b>0.95</b>	<b>0.85</b>	—							
Ca	0.12	−0.11	−0.14	−0.15	<b>0.35</b>	0.23	0.14	0.21	—						
Fe	0.00	<b>0.89</b>	<b>0.55</b>	<b>0.48</b>	<b>0.60</b>	<b>0.95</b>	<b>0.90</b>	<b>0.95</b>	0.09	—					
Al	−0.03	<b>0.77</b>	<b>0.40</b>	<b>0.35</b>	<b>0.59</b>	<b>0.97</b>	<b>0.91</b>	<b>0.94</b>	0.23	<b>0.94</b>	—				
Mn	−0.02	<b>0.74</b>	<b>0.52</b>	<b>0.36</b>	0.31	<b>0.68</b>	<b>0.57</b>	<b>0.74</b>	0.17	<b>0.74</b>	<b>0.65</b>	—			
P	<b>0.37</b>	<b>0.44</b>	<b>0.72</b>	<b>0.80</b>	<b>0.67</b>	0.31	<b>0.44</b>	0.31	−0.01	<b>0.43</b>	<b>0.35</b>	0.19	—		
S	0.30	0.00	<b>0.40</b>	<b>0.46</b>	<b>0.52</b>	0.01	0.12	0.03	0.15	0.04	0.05	−0.21	<b>0.70</b>	—	
POC	0.23	−0.21	−0.19	−0.05	0.24	0.01	0.03	−0.02	<b>0.70</b>	−0.11	−0.01	0.00	<b>0.04</b>	0.21	—

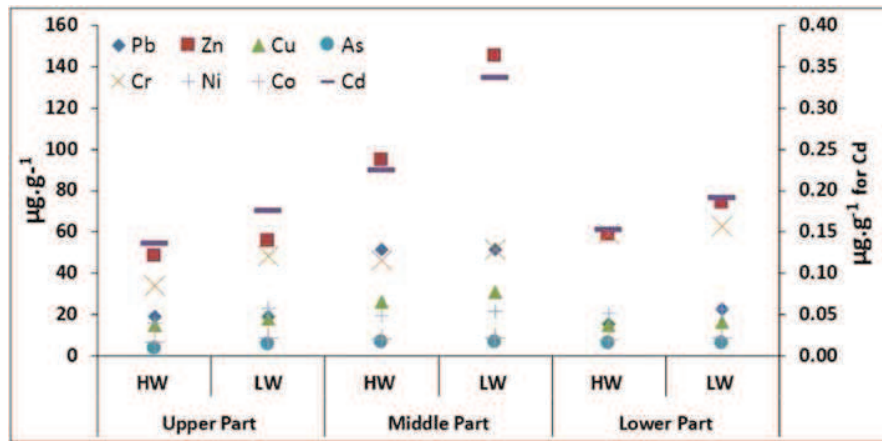


Fig. 2. Distribution of mean total metal concentrations in sediments from the stations located in the upper, middle and lower parts of the Tafna basin during two contrasting hydrological conditions in 2015 (HW: high water flow and LW: low water flow).

2002), the contamination degree (Hakanson, 1980) and the pollution load index (Tomlinson et al., 1980). The objective was to use their different capacities to detect contamination in the Tafna River and furthermore to discuss their strengths and weaknesses.

### 3.4.1. Enrichment factor (EF)

Metal enrichment in sediments was calculated using EF (Eq.1) for two contrasting hydrological conditions (sampling campaigns HW

February 2015 and LW August 2015), using UCC and mean local Tafna bedrock as reference materials (Fig. 3 A/B and 3 C/D respectively).

The most enriched elements were Pb, Cd, Zn and Cu, depending on the stations. Arsenic was only highly enriched (EF > 4) when UCC was the reference material (Fig. 3). In DamB and the stations located after the dam in the middle part of the basin (T6, MG), as well as station S2, the EF exceeded 1.5 for those metals. For the other stations, EF remained low (below 1.5), except for Cr and Co, which slightly exceeded this background value, and also all metals when considering UCC as the

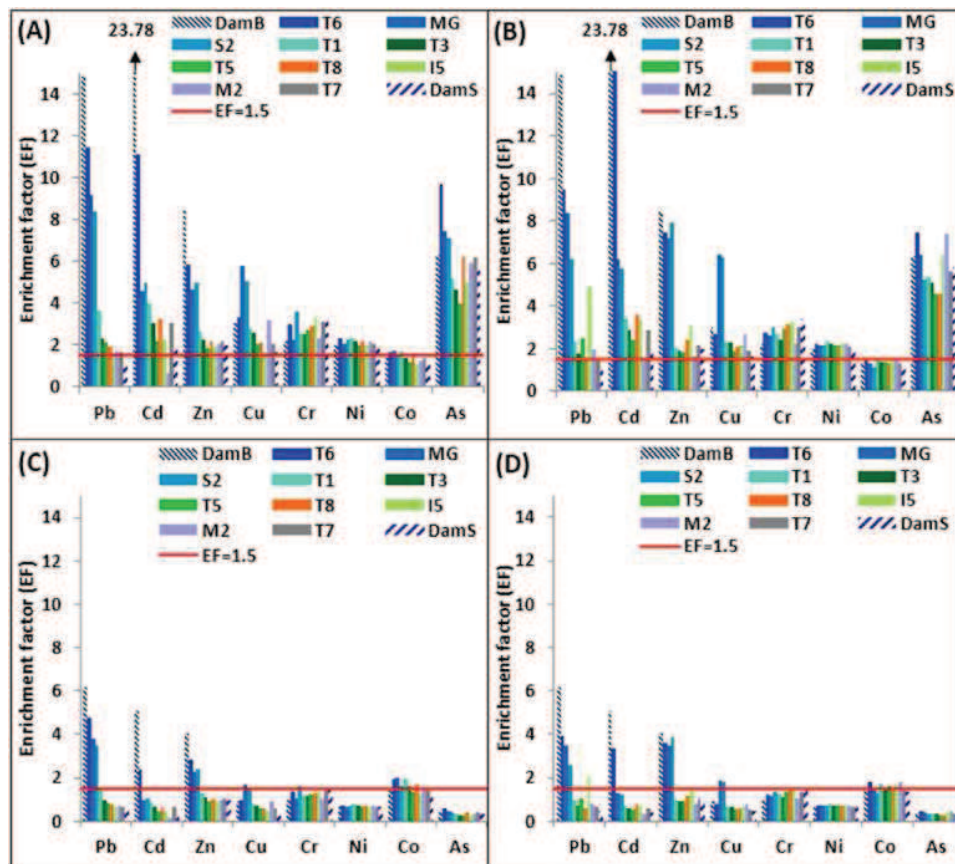


Fig. 3. Enrichment factor (EF) for trace metals in sediments from the different sampling sites (see references in Fig. 1) during two contrasting hydrological conditions (A and C: high water in February 2015, B and D: low water in August 2015) calculated by normalisation using two bedrocks (UCC: A and B and mean local bedrock: C and D). For DamB, only the low water condition (August 2015) was involved. The line indicates an EF value >1.5. Note the outlying value of 23.78 for Cd in DamB (indicated by an arrow).



reference. The highest EF values were observed for Pb (14.83 and 11.42) and Cd (8.43 and 5.85) at DamB (only collected during low water conditions in August 2015) and station T6 located immediately after the dam, respectively.

