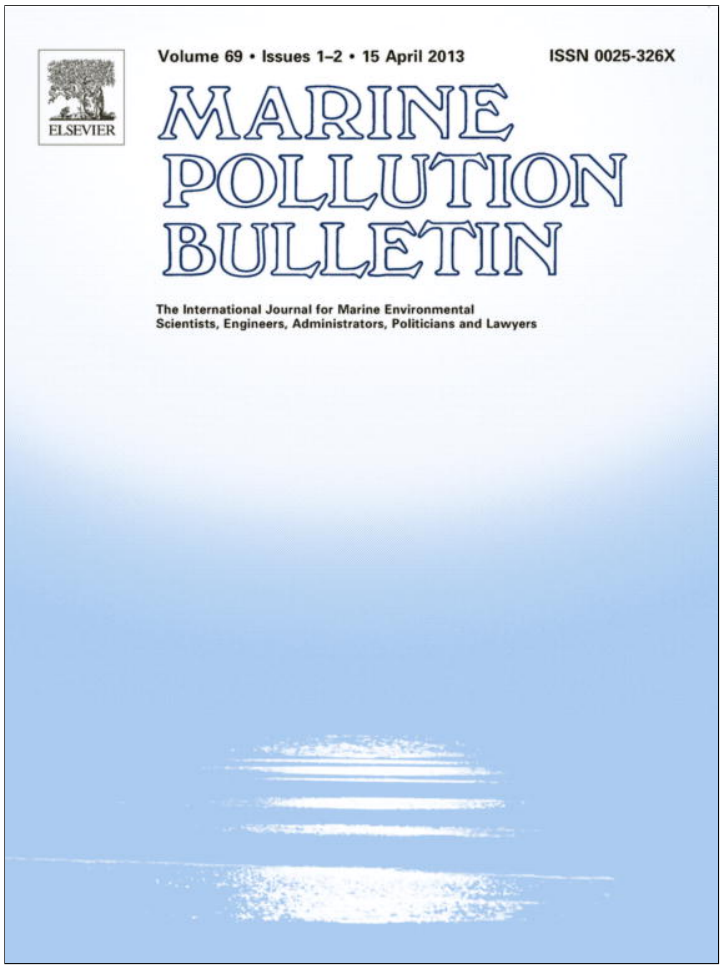
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Dynamics and fates of trace metals chronically input in a Mediterranean coastal zone impacted by a large urban area

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ABSTRACT

Quantification and characterization of chronic inputs of trace metals and organic carbon in a coastal Mediterranean area (the city of Marseille) during the dry season was carried out. The 625 km^2 watershed includes two small coastal rivers whose waters are mixed with treated wastewater (TWW) just before their outlet into the sea. Dissolved and particulate Cu, Pb, Cd, Zn, Co, Ni and organic carbon concentrations in the rivers were comparable to those in other Mediterranean coastal areas, whereas at the outlet, 2- to 18-fold higher concentrations reflected the impact of the TWW. A non-conservative behavior observed for most of the studied metals in the mixing zone was validated by a remobilization experiment performed in the laboratory. The results showed that sorption/desorption processes could occur with slow kinetics with respect to the mixing time in the plume, indicating non-equilibrium in the dissolved/particulate metal distribution. Thus, a sample filtration immediately after sampling is strictly required.

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1. Introduction

Progressive anthropization of coastal areas throughout the world results in changes in the biology and chemistry of coastal seawaters that can drastically alter their ecological and biological dynamics. Coastal inputs of anthropogenic nutrients and contaminants by rivers have proved to play key roles in these changes. Trace metals are of concern because of their potential for long-term accumulation in soils and sediments. Trace metals are natural constituents of crustal materials and can enter into aquatic system through erosion processes (Di Leonardo et al., 2009; Rocha et al., 2011; Weber et al., 2009). Some metals are essential to biota, but all have the potential to be biologically toxic if their concentrations exceed certain levels. Anthropogenic inputs of trace metals to the aquatic compartment often exceed the contributions from natural sources, especially where population density is high. These anthropogenic inputs are mainly due to leaching of impervious urban surfaces (roads, parking lots and roofs) and soil surfaces by runoff and to sewage overflow from sanitary sewer systems during high rainfall events; locally treated wastewater (TWW) discharges and industrial effluents can also be of importance (Bay et al., 2003; Bothner et al., 2002; Gonzalez et al., 1999; Matthai et al., 2002; Nicolau et al., 2012). Wastewater treatment plants have been designed to remove nutrients from wastewaters, but it is also known that large amounts of potentially toxic elements such as metals end up in wastewater. Until recently, the concentrations of trace metals in the effluents from waste water treatment plants (WWTPs) were not routinely tested because of high monitoring costs (Busetti et al., 2005).

