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Dynamics of suspended sediment borne persistent organic pollutants in a large regulated Mediterranean river (Ebro, NE Spain)☆

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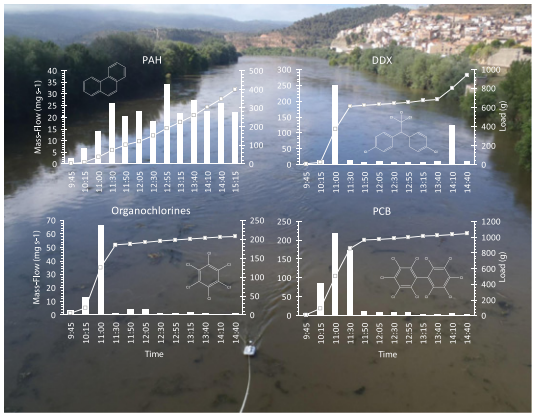
GRAPHICAL ABSTRACT



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ABSTRACT

Mediterranean rivers are characterized by highly variable hydrological regimes that are strongly dependent on the seasonal rainfall. Sediment transport is closely related to the occurrence of flash-floods capable to deliver enough kinetic energy to mobilize the bed and channel sediments. Contaminants accumulated in the sediments are likely to be mobilized as well during such events. However, whereas there are many studies characterizing contaminants in steady sediments, those devoted to the transport dynamics of suspended-sediment borne pollution are lacking. Here we examined the occurrence and transport of persistent organic microcontaminants present in the circulating suspended sediments during a controlled flushing flow in the low part of the River Ebro (NE Spain) 12 km downstream of a well-known contaminated hot-spot associated to a nearby chloro-alkali industry. Polycyclic aromatic hydrocarbons (PAHs) and semi-volatile organochlorine pollutants (DDT and related compounds, DDX; polychlorinated byphenils, PCBs; and other organochlorine compound, OCs) were measured in the particulate material by GC–MS and GC–MS/MS, using previously developed analytical

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methods. The concentration levels observed were compared to previously reported values in steady sediments in the same river and discussed on a regulatory perspective. Hydrographs and sedigraphs recorded showed a peak-flow of 1300 $m^3\ s^{-1}$ and a corresponding peak of suspended sediments of 315 $mg\ L^{-1}$. Combination of flow discharge, suspended sediments and pollutants' concentrations data allowed for quantifying the mass flows (mass per unit of time) and setting the load budgets (weight amount) of the different pollutants transported by the river during the monitored event. Mean mass-flows and total load values found were 20.2 $mg\ s^{-1}$ (400 g) for PAHs, 38 $mg\ s^{-1}$ (940 g) for DDX, 44 $mg\ s^{-1}$ (1038 g) for PCBs and 8 $mg\ s^{-1}$ (200 g) for OCs. The dynamic pattern behavior of PAHs differs substantially to that of organochlorine pollutants, thus reflecting different pollution origins.

1. Introduction

Water scarcity is present in natural conditions in the Mediterranean area due to the characteristic highly variable river flows and the occurrence of low flow characteristic of the Mediterranean climate. Alternation of extreme events such as droughts and flash-floods is common in the region, a fact that will likely accentuate according to the previsions of the IPCC (Lehner et al., 2006). Sediment transport is closely related to the occurrence of flood events (Batalla et al., 1995; Garcia et al., 2000; Vericat and Batalla, 2010) capable to deliver enough kinetic energy to mobilize the riverbed and entrain the sediments. Likewise, it is known that contaminants accumulated in the sediments are mobilized during such energetic events. However, whereas there are many studies characterizing contaminants in steady sediments (Fernández et al., 1999; Carrizo and Grimalt, 2006; Lacorte et al., 2006; Navarro-Ortega et al., 2010), only few are devoted specifically to the transport dynamics of pollutants associated to the suspended sediment load (Gómez-Gutiérrez et al., 2006). In addition, quantitative information concerning the load budgets of persistent organic pollutants associated to particulate material transport is scarce (Schwientek et al., 2013; Rügner et al., 2013). Within this context, flushing flows (FF), which are controlled flood flows performed from a dam for a given environmental and/or engineering purpose (Kondolf and Wilcock, 1996; Batalla and Vericat, 2009), offer some advantageous characteristics (in comparison to natural floods) to examine the role of the suspended loads in entraining and transporting associated contaminants. It has been shown that during FFs suspended sediment concentration doubles that of natural floods, although discharges are typically much lower (Tena et al., 2012b). In turn, flashiness, measured as the rate of discharge increment per unit time, may attain an order of magnitude higher during FFs than during natural events. Consequently, FFs exhibit higher transport capacity than their natural counterparts despite their considerably lower magnitude and duration. Furthermore, and owing to their intrinsic characteristics (i.e. hydrograph design, programmability), they offer obvious practical advantages, particularly in what monitoring logistics is concerned.