For Pb, EF was higher during high water flows (Fig. 3A and C) than during low water flow conditions (Fig. 3B and D), except for the second tributary (I5, as with Cd and Zn). The opposite was observed for Cd, Zn and Cu, particularly at stations T6, MG, S2, and except in the upper part of the basin (T1, T3, T5, Fig. 1 and Fig. 3). Moreover, EF was much higher when using UCC as the reference material (0.64 to 11.42 and 1.1 to 15.63 in high and low water conditions respectively) than with local bedrock (0.14 to 4.74 and 0.28 to 3.95 in high and low water conditions respectively). With regard to UCC and local bedrocks, there was no great difference between the two hydrological conditions for the other elements. DamS presented a low enrichment of around 1.5 for all elements, except for Cr and As (3.37 and 5.79, respectively using UCC as the reference material, and <1.5 using local bedrock as the reference). Metal enrichment at DamS was low compared to DamB.

### 3.4.2. Indices of contamination

Igeo (Eq. (2)), CD (Eq. (3)), SPI (Eq. (4)) and PLI (Eq. (5)) were calculated for different sampling periods (Table 3) to assess the contamination and ecological risk presented by trace elements in the sediments.

During high flow conditions (HW 2014 and 2015), Igeo (Eq. (2)) was low (<1 or <2), indicating a low to moderate metallic pollution. The highest values were for Pb and Zn (Igeo > 2, MG and T6 station in 2015). The contamination degree (Eq. (3)), considering all metals taken together, generally exhibited values of between 12 and 24, which revealed a considerable contamination degree for all stations except for T1, T3, T5 and M2 in 2014. Some values exceeded 24 (MG and T6 in 2015), indicating considerable contamination. In contrast, SPI (Eq. (4)) indicated healthy sediments (SPI < 2), except for MG and T6 in 2014 (poorly polluted sediment, 2 ≤ SPI < 5), and T6 in 2015 (moderately polluted sediment, 5 ≤ SPI < 10).

During low water flow, Igeo was also low for the majority of sites and metals, except Pb in T1 and MG in 2014 (Igeo > 2, moderate to strong pollution) and T5 (Igeo > 5, extreme pollution). In 2015, Igeo was between 2 and 3, indicating moderate to strong pollution for Pb and Zn at MG, T6 and S2 stations, and Cd at T6. The contamination

degree (CD) was higher than during low water flow (particularly for T5 in 2014), except for I5 and T8 in 2014. In 2015, it was generally higher than in 2014 for most of the stations except T5, with the highest values for MG, T6 and S2. SPI was higher in 2015 indicating poorly (MG, S2, T8) to moderately polluted sediment (T6).

DamB in 2015 (not sampled in 2014) exhibited high Igeo values corresponding to strongly to extremely polluted conditions for Pb, Cd and Zn. Accordingly for DamB, the CD and SPI showed extremely high values, confirming the presence of hazardous sediments. In contrast, all indices indicated a low contamination in DamS sediments, but a relatively high CD value.

PLI (Eq. (5)) exceeded 1 at all stations. In 2014, higher values were at T6 during low water and at T5, MG, T6 and T7 during high water flow. In 2015, PLI exceeded 2 for all stations except T1, M2 and T7 in HW, with some stations exhibiting PLI ≥ 3 (MG, T6, S2, T8) in LW.

### 3.5. EDTA extractable fraction of metal

In order to evaluate the potential of a metal to be accessible to living organisms, the available fraction was analysed and expressed as a relative proportion of the total concentration in the sediments during the two hydrological conditions in 2014 (Table 4). Indeed, metal leaching provides information about the metal fraction linked to sediment compounds (Tessier et al., 1979; Leleyter and Probst, 1999). Many extraction protocols have been applied in the literature, but since in sediments a majority of anthropogenic metals are linked to organic matter and oxide compounds, EDTA extraction was used for its greater ability to extract such metal fractions (Beckett, 1989; Leleyter et al., 2012).

Generally speaking, whatever the hydrological conditions, the order of relative metal availability was Cd > Pb > Cu > Zn > Ni > As > Cr, except for stations T1 (Cd > Cu > Co = Zn), MG (Cd > Zn > Cu), T7 (Cu > Pb > Cd) during LW and T5, MG, T6 and S2 (Pb > Cd > Cu) during HW. Of all the metals, the available fraction of Ni, As and Cr was very low (between 0% and 5%). In contrast, the available fraction averaged 36.4 ± 9.8% and 42.4 ± 8.9% for Pb and Cd respectively. The concentrations of the available phase varied between 2.2 µg·g<sup>-1</sup> and 24.0 µg·g<sup>-1</sup> (with a spike of 204 µg·g<sup>-1</sup> in T5 during LW) for Pb, and between 0.02 µg·g<sup>-1</sup> and 0.14 µg·g<sup>-1</sup> for Cd. The available fraction at some stations exceeded 50% for Pb (T3, T8 in LW and T5 in HW) and Cd (T1, T3, I5, T8 in LW). Compared

**Table 3**  
Various indexes of contamination: Igeo, CD (contamination degree), SPI (sediment pollution index), PLI (pollution level index) calculated for sediments from all stations during all sampling campaigns (low water: LW June 2014, August 2015 and high water: HW October 2014, February 2015).