The behavior of trace metals discharging in a coastal zone from a freshwater input depends on the properties of their species and the time of mixing. The differences in physico–chemical conditions between river water and seawater can cause a redistribution of metals between solution and suspended particulate matter (SPM) phases. Mobilization of dissolved metals from the solid phase is, indeed, the subject of considerable interest, and numerous field data confirm the significance of metal release from river SPM in salinity gradients (Kraepiel et al., 1997). During the mixing of fresh and salty waters, the partitioning of metallic species between the solution and SPM phases is controlled by two major processes: the removal of metals by flocculation of humic and fulvic acid-metal complexes and the desorption of metals from river particles or from resuspended sediment (Roux et al., 1998; Wang and Liu, 2003). Trace metal behavior varies according to metal and estuary. Conservative behavior was reported for Cu in the Rhône estuary (Dai et al., 1995; Elbaz-Poulichet et al., 1996), the Gironde estuary (Kraepiel et al., 1997) and the Loire estuary (Waeles et al., 2009), for Zn in the Scheldt estuary (Zwolsman et al., 1997) and for Pb in the Gironde estuary (Kraepiel et al., 1997). Contrastingly, Cu release into solution was shown in the Changjiang Estuary (Wang and Liu, 2003), the San Francisco Bay Estuary (Sañudo-Wilhelmy et al., 1996) and the Penze Estuary (Waeles et al., 2008). Cd also showed non-conservative behavior in various estuaries

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(e.g., Elbaz-Poulichet and Martin, 1987; Waeles et al., 2009). The characteristics of a river or estuary's watershed such as climate (e.g., rain frequency and intensity), morphology, hydrology, geology and land use drive estuarine dynamics, particularly flushing times of waters and particle concentrations and residence times, which are among the most important factors controlling metal reactivity in estuaries (Elbaz-Poulichet, 2005). Additional parameters such as redox conditions (Zwolsman et al., 1997) or presence of dissolved organic matter (DOM) (Louis et al., 2009) have also been reported to control the fate of metals in estuaries. In aquatic systems, DOM plays a major role in metal speciations, affecting their bioavailability and toxicity towards micro- and macro-organisms (Bruland and Lohan, 2003). Among possible DOM sources, WWTP effluents bring high quantities of dissolved and particulate carbon forms to rivers or estuaries, influencing metal speciations significantly, which implies a need for DOM characterization (e.g., Buzier et al., 2011; Pernet-coudrier et al., 2008).

Only a few studies have dealt with the Mediterranean area despite its rapid anthropization due to present-day heliotropism from Northern Europe and despite its climate specificities. Among all the possible sources of marine pollution, large coastal cities are among the most worrying, especially in the Mediterranean Sea. A typical example is Marseille, the largest Mediterranean French city, with over 1.7 million inhabitants. Two small rivers, the Huveaune and the Jarret, run through the agglomeration and join before their outlet to the sea (Fig. 1). Despite their low flow, they can have a large local ecological impact. Some studies have been performed on the dynamics of elements in Mediterranean estuaries of large or small rivers (e.g., Dassenakis et al., 1997; Elbaz-Poulichet et al., 1991; Elbaz-Poulichet, 2005; Ollivier et al., 2011), but a system such as Marseille is not commonly examined. The uniqueness of this system is that the river waters are mixed with the city WWTP effluents and then rapidly discharged into the open sea without passing through an estuary, so that the WWTPs' contribution to the water characteristics at the outlet is most likely predominant during baseflow periods. These inputs have a certain impact on the local coastal ecosystem, however, a high number of such anthropized sources along the coast is likely to impact the whole Mediterranean Sea.

In this context, the aims of the present study were (1) to quantify and characterize carbon and trace metal inputs to the sea during dry periods near the Marseille urban area, (2) to identify the specific contribution of the WWTP and (3) to understand the transfer mechanisms that operate in the mixing zone.

2. Materials and methods

2.1. Study site

The climate of the studied area is typically Mediterranean, with wet temperate winters and dry, hot summers. The average annual rainfall is 551 mm. Rainfall is strongly seasonal as more than 75% of the rains occur between September and January. The rains are frequently of high intensity, promoting high rates of terrestrial runoff and can occur after long, dry periods that allow contaminant accumulation on the watershed surfaces. Another rainfall period occurs in spring between March and May, during which rainfalls can be of longer duration and lower intensity. Long dry periods (less than 30 mm of rain per month) occur from January to March and from May to September. As in most of the Mediterranean area, the spatial and seasonal variability of the rainfall follows a complex pattern with wide and unpredictable rainfall fluctuations from 1 year to another (Martínez-Casasnovas et al., 2002).