FFs have been used typically to mitigate dam-induced impacts, mobilizing accumulated sediment and scouring the channel (Milhous, 1982), and maintaining large morphological features (Reiser et al., 1989). Under appropriate conditions, they are increasingly used as a tool for the maintenance and enhancement of aquatic and riparian habitat (Brookes, 1995; Kondolf and Wilcock, 1996; Downs et al., 2002). In particular, FFs have been implemented in the lower Ebro River since 2002 and have been extensively monitored and subsequently analyzed, even modeled (Batalla and Vericat, 2009; Tena et al., 2011, 2012a, 2012b). In the present work, we examine the dynamics of persistent organic microcontaminants associated to the suspended sediments during a particular FF that was performed in the lower River Ebro (NE Spain) in June 2012. Measurements were taken 12 km downstream of a well-known contaminated hot-spot (Amaral et al., 1996; Olivares et al., 2010; Soto et al., 2011) associated to a nearby chloro-alkali industry (Flix) (Fig. 1).

A total of 42 semi-volatile persistent organic compounds corresponding to the families of polycyclic aromatic hydrocarbons (PAHs), DDT and its metabolites (DDX), polychlorinated biphenyls (PCBs) and other organochlorine compounds (OCs) were monitored. The objectives of the paper are (a) to analyze the presence of persistent organic pollutants associated to the suspended sediment load; (b) to characterize their variation during one of the artificial releases (flushing-flow) that are regularly performed in this river; (c) to provide a quantitative assessment of the mass-flows and load budgets of the organic microcontaminants transported during the FF; and (d) to assess the risk associated to such transport, also by putting the results in the current regulatory context.

2. Site description: The lower Ebro

The Ebro is the largest river in the Iberian Peninsula flowing into the Mediterranean Sea, with a basin draining a total of 85,534 km^2 (Fig. 1). It is characterized by an interannual variability associated with its intrinsic Mediterranean character. Mean discharge recorded in Tortosa (i.e. the lowermost downstream gauging station) for the period 1912–2012 is 436 $m^3\ s^{-1}$, but flows vary from less than 50 $m^3\ s^{-1}$ in the very dry seasons to more than 12,000 $m^3\ s^{-1}$ (i.e. the major flood recorded ever that occurred in October 1907 Novoa, 1984).

Runoff in the Ebro is regulated by a series of dams. In particular, in the lower Ebro (where we focus our study) the Mequinenza–Ribarroja–Flix dam complex is located; it owns a total storage capacity of ~1.7 km^3 (i.e. 1 $km^3 = 1 \times 10^9\ m^3$), the largest in the catchment. Regulation has led to a decrease of an average of 25% the magnitude of natural frequent floods (i.e. Q_2–Q_{25}, where Q_i is the discharge associated with i years recurrence interval) in the reach downstream the dams (Batalla et al., 2004). Sediment transfer has also been altered; for instance, Vericat and Batalla (2006) reported a mean trapping efficiency for suspended sediment at around 90% in the dam complex, whereas bedload is fully captured. Together with hydrological and sedimentological alterations because of regulation (Batalla et al., 2004; Vericat and Batalla, 2006; Tena et al., 2012a) ecological consequences have also been observed in the lowermost part of the catchment (Prats et al., 2011; Sabater et al., 2011); for instance, the massive growth of macrophytes (Batalla and Vericat, 2009; Tena et al., 2012a). Within this context, FFs have been designed and implemented in the lower Ebro since 2002 with a twofold objective: (i) controlling macrophyte populations and (ii) maintaining certain degree of sedimentary activity in the channel. However, river regulation is not the only impact in the lower Ebro. The Flix Reservoir is heavily affected by wastes from a chloro-alkali plant. The result of the accumulation of waste disposal from the factory through decades is a deposit of hazardous industrial solid waste (200,000–360,000 T) which contains large amounts of PCBs, DDT, hexachlorocyclohexane (HCB) and heavy metals (Hg) (Fernández et al., 1999). Today, this deposit is a major concern and decontamination works are being carried out. This decontamination involves the removal of the contaminated sludge of the river by dredging, a subsequent processing at a nearby treatment plant, transportation and disposal in landfill of contaminated wastes. Consequently, the present study can be used as a tool for the evaluation of the effects of this dredging process on the Ebro River downstream from Flix.