Stations	Igeo 2014							Igeo 2015							CD (2014)	CD (2015)	SPI (2014)	SPI (2015)	PLI (2014)	PLI (2015)
	Pb	Cd	Zn	Cu	Ni	Cr	Co	Pb	Cd	Zn	Cu	Ni	Cr	Co						
T1 HW	-0.41	-0.73	-0.08	-0.50	-0.27	0.36	0.82	0.66	-0.19	0.41	-0.25	-0.33	0.25	0.99	10.3	12.9	0.92	1.33	1.3	1.7
T3 HW	-0.18	-0.56	0.20	-0.40	-0.26	0.35	0.77	0.47	-0.10	0.64	0.12	0.05	0.74	1.24	10.9	15.03	1.03	1.42	1.4	2.1
T5 HW	1.39	-1.65	-0.71	-1.32	-1.38	-0.49	-0.04	0.61	-0.28	0.65	0.08	0.18	1.13	1.28	9.0	16.07	0.54	1.27	1.0	2.2
MGHW	0.85	-0.32	1.14	0.28	-0.61	0.40	0.35	2.69	0.71	1.92	1.51	0.19	0.79	1.77	13.9	31.5	1.23	2.60	1.7	3.9
M2 HW	-0.20	-1.61	-0.46	-1.06	-1.04	-0.07	0.24	0.43	-1.96	0.92	0.82	0.45	1.00	1.46	7.5	17.09	0.51	0.45	1.0	2.0
T6 HW	1.21	1.59	1.57	-0.01	-0.65	0.24	0.52	2.88	1.88	2.14	0.58	0.22	1.08	1.58	18.8	34.76	4.43	5.55	2.1	4.2
T7 HW	0.15	0.07	0.68	-0.10	-0.01	0.96	1.10	-0.01	-0.08	0.63	-0.17	-0.01	1.05	1.20	14.7	14.61	1.58	1.43	1.8	1.9
S2 HW	0.71	-0.82	0.74	0.30	-0.97	0.11	0.16	1.79	0.07	1.25	0.56	-0.44	0.70	0.70	11.7	18.53	0.89	1.65	1.5	2.4
I5 HW	0.64	-0.39	0.80	-0.42	-0.08	1.00	0.91	0.55	0.08	1.06	0.11	0.51	1.75	1.48	14.4	19.88	1.18	1.61	1.8	2.6
T8 HW	-0.01	0.30	0.89	-0.34	-0.25	0.71	0.92	0.24	0.05	0.69	-0.12	0.13	1.01	1.35	13.9	15.6	1.84	1.56	1.7	2.1
T1 LW	2.81	-1.78	-0.53	-0.95	-0.89	-0.03	0.43	0.76	0.31	0.74	0.19	0.41	1.07	1.54	17.1	18.13	0.61	1.88	1.3	2.5
T3 LW	1.41	-1.76	-0.45	-1.09	-1.01	-0.17	0.06	0.37	0.13	0.71	0.25	0.35	0.96	1.48	9.9	16.85	0.51	1.65	1.1	2.3
T5 LW	5.39	-0.43	0.51	-0.32	-0.28	0.60	0.88	0.88	-0.11	0.67	-0.03	0.32	1.28	1.52	73.4	17.85	2.11	1.43	2.5	2.4
MGLW	2.12	-0.02	1.72	0.58	-0.46	0.32	0.69	2.53	1.13	2.53	1.63	0.21	0.98	1.30	20.6	33.62	1.58	3.39	2.2	4.2
M2LW	0.47	-1.12	1.25	0.03	0.09	0.50	1.22	0.53	-0.76	0.52	0.5	0.41	0.87	1.71	15.1	16.95	0.74	0.93	1.8	2.2
T6 LW	1.13	1.45	1.63	-0.62	-0.75	0.16	0.69	2.64	2.39	2.51	0.29	0.21	0.99	1.50	18.0	36.54	4.04	7.81	2.0	4.3
T7 LW	1.23	1.71	1.58	-0.32	-0.64	0.16	0.65	0.29	0.21	0.99	0.06	0.37	1.40	1.55	19.1	18.39	4.81	1.75	2.1	2.4
S2 LW	0.86	-0.22	1.18	0.43	-0.72	0.33	0.36	2.24	1.16	2.82	1.75	0.36	1.34	1.22	14.2	35.31	1.32	3.44	1.7	4.4
I5 LW	-0.01	-0.58	0.42	-0.59	-0.26	0.71	0.83	1.47	-0.06	1.04	-0.21	-0.01	1.03	1.18	11.9	17.91	1.02	1.49	1.5	2.3
T8 LW	-0.30	-1.22	-0.02	-1.11	-0.84	0.15	0.31	0.37	0.76	1.35	0.43	0.63	1.68	1.76	8.4	22.51	0.66	2.54	1.1	3.0
DamB	-	-	-	-	-	-	-	4.39	4.11	3.80	1.60	1.14	1.78	2.42	-	99.42	-	25.69	-	10.1
DamS	-	-	-	-	-	-	-	-0.03	-0.3	1.05	0.07	0.53	1.75	1.54	-	18.95	-	1.25	-	2.4

**Table 4**

Metal concentration of the available fraction (in  $\mu\text{g}\cdot\text{g}^{-1}$ ) and its proportion of the total concentration (in %) in sediments from the different stations, using EDTA extraction, for low water (LW) and high water (HW) conditions in 2014.