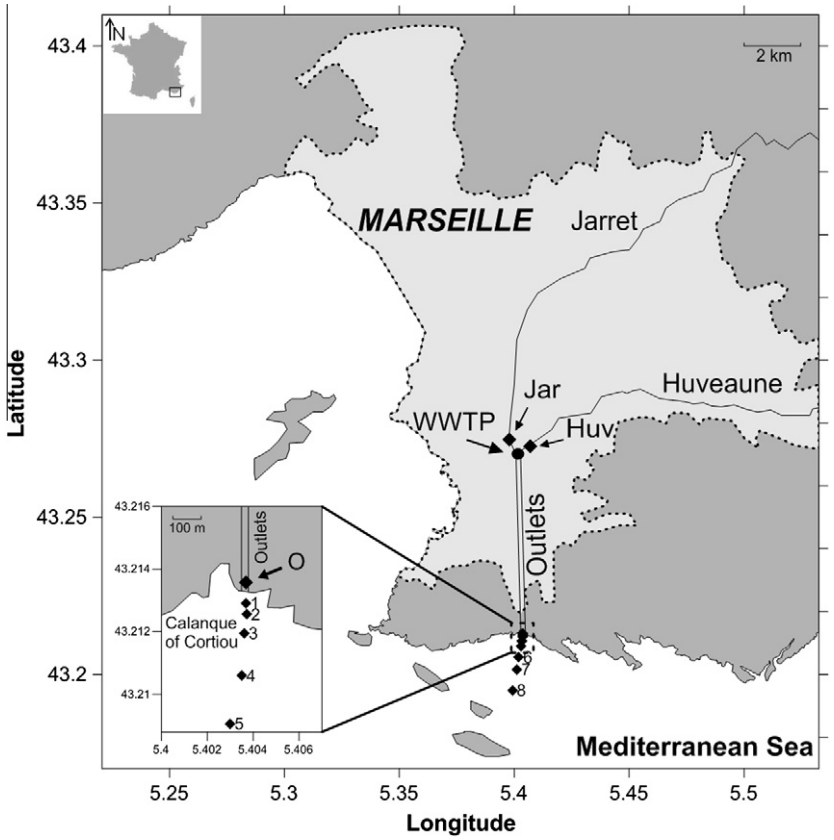


Fig. 1. Map of the studied site: the dotted area represents the urbanized zone of Marseille, (inset) position of the sampling sites, in the vicinity of the effluent outlets. Sampling points: O: outlet; Jar: Jaret River; Huv: Huveaune River; 1–8: surface sampling points at sea.

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The Huveaune River extends over 48.4 km and runs through a watershed with an area of 523 km^2 that consists of a karstic formation (60%) and detrital sediments. Land use in the downstream part of the watershed is urban and industrial. The Jarret extends over 21 km with a 102 km^2 watershed that is mainly urban and industrial. These two rivers merge in Marseille. The resulting river water is mixed with the effluent water coming from the Marseille City WWTPs and then channeled to the sea at the Calanque of Cortiou (Fig. 1). This treatment plant, one of the largest in Europe (1.7 million inhabitant eq.), uses both physical and biological treatment processes. At the Calanque of Cortiou, freshwater–seawater mixing occurs directly at the surface of the sea and presents a rapid mixing time.

The Huveaune's base flow ranges from 1 to 5 $m^3 s^{-1}$ (1.7 $m^3 s^{-1}$ on average), the Jarret's from 0.5 to 3 (0.8 $m^3 s^{-1}$ on average) and the WWTPs' effluent ranges from 0.4 to 3.8 $m^3 s^{-1}$ (3.0 $m^3 s^{-1}$ on average), so that half of the flow at the outlet is due to the WWTP discharge.

2.2. Sampling

All bottles (FEP and HPED, from Nalgene) used throughout the sampling and conditioning were previously cleaned with 10% nitric acid prepared from 70% HNO_3 of analytical reagent grade (Fisher Scientific), rinsed with milli-Q water (Millipore 18.2 MΩ), filled with milli-Q water and acidified at 0.1% with s.p. HNO_3 (Merck) until use.

Five sampling campaigns (16/02/2010, 18/03/2010, 26/04/2010, 28/06/2010, 22/03/2011) were conducted during dry periods but under contrasting conditions with regard to season, wind and waves. A sixth campaign conducted on 18/04/2012 allowed identification of an abnormal event characterized by very high DOC and metal concentrations and will be discussed separately in the text. For tributaries, 15 (Huveaune, Jarret) and 25 (Outlet) additional samples were collected at various dates in between these campaigns to better take into account input variabilities and thereby evaluate more accurately their contributions to the average flux of elements to the coastal zone.

Sampling locations (Fig. 1, inset) were selected to cover the whole freshwater–seawater mixing zone. Eight profiles of salinity, temperature and dissolved O_2 were assessed along a north–south transect from the outlet to over 2 km offshore using a HACH LANGE multi-probe calibrated before each campaign.

Surface samples were collected in the Huveaune and Jarret Rivers upstream of their confluence, while mixed river and WWTP water was collected just upstream of the outlet (continental end-member). Along a transect at sea, four samples were taken at ≈5 m from the outlet (surface, 0.5, 1.5 and 2.5 m in depth), two samples at 2 km offshore (surface and 4 m in depth, this latter defining the marine end-member), and six surface samples between these two limits. Considering the high salinity stratification of the plume, sampling was performed using a 2.2 L horizontal sampler (Wildco) that allowed a 10-cm thick water layer resolution. Samples were partitioned in 1 L FEP bottles for metal analysis and 1 L HDPE bottles for organic matter (OM) analysis. After sampling, the bottles were stored in a cooler, brought back to the laboratory and immediately filtered. Additionally, during the two last campaigns, at each sampling site, an aliquot was also immediately filtered on board.

2.3. Sample filtration, conditioning and treatment

Samples for DOC/POC analyses were filtered through 25 mm glass filters (Whatman GFF, 0.7 μm). Particulate organic carbon (POC) was quantified using these filters. The dissolved fraction was preserved using 25 μL 1 M NaN_3 (NaN_3 >99%, Aldrich) and stored at 4 °C in 24 mL glass tubes (Wheaton, equipped with Teflon/silicone septa) prior to analysis of dissolved organic carbon (DOC). All tubes, filters and glass filtering systems (Wheaton) were previously cleaned with 10% HNO_3, milli-Q rinsed and calcinated for 4 h at 450 °C.

Samples stored in 1 L FEP bottles for dissolved/particulate metal analyses were filtered through 47 mm cellulose nitrate filters (Sartorius, 0.45 μm). The filters were dissolved by microwave digestion (AntonPaar Multiwave 3000) in aqua regia (trace metal grade acids, Fisher Scientific) for further analysis of metals in the particulate fraction following a previously validated procedure (Tessier et al., 2011). The filtrate (dissolved fraction) was stored in 60 mL FEP bottles, acidified with 60 μL HNO_3 (supra pure 65%, Merck) and digested for 2 h under UV irradiation (Metrohm 705, 500 W) for further analysis of total dissolved metal concentrations (Louis et al., 2009).

