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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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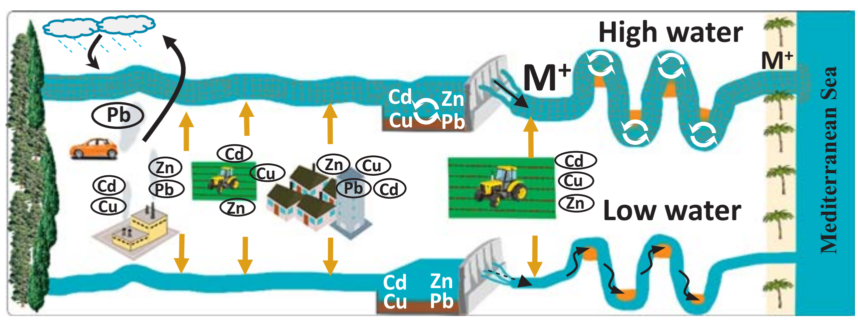
HIGHLIGHTS

- 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



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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.

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-Garcıa 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 resuspended 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^2, 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