2014	Pb		Cd		Cu		Zn		Co		Ni		As		Cr		
	$\mu\text{g}\cdot\text{g}^{-1}$	%	$\mu\text{g}\cdot\text{g}^{-1}$	%	$\mu\text{g}\cdot\text{g}^{-1}$	%	$\mu\text{g}\cdot\text{g}^{-1}$	%	$\mu\text{g}\cdot\text{g}^{-1}$	%	$\mu\text{g}\cdot\text{g}^{-1}$	%	$\mu\text{g}\cdot\text{g}^{-1}$	%	$\mu\text{g}\cdot\text{g}^{-1}$	%	
LW	T1	2.19	2	0.03	74	1.68	21	2.29	10	0.47	11	0.53	5	0.11	4	0.16	1
	T3	23.97	70	0.03	63	1.38	19	3.77	15	0.34	10	0.31	3	0.09	4	0.15	1
	T5	204.00	38	0.05	47	2.66	22	3.58	7	0.49	8	0.45	3	0.12	3	0.14	0
	MG	-	-	0.07	45	4.80	21	34.26	31	0.42	8	0.94	7	0.22	6	0.14	0
	M2	6.99	39	0.03	36	2.89	18	2.46	3	0.49	7	0.73	4	0.10	2	0.12	0
	T6	10.39	37	0.14	33	2.29	23	11.98	12	0.42	8	0.36	3	0.18	3	0.15	1
	T7	6.69	22	0.07	14	4.58	37	6.144	6	0.49	10	0.52	5	0.15	2	0.16	1
	S2	11.58	39	0.05	36	5.19	18	17.69	3	0.34	7	0.56	4	0.14	2	0.14	0
	I5	3.59	28	0.05	51	2.30	22	3.69	8	0.45	8	0.43	3	0.11	3	0.15	0
	T8	5.68	54	0.04	60	1.25	17	2.67	8	0.51	13	0.31	3	0.12	3	0.16	1
LW	T1	2.24	23	0.03	35	1.53	14	1.95	6	0.56	10	0.74	5	0.10	3	0.16	1
	T3	3.45	30	0.04	42	2.11	18	3.94	10	0.46	9	0.51	3	0.12	3	0.16	1
	T5	17.08	51	0.02	37	0.78	13	1.20	6	0.27	9	0.13	2	0.08	3	0.16	1
	MG	10.37	45	0.05	44	5.55	30	21.60	29	0.18	5	0.47	4	0.15	5	0.16	1
	M2	-	-	0.02	40	0.81	11	1.67	7	0.31	8	0.15	2	0.12	4	0.17	1
	T6	10.54	35	0.14	30	3.96	2	13.78	14	0.33	7	0.39	3	0.09	2	0.16	1
	T7	4.90	34	0.07	44	2.77	19	5.16	10	0.45	7	0.49	3	0.12	2	0.17	0
	S2	9.02	43	0.03	40	3.24	17	11.84	21	0.25	7	0.40	4	0.13	4	0.14	1
	I5	6.54	33	0.04	38	1.75	15	3.97	7	0.45	8	0.44	3	0.11	2	0.18	0
	T8	4.07	32	0.07	39	2.46	20	5.70	9	0.42	7	0.32	2	0.12	3	0.15	0

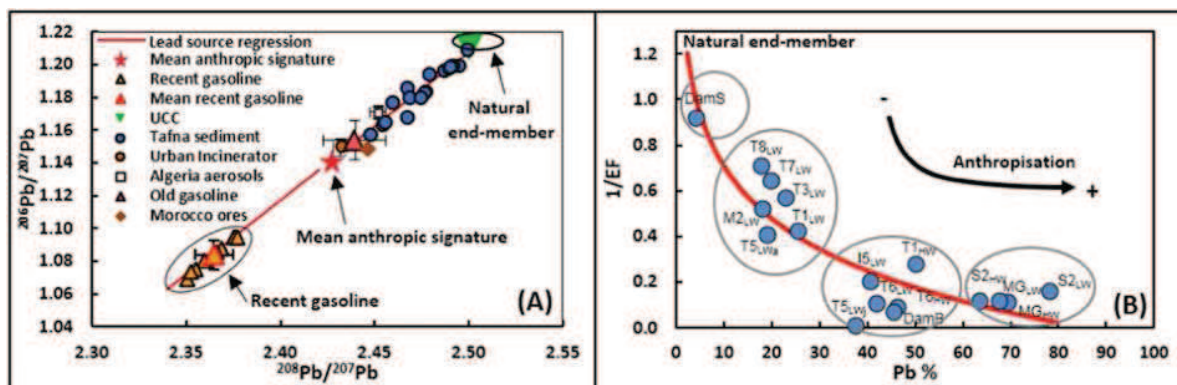
with high flow conditions, higher concentrations were mostly observed during low water conditions, with exceptions depending on the metals and the stations. This was also true for the relative percentage, except for Cd (T7) and Cu (MG). In contrast Pb and Zn were relatively more available during HW (except T3, T8 and T1, T3, MG respectively). The standard deviation of the mean percentage for all the stations was also higher during LW compared with HW conditions (average values: Pb  $36.6 \pm 12.8\%$  vs.  $36.2 \pm 6.7\%$ ; Cd  $45.9 \pm 13.1\%$  vs.  $38.9 \pm 3.1\%$ , Cu  $21.8 \pm 3.4\%$  vs.  $18.3 \pm 4.4\%$ , respectively).

As shown in Table 4, a high concentration in the available fraction did not necessarily mean a high proportion of the available phase, as for example Pb ( $204 \mu\text{g}\cdot\text{g}^{-1}$  in T5 during LW corresponded to only 38% of Pb available). However, except for this value, the high concentration observed for Pb in T3 during low water was consistent with a high relative availability (70%). Generally speaking, while the relationship between the concentration and percentage of the available fraction was significant for Cu ( $y (\%) = 2.77x (\mu\text{g}\cdot\text{g}^{-1}) + 12.58$ ;  $r^2 = 0.45$ ;  $n = 20$ ;  $p < .01$ ) and for Zn ( $y (\%) = 0.71x (\mu\text{g}\cdot\text{g}^{-1}) + 5.45$ ;  $r^2 = 0.60$ ;  $n = 20$ ;  $p < .001$ ), this was not the case for Pb and Cd.

### 3.6. Lead isotopes

The relationships  $^{206}\text{Pb}/^{207}\text{Pb}$  vs.  $^{208}\text{Pb}/^{207}\text{Pb}$  (Fig. 4A) and  $^{207}\text{Pb}/^{206}\text{Pb}$  vs.  $^{208}\text{Pb}/^{206}\text{Pb}$  (not shown) were investigated to assess the contribution of the dominant sources of lead to the lead composition of the Tafna sediments. In the  $^{206}\text{Pb}/^{207}\text{Pb}$  vs.  $^{208}\text{Pb}/^{207}\text{Pb}$  diagram (Fig. 4A), sediments samples ( $n = 17$ ) were plotted with literature data. These data referred to natural (UCC) and various potential anthropogenic lead sources (see Fig. 4A). For the Tafna sediments, the  $^{206}\text{Pb}/^{207}\text{Pb}$  vs.  $^{208}\text{Pb}/^{207}\text{Pb}$  in river sediments ranged between 1.1568 and 1.2086 and 2.448–2.500, respectively. These values were consistent with those of Roussiez et al. (2005) for the sediments from the Gulf of Lion in the western Mediterranean Sea and of N'Guessan et al. (2009) for the Gascogne streams (SW France).