Onboard filtration was achieved using 0.2 μm in-line syringe cellulose nitrate filters (Sartorius). Filtrates were stored in 60 mL FEP bottles for dissolved metal analysis and in 24 mL glass tubes for DOC analysis. Similar conditioning protocols were applied as for the laboratory-filtered samples.

2.4. Remobilization experiment

For a better understanding of the mechanisms that operate in the salinity gradient, a remobilization experiment designed to simulate the mixing of the outlet effluent with seawater was performed in the laboratory. A 10 L sample of composite outlet water was obtained during the 28 June 2010 campaign by collecting ten 1 L samples during ~ 15 min to obtain a representative outlet sample. Filtered marine end-member water was mixed in 1 L FEP bottles with the unfiltered outlet water to cover a range of salinity: 1, 2.5, 5, 10 and 25. The 1 L FEP bottles were placed on an agitation system (Reax 20, Heildolph) and aliquots were sampled at 15 min, 1 and 6 h of mixing time using pre-cleaned syringes and then filtered through pre-cleaned 0.22 μm in-line filters (Sartorius). Filtrates were stored and analyzed for DOC and dissolved trace metals as explained below.

2.5. One-day monitoring of the outlet waters

A 1-day monitoring of the outlet effluent was performed from 21/03/2011 21 h to 22/03/2011 21 h using a mobile refrigerated automatic sampler (Hydreka) installed in the outlet upstream of the mixing of the TWW with the river waters, thanks to the logistics of the SERAM company. In all, 24 1-L composite samples were each collected by sampling 100 ml of water every 6 min over the course of 1 h. The samples were then treated in the laboratory using the protocol described previously.

2.6. Carbon analysis

POC contents on filters were determined using a TOC-V_{CSH} analyzer (Shimadzu), coupled with an SSM-5000A module. The GFF filters were dried to constant weight at 60 °C, and then exposed to HCl fumes for 4 h to remove all of the inorganic carbon (Lorrain et al., 2003). The organic carbon content was determined using the high-temperature (900 °C) catalytic oxidation method with CO_2 IR detection (Ammann et al., 2000; Callahan et al., 2004), calibrated using glucose (Analytical reagent grade, Fisher Scientific), with an accuracy of 0.1 mg C.

DOC and DIC concentrations were determined using the same TOC-V_{CSH} analyzer, calibrated using hydrogenophtalate (Shimadzu) and $NaHCO_3$/Na_2CO_3 standard solutions, respectively, with an accuracy of 0.02 mg C L^{-1} (Louis et al., 2009). DOC and DIC anal-

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yses were validated using a certified reference material (MISSIPPI-03, Canada); values obtained remained within the certified limits.

2.7. Analyses of major elements and trace metals

2.7.1. Dissolved trace metals in salt samples

Total dissolved metal (Cd, Cu, Pb and Zn) concentrations were determined using Differential Pulse Anodic Stripping Voltammetry (DPASV). Measurements were carried out using an AutolabIII (EcoChemie) potentiostat controlled by GPES 4.9 software (EcoChemie) coupled with a three-electrode cell (663 VA Stand, Metrohm) (Louis et al., 2009) with a Ag|AgCl|KCl 3 M electrode as the reference, a Pt wire as the auxiliary and a static mercury drop (SMDE) as the working electrode. Parameters of the DPASV procedures were adapted from (Omanović et al., 2006) and (Jean et al., 2012). Total dissolved Co and Ni were determined only for samples of the last three campaigns using Differential Pulse Adsorptive Cathodic Stripping Voltammetry (DPAdCSV) using the same instrument and a procedure adapted from (Vega and van den Berg, 1997). Trace metal determinations were performed using a fully automatic standard addition method using Cavro XE 1000 Syringe Pumps and the voltammograms obtained were treated (2nd derivative) using ECDSOFT software (Omanović et al., 2006). Standard deviations of the measured metal concentrations remained below 5%.

Analyses were validated using a certified "Nearshore Seawater Reference Material for Trace Metals" – CASS5 (NRC CNRC). All metal determinations remained within the certified limits.

2.7.2. Major ions in freshwater samples

Major ions were analyzed using ionic chromatography (Dionex, DX-120) to measure F^-, Cl^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}. Anionic and cationic columns were loaded with quaternary ammonium- (AS9-HC) or carboxylate-functionalized (CS12-A) groups, respectively. Anionic and cationic eluents were 9 mM Na_2CO_3 and 20 mM CH_4SO_3, respectively. In both cases, the flow rate was 1 mL min^{-1} and the separated ions were quantified using conductimetry. Analyses were validated using a "River Water Reference Material" (MISSIPPI-03, Environment Canada).

2.7.3. Trace dissolved metals in freshwater samples and particulate metals

Particulate metals on the acid-digested filters were quantified using *High Resolution Inductively Coupled Plasma Mass Spectrometry* (*HR ICP-MS* Element 2, Thermo Finnigan). The instrument was calibrated using standard solutions and an In internal standard was added to the samples (Lenoble et al., 2013). Quality control of the HR ICP-MS measurements was performed by determination of element concentrations in a Certified Reference Material (SLRS-4 river water, PACS-2 sediment, National Research Council Canada). All results showed good agreement with the certified data. Trace metal concentrations in the freshwater samples were analyzed following the same procedure.

In the following, concentration and content terms refer to mass/mol per unit volume (e.g., mg L^{-1}) and mass/mol per unit mass (e.g., mg g^{-1}), respectively.

3. Results and discussion

3.1. Dynamics of elements in the mixing zone

Table 1 gives the averages and ranges of variation of the measured parameters in the Huveaune and Jarret Rivers, at the outlet and in the seawater end-member compared with the world averages for rivers (Gaillardet et al., 2003) and with values observed in the Eygoutier River, a small coastal river in the same geographic area (Nicolau et al., 2012).

3.1.1. Salinity, dissolved oxygen and SPM

The dispersion of freshwater in seawater during dry weather conditions can be tracked according to salinity (Supplementary material Fig. SI1). The sea salinity near Marseille is approximately 38.2. The river/effluent outlet salinity, which is lower than 0.5, will be considered as null. The freshwater plume thickness decreased from 4 to 1 m along the first 400 m of the transect and then remained lower than 1 m until 1000 m.

In the rivers, dissolved oxygen varied from 98% to 104.2% for the Huveaune and from 83.6% to 94.3% for the Jarret, values similar to other Mediterranean rivers. In outlet discharge water, dissolved oxygen varied from 69.5% to 82.2%. The decrease in the dissolved oxygen in the outlet waters was due to high DOC/POC concentrations in the TWW that stimulated oxygen-consuming biologic activity. In the plume, dissolved oxygen increased and closely followed the salinity variation due to dilution with seawater whose oxygen saturation is close to 100% (Zwolsman et al., 1997).

In Huveaune water, Suspended Particulate Matter (SPM) varied from 2.1 to 21 mg L^{-1}, and in Jarret water, from 4.6 to 30 mg L^{-1} (Table 1). These values were comparable to those of other Mediterranean rivers such as the Rhone (close to 6 mg L^{-1} (Ollivier et al., 2011) and the Eygoutier (13 ± 3.7 mg L^{-1})) under similar conditions. At the outlet, the SPM value was higher (between 9.8 and 83 mg L^{-1}) due to the TWW that contained a high quantity of particles. Along the salinity gradient, the SPM was conservative with the salinity and decreased to 4.5 mg L^{-1} in the seawater end-member, a value typical of the north-east Mediterranean Sea (Chronis et al., 2000). These results indicate that no significant sedimentation processes occurred at the beginning part of the plume, which means that the particles were low-weighted, such as organic matter (OM), or small-sized, such as oxide or clay particles. This suggests that, during dry conditions, no significant sedimentation occurs and that most of the metal and OM inputs from the Marseille urban area remain suspended in seawater.

3.1.2. Organic matter

DOC and POC variations as functions of salinity are given in Fig. 2. Throughout the campaigns, DOC concentrations varied from 1 to 1.8 mg C L^{-1} in the Huveaune and from 1.1 to 2.9 mg C L^{-1} in the Jarret (Table 1). These values are in the range of those observed in the Eygoutier River (4.1 ± 3.5 mg C L^{-1}) and in the Rhône river (1.7 mg C L^{-1}, (Dai et al., 1995)). At the outlet, the DOC fluctuated from 4 to 10 mg C L^{-1} (6.2 mg C L^{-1} on average), these high values being explained by the DOC concentrations in the TWW being higher than 40 mg C L^{-1} as observed by Drewes and Jekel (1998). In the mixing zone, the DOC concentration progressively decreased to less than 1 mg C L^{-1} in the seawater end-member, following the mixing line, which indicates conservative behavior (Fig. 2A). The same behavior was observed in various estuaries such as the Rhône Estuary (Dai et al., 1995), the Mississippi River plume (Guo et al., 2009) and the Bay of Saint Louis (Cai et al., 2012) as well as the Humber Estuary (Álvarez-Salgado and Miller, 1998; Cai et al., 2012). As observed in other studies, increased DOC at low salinity was due to (1) lysis of freshwater phytoplankton cells in seawater (Morris et al., 1978), (2) deflocculation of SPM aggregated colloids affecting only the <3 nm DOC fraction (Dai et al., 1995) or (3) bacterial decomposition of SPM-OM where turbidity is high (Álvarez-Salgado and Miller, 1998). Such DOC behavior was not observed in the studied system.

Throughout the campaigns, the POC content varied from 55 to 160 mg C g^{-1} in Huveaune water, from 130 to 320 mg C g^{-1} in Jarret water and from 110 to 420 mg C g^{-1} at the outlet (Table 1). As for the DOC, higher values and variability at the outlet are ex-

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Table 1
Variations of dissolved (D) and particulate (P) elements concentrations in the rivers, at the outlet and in the seawater end-member compared to the world rivers average (Gaillardet et al., 2003) and to the Eygoutier River (Nicolau et al., 2012).