A linear regression was drawn between anthropic sources, the natural end-member and the Tafna sediments ( $Y = 0.9063X - 1.0582$ ;  $r^2 = 0.999$ ;  $n = 39$ ;  $p < .0001$ ). A mean anthropogenic isotopic signature was calculated as the mean of the isotopic values of all the above anthropic sources (Mean =  $^{206}\text{Pb}/^{207}\text{Pb} = 1.141$  and  $^{208}\text{Pb}/^{207}\text{Pb} =$



**Fig. 4. A:** Relationship between lead isotopic ratios  $^{206}\text{Pb}/^{207}\text{Pb}$  versus  $^{208}\text{Pb}/^{207}\text{Pb}$  in some samples of the Tafna sediments ( $n = 17$ , this study), literature data: UCC (Millot et al., 2004), recent (Monna et al., 1997) and old (Chow et al., 1974) gasoline in Europe, urban incinerator (Monna et al., 1997), Algerian aerosols (Bridgestock et al., 2016) and Moroccan ores (Maring et al., 1987). The mean anthropic isotopic signature was calculated as the mean of all the above anthropic sources. The continuous line is the regression between anthropic sources and the natural end-member including the Tafna sediments ( $Y = 0.9063X - 1.0582$ ;  $r^2 = 0.999$ ;  $n = 39$ ;  $p < .0001$ ). **B:** Relationship between  $1/EF$  and the anthropic contribution for lead (Pb %; see Eq. (6)) calculated by a mixing model on the basis of the regression line (Fig. 4A) for samples of the Tafna sediments collected during low water (LW) and high water (HW) conditions (see paragraph 2.3). Note that T5<sub>LW</sub> and T5<sub>HW</sub> means June 2014 and August 2015, respectively. The anthropisation intensity is indicated and follows the general logarithmic equation ( $Y = -0.327\ln(x) + 1.4569$ ,  $r^2 = 0.7897$ ;  $n = 17$ ;  $p < .0001$ ).

2.427), which was assumed to be representative of the influencing anthropic end-member with regard to the different anthropogenic sources in the area (Fig. 4A). On the  $^{207}\text{Pb}/^{206}\text{Pb}$  vs.  $^{208}\text{Pb}/^{206}\text{Pb}$  diagram, the sediment samples fall on a linear line ( $Y = 0.706X - 0.632$ ;  $n = 17$ ;  $r^2 = 0.936$ ;  $p < .0001$ ), parallel and close to the ESLP (European Standard Lead Pollution, Haack et al., 2003), but samples are less and more enriched in  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$  respectively.

To determine the contribution of anthropogenic Pb to the Tafna sediments, the percentage of anthropogenic Pb (Pb %) was calculated on the basis on the equation below (Eq. (6)) for each sediment sample using a mixing model on the basis of the first regression above:

$$\text{Anthropic contribution\%} = \frac{(^{206}\text{Pb}/^{207}\text{Pb})_{\text{Sediment}} - (^{206}\text{Pb}/^{207}\text{Pb})_{\text{Natural}}}{(^{206}\text{Pb}/^{207}\text{Pb})_{\text{Anthropic}} - (^{206}\text{Pb}/^{207}\text{Pb})_{\text{Natural}}} * 100 \quad (6)$$

where  $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{Sediment}}$  is the averaged value of the concerned Tafna sediment,  $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{Natural}}$  is the signature of UCC and  $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{Anthropic}}$  is the mean value for the anthropic end-member (see text and Fig. 4A).

The average anthropic contribution for the whole basin was assessed to be equal to 39%. In order to evaluate the range of anthropogenic Pb contributions at the basin scale and by combining different indicators, 1/EF was plotted against the percentage of anthropogenic Pb calculated using Eq. (6) (Fig. 4B). A significant relationship between 1/EF and %  $\text{Pb}_{\text{anthropic}}$  ( $Y = -0.327\ln(x) + 1.4569$ ,  $r^2 = 0.7897$ ;  $n = 17$ ;  $p < .0001$ ) was observed, but with a slight dispersion for low 1/EF values. When 1/EF tended towards zero, i.e. high anthropogenic contribution, the anthropogenic contribution assessed by lead isotopes ranged between 40 and 80%. Four sets of samples can be identified (circled in Fig. 4B): DamS close to the natural end-member ( $\text{Pb}_{\text{anthropic}}$  4%), a second set ( $\text{M2}_{\text{LW}}$ ,  $\text{T8}_{\text{LW}}$ ,  $\text{T7}_{\text{LW}}$ ,  $\text{T1}_{\text{LW}}$ ,  $\text{T5}_{\text{LW}}$ ,  $\text{T3}_{\text{LW}}$ ) moderately contaminated ( $\text{Pb}_{\text{anthropic}}$  18%–25%), a third set ( $\text{I5}_{\text{LW}}$ ,  $\text{T1}_{\text{HW}}$ ,  $\text{T5}_{\text{LW}}$ ,  $\text{T6}_{\text{LW}}$ ,  $\text{T6}_{\text{HW}}$ , DamB) severely contaminated ( $\text{Pb}_{\text{anthropic}}$  38%–50%) and a final one (MG and S2) extremely contaminated ( $\text{Pb}_{\text{anthropic}}$  63%–78%) by lead.

## 4. Discussion

### 4.1. Anthropogenic influences and geochemical controlling factors

The metal concentrations in sediments from the Tafna basin exhibited values in the range of those observed in other similar basins from the Mediterranean area (Llobregat, Spain, Casas et al., 2003; Rhône, France, Ferrand et al., 2012), even though higher values were observed for Zn, Pb and Cd.

The different indicators of anthropogenic contamination (EF, Igeo and SPI, Table 3) indicated convergent results concerning Pb, Zn, Cd and Cu, which in some places were very enriched in sediments whatever the reference material used to calculate EF (Fig. 3 and Table 3, Reimann and De Caritat, 2005; Hernandez et al., 2003). However, the intensity of the enrichment depended on the reference material used (UCC vs. Tafna bedrock, Fig. 3). This has already been observed elsewhere, indicating the discrepancy between general and local references (Reimann and De Caritat, 2005; N'Guessan et al., 2009). Indeed, the enrichment was probably between the two values, since the Tafna bedrock sometimes indicated EF of <1, indicating that it had been subjected to weathering processes that have modified the initial composition. Moreover, these rocky outcrops were sampled locally at the sediment sampling site and thus may not be as representative of the drainage sub-catchment as expected, in contrast to the sediments. Generally speaking, Pb and Cd exhibited the greatest anthropogenic influence as regards the different indicators (EF, Igeo and SPI, Table 3), but the intensity varied within the basin depending on the local sources and the environmental factors (see paragraph IV.2). Moreover, the availability for Cd and Pb was highest among the considered metals (14–74%, 2–70%

respectively, Table 4, Fig. 5), which confirms the adsorption/complexation of the anthropogenic fraction mainly onto organic matter and oxides (Bur et al., 2009; Ni et al., 2016).

Lead isotopes reinforced the idea that in some places the basin suffers from a strong influence of anthropogenic lead contamination since sediments are integrated into the anthropogenic regression line (Fig. 4A, B). This contamination comes from global atmospheric contamination source of recent gasoline, as mentioned in several parts of the world (Agnan et al., 2015) but also from others sources such as old leaded gasoline and from local sources (incinerators, factories and ores). Indeed, sediments originate from soil erosion and thus testify to lead deposition accumulated in soils over decades in the upper basin (Bacon et al., 1992). This mix of anthropogenic sources justified the choice of a mean anthropogenic signature to evaluate Pb contamination (Komárek et al., 2008), which was in the range of 4% to 78%, depending on the location in the basin.

As attested by the low enrichment ( $\#EF < 2$ ) irrespective of the reference material used and also the low Igeo in 2014 and 2015 (Table 3), the anthropogenic contribution for Co, Ni, Cr, Al and Fe was weak (except for Co in some places, Fig. 3). For arsenic (and to a lesser extent Ni), the enrichment greatly depended on the selected reference material. This metalloid is of concern since it has been classified as a priority pollutant by the United States Environmental Protection Agency (USEPA, 1988) because of environmental toxicity regarding its speciation (Akter et al., 2005). In the Tafna basin, it can be associated with agriculture and forestry practices such as pesticide (Akter et al., 2005) and herbicide inputs, and in more limited amounts as an additive in the glass and ceramic industries and in feed additives (Patel et al., 2005). The absence of enrichment when using local bedrock (Fig. 3) rather than UCC ( $EF > 4$ ) as the reference material has already been mentioned in other studies (Agnan et al., 2015; N'Guessan et al., 2009). This is explained by the weak UCC content as regards local/regional bedrocks. Moreover, the availability of those metals (As, Co, Ni, Cr, Al and Fe) was weak (Table 4), indicating that they are associated with the mineral lattice (Morillo et al., 2002). Indeed, even though these elements can be produced by industry and mine ores, the anthropic influence remains low in the sediment from the Tafna basin. Consequently, it can be assumed that their impact on living organisms in the area is low.

A PCA was performed by combining metal concentrations from all the river sediments and differentiating between hydrological conditions (Fig. 5). The PCA synthesised what had already been observed when considering the factors separately (Table 2). Component 1 distinguished between the metals that are anthropogenically influenced the least (Cr, Co, Ni, As), which are linked to Al, Fe and Mn oxides (Filgueiras et al., 2004, Fig. 5, Table 2) and/or clay minerals (Suresh et al., 2012) in high water conditions. During LW conditions, As, Fe and Mn are discarded, demonstrating the affinity of As to Mn and Fe oxides (Chaillou et al., 2003) (Fig. 5). In contrast, the relationships between Cu and S (Fig. 5), and to a lesser extent P, indicated their main origin to be from fertiliser or pesticide inputs (Han et al., 2001). Component 2 isolated the most anthropogenically influenced metals and indicated that Cd and Zn was linked to P while POC was linked to Ca in both hydrological conditions. It was proposed that Cd mostly originated from agricultural sources due to fertiliser inputs, particularly associated with arable soil erosion during high water conditions. Lead was related equally to axis 2 and axis 3 ( $R = -0.59$  and  $-0.62$ ) and to the above contaminants (Cd, Zn, Cu). Indeed the most enriched stations were those draining the upper basin (Fig. 3), which also had the highest Ca content in sediment due to the presence of carbonate bedrock in this area. However the poor Pb content in carbonate (Erel et al., 2004) suggested the absence of any correlation between them (Table 2).





The T6 station showed the highest level of contamination, particularly for Pb and Cd (as indicated by the set of anthropogenic indicators (Fig. 3, Table 3)), and exceeded the contamination of the upper stations M2, MG and T5. Indeed, the largest dam in the basin (DamB, see introduction and Fig. 1) is situated between these three stations and T6, and its sediment is highly contaminated by Pb and Cd (Table 3). Pb and Cd supplied to the river can be strongly adsorbed onto the particles originating from erosion processes in the upper sub-basin and accumulated in the dam (Audry et al., 2004). During high water flow, frequent dam releases occur for water management purposes, resulting in a release downstream of metal-enriched particles (Varol, 2013). These dam releases as well as the enrichment observed in the upper stations during high water flow can contribute to metal enrichment at the T6 station. In contrast, a dilution process upstream can reduce the contamination (cf. Table 3 and Fig. 3) for Cd and Zn in MG, M2 and T6, since those elements are less adsorbed onto particles than Pb (Bur et al., 2009; Roussiez et al., 2013). The upper Tafna river (T5 station) can also contribute to lead contamination (Table 3), particularly in DamB and thus the T6 station. The riverine transfer of metal contamination downstream is delayed due to the presence of dams, which limits the natural transfer of water, thus decreasing the flow velocity and consequently increasing sediment residence time and favouring their deposition (Frémion et al., 2016). However with water releasing processes, dams represent a secondary source of metals by remobilising particles from the dam (i.e. Coynel et al., 2007) and leading to downstream contamination (Wildi et al., 2004) with a high toxicity risk (SPI > 20, Table 3), which endangers the downstream stations (i.e. T6 station Cd and Pb availability >30%). Indeed, this group of stations exhibited a considerable threat of metal toxicity for living organisms since the metal availability in the sediments was high with ranges as follows: MG 21–45% > S2 3–43% > T6 2–37%. The middle part of the Tafna basin was thus the location most at risk because of the presence of several industrial units and a high level of urbanisation that are sources of heavy pollution with metals easily accessible to living organisms.

The enrichment of Cd, Zn and Cu during the low water flow period at S2, MG and T6, except for Cu at T6 station (Fig. 3 and Table 3), can be related to the influence of the local waste inputs upstream from the different anthropogenic activities (industrial wastes, domestic pollution, agricultural fertilisers, vineyard treatments etc.) that cannot be diluted (Thilagavathi et al., 2011), in contrast to the sediments washing up during high water flows.

For this group of stations, weak correlations were identified between POC and metals, but the high availability (cf. EDTA extraction) indicated that other compounds such as clay minerals and oxides are, in addition to organic matter, preferential controlling factors of the anthropogenic fraction of Pb, Cd, Zn and Cu.