	SPM (mg L^{-1})	DOC (mg L^{-1})	POC (mg g^{-1})	Cu (nM)		Pb (nM)		Cd (nM)		Zn (nM)		Co (nM)		Ni (nM)	
				D	P	D	P	D	P	D	P	D	P	D	P
Huveaune-average	9.1	1.3	110	27	15	0.64	5.2	0.07	0.07	52	47	6.9	1.4	43	7.3
(min–max)	(2.1–21)	(1.0–1.8)	(55–160)	(11–42)	(4.2–32)	(0.26–1.6)	(0.95–14)	(0.02–0.18)	(0.02–0.2)	(18–97)	(4.4–115)	(1.3–13)	(0.36–3.7)	(7.8–72)	(1.4–24)
Jarret-average	13	1.8	230	28	27	0.37	2.7	0.07	0.07	73	87	4.1	2.1	29	7.5
(min–max)	(4.6–30)	(1.1–2.9)	(130–320)	(9.4–50)	(8.1–260)	(0.17–0.81)	(1.0–4.8)	(0.02–0.18)	(0.02–0.14)	(17–170)	(13–260)	(1.5–6.6)	(0.49–4.1)	(11–44)	(0.2–19)
Outlet-average	22	6.2	250	33	150	0.88	8.2	0.12	0.29	200	300	7.4	1.7	50	17
(min–max)	(9.8–83)	(4.0–10)	(110–420)	(16–60)	(56–270)	(0.35–1.4)	(3.4–18)	(0.05–0.20)	(0.13–0.69)	(110–330)	(91–760)	(2.5–13)	(0.60–5.2)	(24–76)	(4.5–57)
Seawater-average	4.5	1	43	3.3	5.2	0.25	0.26	0.07	0.04	21	120	0.52	0.24	8.4	14
(min–max)	(3.1–6.0)	(0.8–1.2)	(21–65)	(1.6–4.1)	(1.9–9.2)	(0.14–0.36)	(0.04–0.37)	(0.05–0.08)	(0.01–0.09)	(14–31)	(61–160)	(0.22–1.0)	(0.06–0.55)	(5.7–9.9)	(6.1–20)
World average river				23		0.38		0.71		9.2		2.5		14	
Eygoutier-average	13	4.1	240	55	60	2.9	10	0.36	1.4	280	350				

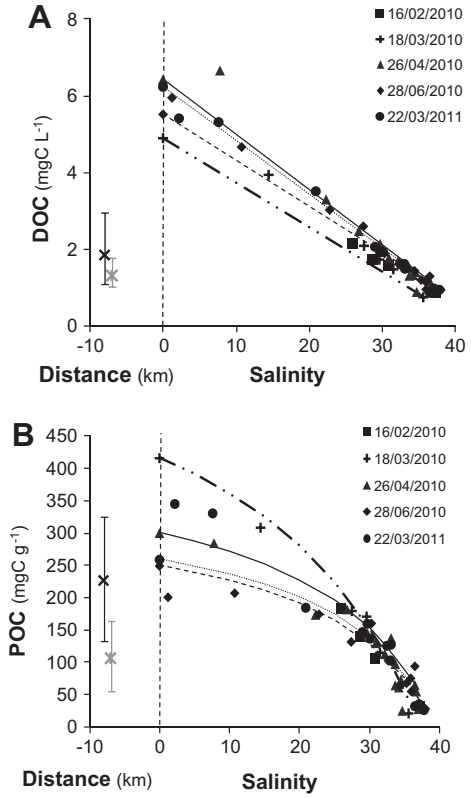


Fig. 2. Variation of DOC (A) and POC (B) in Huveaune (*) and in Jarret (×) rivers, as a function of the distance until outlet, and from outlet to seawater, as a function of the salinity gradient, for each sampling campaign. Vertical lines at river points join maximum and minimum values. Mixing lines are given for the 18/03/2010 (dotted-dashed line), 26/04/2010 (solid line), 28/06/2010 (dotted line) and 22/03/2011 (dashed line) campaigns.

plained by the TWW POC content: at the outlet, the variability of both DOC and POC was controlled by the TWW inputs that were superimposed onto the river fluctuations. For all the campaigns, the POC content decreased with increasing salinity down to the value of the seawater end-member (43 mg C g^{-1} on average), as observed elsewhere (Cai et al., 2012; Saliot et al., 2002; Savoye et al., 2012). Globally, the POC content showed a conservative trend for all of the campaigns (Fig. 2B). The sample variability compared to the conservative curve was due to the heterogeneity of the source.

Fig. 3 gives DOC as a function of POC expressed in mg C L^{-1}. In the Huveaune, the DOC fraction is dominant, whereas in the Jarret river, it is the POC fraction. Finally, at the outlet, the DOC and POC are in the same range but in higher concentrations, which implies high DOC and POC inputs in the TWW. Along the salinity gradient, the DOC increased from 50% of the total organic carbon at the outlet to 90% in the marine end-member as observed elsewhere (Cauwet et al., 1997).

3.1.3. Dissolved and particulate metals

Variations of dissolved metal concentration as a function of salinity from the river points to the marine end-member and dissolved concentration as a function of particulate concentration are depicted in Fig. 4 for each metal studied. The eq:eq line permits comparison of dissolved and particulate fractions for the same element. For each element, the Huveaune/Jarret data points and error bars represent average values and min–max ranges, respectively, calculated from the full set of analyzed samples (see Section 2.2).

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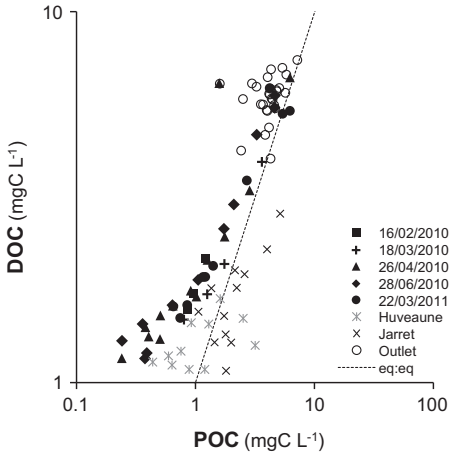


Fig. 3. DOC as a function of POC expressed in mg C L^{-1}. The dotted line (eq:eq) represents the same carbon concentration in the dissolved and particulate phases.

Cu concentrations measured in the Huveaune and Jarret Rivers were in the same range, either as dissolved or particulate (Table 1), but lower than in the Eygoutier River (Nicolau et al., 2012). Dissolved Cu was close to the world average river value (Table 1). Cu was mainly in the dissolved fraction in Huveaune water and equidistributed between the dissolved and particulate fractions in Jarret water (Fig. 4B). The higher particulate/dissolved Cu ratio at the outlet compared to the rivers indicates a high input of particulate Cu by the TWW. Dissolved Cu represented 20% and 80% of total Cu at the outlet and at the marine end-member, respectively. Dissolved Cu concentrations in the marine end-member (3.3 nM on average) were in the range of those reported for Western Mediterranean surface water (Morley et al., 1997) and coastal waters of Toulon Bay (Jean et al., 2012). Dissolved Cu at the outlet was therefore 10 times higher than the typical seawater value. Diminution of Cu with increasing salinity followed different patterns, depending on the campaigns: slightly below the conservative mixing line for the March 2011 campaign, which indicates a probable adsorption of dissolved Cu onto SPM; significantly above the line for the March, April and June 2010 campaigns (Fig. 4A), which indicates, instead, a release of dissolved Cu from SPM as previously observed in the Loire Estuary (Waeles et al., 2004). This contrasts with the conservative behavior of Cu reported for the Rhone (Elbaz-Poulichet et al., 1996) and Danube (Guieu et al., 1998) Estuaries.

Pb was mainly found in the particulate fraction in the Huveaune and Jarret rivers and at the outlet, whereas in the seawater end-member dissolved Pb was higher (Fig. 4D). In the Huveaune and Jarret rivers, both particulate and dissolved Pb values were lower than those observed in the Eygoutier River and, regarding dissolved Pb, of the same order of concentration as the world river average (Table 1). Concentrations of both fractions were approximately 2-fold higher at the outlet than in the rivers, indicating a significant Pb input from the TWW. Dissolved Pb represented 15% and more than 50% of total Pb at the outlet and at the sea-end-member, respectively. Dissolved Pb at the marine end-member (0.25 nM on average) was higher than the average surface Pb of 0.085 nM measured in western Mediterranean waters (Morley et al., 1997) but was close to the value recorded in the open part of Toulon Bay (0.19 nM, (Jean et al., 2012)). For the April 2010 campaign, dissolved Pb showed a behavior close to the conservativity in the salinity gradient, as reported for the Gironde (Kraepiel et al., 1997) and in the Rhône Estuaries (Elbaz-Poulichet et al., 1996). For the other campaigns, data points were above the conservative mixing line, indicative of the release of dissolved Pb from SPM that was maximal at salinities close to 10 (Fig. 4C).

The Huveaune and Jarret Rivers showed the same average concentrations of particulate and dissolved Cd. These values were lower than those observed in the Eygoutier River and than those in the world river average (Table 1). Such low dissolved Cd values are likely due to the geology of the Huveaune and Jarret watersheds. The TWW brought particulate Cd in higher proportion compared to the river values (Fig. 4F). Dissolved Cd represented 15% and more than 90% of total Cd at the outlet and at the marine end-member, respectively. Dissolved Cd at the marine end-member (0.07 nM on average) was higher than the mean value observed in the 1–100 m layer in the western Mediterranean (0.044 nM, (Morley et al., 1997)) but lower than values observed in the eastern Mediterranean (0.018–0.278 nM, (Zeri and Voutsinou-Taliadouri, 2003)) and close to the ones measured in coastal waters of Toulon Bay (Jean et al., 2012). On average, dissolved Cd was 2-fold more concentrated at the outlet than at the marine end-member. For the April and June 2010 campaigns, points above the conservative mixing line (Fig. 4E) indicate the release of Cd from particles. This mechanism is well documented and corresponds to the formation of stable and soluble chlorocomplexes from particle-desorbed Cd (Dai and Martin, 1995; Elbaz-Poulichet et al., 1987; Waeles et al., 2008; Wang and Liu, 2003; Yang and Sañudo-Wilhelmy, 1998). This phenomenon was principally observed at salinities greater than 25. Two possibilities were suggested: (1) the desorption was more efficient at high quantities of chlorides, or (2) the mixing time was too short at low salinities to allow release of Cd into the dissolved phase. On the contrary, the data points for the March 2011 campaign were below the mixing line up to a salinity of 25 and above the mixing line thereafter (Fig. 4E), which indicated an adsorption of Cd onto particles up to a salinity of 25 followed by a release of Cd from particles to the dissolved phase above a salinity of 25.