#### 4.2.2. Group 2: T1, T3, T5

These three stations represent the upper Tafna river basin conditions. Of these three stations, the upper one T1 was generally the most contaminated one (Fig. 3 and Igeo, Table 3). However, T5 station remained more enriched in Pb during low water conditions (Fig. 5c). The T1 station was impacted by the main gasoline station used by vehicles on the main road towards the Sahara Desert. The anthropogenic influence was more detectable during high water flow, probably as a result of the washing of the road surface (Figs. 3 and 4 and Table 3). Moreover, Pb and Cu enrichment could be due to the impact of textile manufacturing activities.

Station T3 exhibited moderate contamination (Figs. 3 and 4, and Table 3), except in Pb during the most severe hydrological conditions (low water flow, August 2015 and high water flow, February 2015). It could therefore be assumed that lead from the upstream station T1 is transported downstream by suspended matter during flood events (Roussiez et al., 2013; Ulses et al., 2008).

The metal contamination decreased in T5 compared with T1 and T3 (Figs. 3 and 4, Table 3), with the exception of lead during low water

flow. The presence of DamE (Beni Bahdel, Fig. 1) between those stations was probably led to the water being affected to a small extent by metal remobilisation downstream, in contrast to the situation at DamB, due to its smaller size (cf. § 2.1) and limited water release. However it could be assumed that some re-suspension of lead-enriched particles accumulated behind the dam may influence the enrichment observed at the T5 station owing to the strong affinity of lead to particles (Jain and Ram, 1996). The CD index exhibited a high value in 2014, which reflected a polymetallic contamination. Agricultural activities also take place along the river, and the farmers use gasoline pumps for irrigation, which might be a local, irregular but nevertheless hazardous source of gasoline lead.

The available metal fraction was 35–74% and 2–70% for Cd and Pb respectively at stations T1, T3 and T5. Similarly to the stations of the first group, they represent important risks of contamination (Eggleton and Thomas, 2004) for living organisms. Although the contamination is lower than with the first group of stations, the risk might be higher for Pb and Cd at these stations (Table 4).

#### 4.2.3. Group 3: M2, I5, T7, T8, DamS

Generally speaking, these stations were the least contaminated ones in the basin, even though some contamination occurred at I5 (Pb, Cd, Zn) during low water conditions, and at T8 and to a lesser extent at T7 (Cd) for both hydrological conditions (Fig. 3 and Fig. 4, Table 3). The stations T7, T8, I5 are located in the downstream part of the Tafna basin, along the main channel (T7 and T8) and on the major right-hand Tafna tributary Isser (I5). As in the upstream part of the basin, but to a lesser extent, Pb, Cd, Cu, Zn contamination could be linked to the influence of several anthropogenic activities (fertiliser inputs due to large agricultural land use upstream, domestic waste, atmospheric deposition etc.). The relative lower contamination in I5 compared to S2 (upper part of the basin, see above paragraph) could be explained by a strong dilution by the Isser wadi (Fig. 1). This is supported by the metal composition of the accumulated sediment behind DamS, which indicates no contamination (Tables 2 and 3, and Fig. 4). Indeed, this area is under the influence of the highest mechanical erosion rate (Bouanani et al., 2013; Zettam et al., 2017) in this sub-basin, which can reach up to  $745 \text{ t} \cdot \text{km}^{-2} \cdot \text{yr}^{-1}$  (Bouanani et al., 2013). Consequently this leads to a particle dilution effect (Benoit and Rozan, 1999) regarding the upper metal contamination observed at S2. A comparable dilution was observed at the M2 station located after the confluence between the Mouillah River and the Ourdeffou River (Fig. 1), which explains the relatively low contamination at M2 compared to MG (Fig. 5c).

Sediment settling in the middle course of the Tafna (between T6 and T7 stations) could explain part of the lower contamination in T7 station compared to T6 located immediately after the very contaminated DamB (Fig. 1 and the paragraph above). In this part, the geomorphology (lower slope) has led to very significant meanders and thus sedimentation and metal storage along the river course (Ciszewski et al., 2004).

The moderate contamination found at the outlet of the Tafna (station T8) could be due to the dilution by the moderately contaminated Isser tributary (Fig. 1) and the reduced contamination upstream (cf. T7 station pattern). Indeed the contamination at T8 was higher during low water flow (cf. Table 3 and Fig. 5c). The successive Mediterranean-type storm events, which are very erosive due to their high discharge intensity, may act as a contamination regulator downstream (T8) due to particle dilution and/or washing out the metals by desorption processes (Martínez-Santos et al., 2015). However, this means that the metal contamination is irredeemably leached towards the Mediterranean Sea and accumulated in marine sediments (Roussiez et al., 2006).

It should also be noted that although metal contamination at the outlet station remained moderate, the availability of metals Cd and Pb was high (60 and 54% respectively). This station is therefore the station



in the basin most at risk from these contaminants under changing physicochemical conditions (Table 4).

Indeed, during high flow conditions, but only for group 2 and 3 stations (low to medium contamination), organic matter acted as an anthropogenic metal trapping agent, as indicated by the linear regression between Pb and Zn enrichment and POC ( $EF_{Pb} = 0.290 \text{ POC} + 1.111$ ,  $r^2 = 0.88$ ;  $n = 8$  and  $EF_{Zn} = 0.078 \text{ POC} + 1.89$ ;  $r^2 = 0.60$ ;  $n = 8$ , with POC in %).

As a whole in the basin, the middle part appeared to be the most contaminated area (MG, M2, T6 and S2, Fig. 2 and Fig. 3). Upstream contamination, sediment settling due to the presence of dams, lower slopes and river channel geomorphology favours metal enrichment in sediment in the middle and downstream parts, which undergoes a delayed remobilisation/release downstream during high flow conditions (Gaiero et al., 1995; Martínez-Santos et al., 2015). All the stations in the basin exhibited low contamination by As, Co, Ni, Cr, Al and Fe, despite potential industrial sources. The only exception concerned stations T6, S2, I5, T7 T8, where chromium was moderately enriched ( $EF\#2$  and Igeo #1). The contamination at T6 could not only be due to sediment release from DamB, but was probably also due to more local sources since the enrichment was lower.

#### 4.3. Interest of a multi-indicator approach

The different contamination indicators used in this study (EF, Igeo, CD, SPI, PLI, Pb isotopes and fraction of extractable metal) helped determine the anthropogenic influence in terms of single metal contamination, polymetallic pollution, sources of lead and risk of transfer to organisms. Indeed each indicator has its own advantages and limits.

Lead isotopes are a very powerful tool for identifying the origin and quantifying precisely the respective contributions of the end-member sources of anthropogenic vs. natural lead to the fluvial sediment (Fig. 4). However, they are only relative to a single metal among a polymetallic contamination such as in the Tafna basin (Table 3 and Figs. 3 and 5). The enrichment factor provides evidence of the intensity of the anthropogenic contamination for each metal, but is highly dependent on the reference bedrock as well as to a lesser extent on the reference element. The case of As is very illustrative (Fig. 3) and could lead to an incorrect perception in term of sources (between anthropogenic activities and natural weathering processes) and thus of contamination occurrence. Igeo is also a single metal indicator of contamination based on the local bedrock as a reference, which makes it close to field conditions. However it has a low discrimination power due to negative values and a low range of values, except for very contaminated sites (i.e.  $T6_{HW}$  in 2015, Table 3). In contrast, the contamination degree (CD) and pollution level index (PLI) evaluate the global metal contamination of a site by combining all metals with reference to the enrichment to the local bedrock. If they are also close to field conditions, single anomaly metal contamination can lead to a bias of the global contamination perception: for example lead in T5 LW 2014 contributed to  $CD = 73.4$ , whereas all other metals exhibited low Igeo values (Table 3). Moreover, the calculation methods and the use of different types of ranges for those indices can also influence the contamination evaluation: e.g. for station T8, the Igeo LW 2015 indicated a low to moderate contamination degree (0.37 and 1.76), whereas  $CD = 22.51$  suggested considerable contamination (Table 3). Moreover these indices do not evaluate the risk of metal contamination. Only SPI takes risk into account, but by attributing an *a priori* toxicity weight to each metal. Consequently, the resulting summary is very much influenced by this weight: e.g. T7 LW 2014,  $SPI = 4.81$  due to a Cd weight of 300, whereas Igeo varied between 0.32 and 1.71 (Table 3). The highest availability of a given metal did not necessarily correspond to the most concentrated elements and the most contaminated stations. For example, T3 and T8 stations in LW 2014 were not very highly contaminated (Table 3), but the percentage of available Cd and Pb was fairly high (54% to 70%, Table 4). Such risk indicators must thus be considered in addition to evaluating

the sources and intensity of the contamination given by other indicators. Metal availability is one example of these since the toxicity risk is related to the weakness of the links between metals and sediments particles and to changes in environmental conditions (flood, geochemical factors etc.).

The combination of all the above indices used during different water flow conditions helped determine the most anthropogenic-derived elements, the most contaminated stations, as well as the distinctive features of metal contamination, and moreover highlighted the greatest potential threats to living organisms and aquatic ecosystems. Nevertheless, it offers a basic blueprint for the development of further more in-depth investigations using ecotoxicity tools to evaluate real ecotoxicological impacts.

## 5. Conclusions

This study aimed to evaluate metal contamination in the Tafna basin based on fluvial sediment investigations. The contamination was heterogeneous within the basin and concerned some specific trace metals: the most enriched metals were  $Pb > Cd > Zn > Cu$ , with very high contamination observed in the middle part of the Tafna basin (especially the stations MG, S2, T6 and DamB). The different geochemical indicators (EF, Igeo, CD and SPI) used in this study gave fairly consistent results to indicate contamination due to anthropogenic activities. Several sources of contamination were identified from local permanent or occasional pollution (industrial units, domestic wastes and agricultural activities) to more diffuse pollution (atmospheric deposition, recent and old gasoline, mining wastes exploitation, incinerators and factories). The variety of anthropogenic Pb sources led to the identification of a mean anthropic contributory end-member using lead isotopes, which was shown to strongly influence sediment enrichment for the stations mentioned above. The links between those metals and other chemical or mineralogical compounds of the sediments indicated that Cd, Zn and Cu were impacted by fertiliser inputs, and that Pb enrichment was linked to POC, except at the most contaminated stations. The other trace metals (Co, Ni, Cr and As) exhibited a low level of contamination and were controlled by Al, Fe and Mn oxides. Indeed for As, it was important to apply the reference bedrock used in the EF calculation: local bedrock was recommended to avoid overestimation and misinterpretation of the anthropogenic influence.

Dams may play contrasting roles as: (i) a secondary source of metals for downstream parts of the river basin due the remobilisation during high flow of sediments previously stored behind the dams (as was the case for DamB, leading to the heavy contamination downstream of station T6) and (ii) a diluter of contamination by eroded particles in the context of a strong physical erosion rate in the surrounding area (as was the case for DamS, which contributed to dilution of local contamination (S2) transferred downstream (I5).

In the downstream part of the basin, the river geomorphology (density of meanders) slowed the contamination transfer by decreasing the flow rate of the Tafna, leading to sediment deposition and therefore the associated metal contaminants (pattern between T6 and T7 stations). However under these Mediterranean hydroclimatic conditions, the rapid and intense storm flows contributed to washing away the anthropogenically-derived metals adsorbed onto particles and accumulated in the sediments during previous low water conditions. Consequently, the contamination was diluted and leached downstream towards the Mediterranean Sea, contributing to marine sediment enrichment.

The potential ecotoxicity of the trace metals depended initially on their availability, which was assessed in this study by their EDTA extractability. Cd and Pb were found to be the most available metals. If significant relationships were detected between the concentration of the extractable fraction and its percentage of the total concentration in the sediment for Cu and Zn, the availability was not strictly related to the contamination degree for Cd and Pb. Within the Tafna basin, the sites where the trace element availability in the sediments represented the

greatest threats for organisms and aquatic ecosystems were T8 (outlet) and T3 (upstream), while T6, Mg and S2 were the most contaminated sites.

The different indicators used in this study have been discussed (strengths and weakness) and their combined consideration recommended because it provides an integrated view of the contamination patterns (local vs. generalised, multi or single, risky or not etc.). However, further investigations are required using ecotoxicological tools to characterise the impact of contamination on living organisms in terms of aquatic biodiversity and ecosystem health.

## Acknowledgements

The authors would like to thank the technicians and engineers from the EcoLab technical platforms (Marie-José Tavella, Virginie Payre-Suc, Frédéric Julien and David Baqué) and from the ICPMS platform at OMP (Aurélien Lanzanova and Frédéric Candau) for their help with preparing samples and/or for elemental analysis, and for their assistance during the ICP analyses and the cleanroom dissolution procedure. Ibrahim Zenagui, Hannane Sebbagh and Zineb Benkebil are also thanked for their help with field sampling. Amine Benabdelkader received a financial fellowship from The Algerian Ministry of Higher Education. This work was supported by the CNRS in France at EcoLab and the University of Tlemcen in Algeria.

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