Particulate and dissolved Zn concentrations in the Huveaune and Jarret Rivers were lower than in the Eygoutier River. At the outlet, they were in the same range as in the Eygoutier River. Dissolved Zn concentrations in the Huveaune and Jarret rivers were 6–8-fold higher than the world river average (Table 1). In the rivers, Zn was evenly distributed between the dissolved and particulate fractions, but at the outlet, particulate Zn was in higher proportion (Fig. 4H). The dissolved Zn decreased with increasing salinity from values higher than 110 nM at the outlet to 21 nM at the marine end-member (Fig. 4G), this latter value being higher than those reported in surface Mediterranean waters: 4–5 nM in surface western Mediterranean waters (Morley et al., 1997) and and close to 9 nM in the open part of Toulon Bay (Jean et al., 2012). For the June 2010 and March 2011 campaigns, points above the conservative mixing line (Fig. 4G) indicate a release of Zn from SPM at low salinity as previously reported for the Scheldt (Zwolsman et al., 1997) and Rhone (Elbaz-Poulichet et al., 1996) Estuaries. Such results contrast with the conservative behavior found in the Danube estuary (Guieu et al., 1998). For the other campaigns, no trend was clearly defined.

Co was mainly found in the dissolved fraction for all points: rivers, outlet and sea (Fig. 4J), contrary to what was observed, for instance, in the Hudson River Estuary or San Francisco Bay (Tovar-Sánchez et al., 2004). Concentrations of dissolved Co in rivers were 2–3-fold higher than the world river average (Table 1). Dissolved Co increased at the outlet compared to the river values, which indicates an input of dissolved Co by the TWW. The dissolved Co decreased from 7.4 nM on average at the outlet to 0.52 nM at the marine end-member, this latter value being high when compared with the average of 0.078 nM in surface western Mediterranean waters (Morley et al., 1997). Along the salinity gradient, the proportion of dissolved Co remained at approximately 80% of the total Co. Data from the June 2010 campaign were above the conservative mixing line; for the March 2011 campaign, samples were

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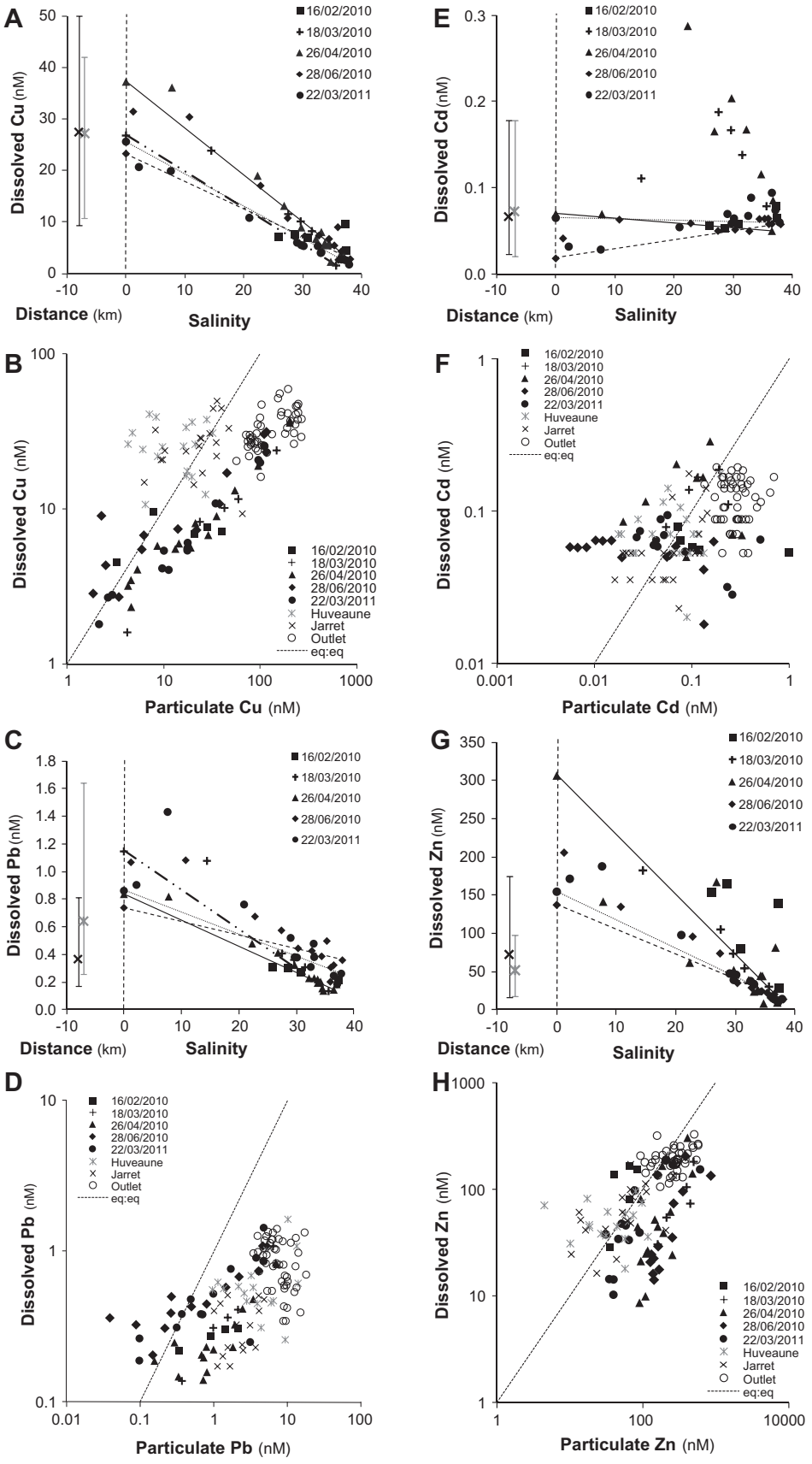


Fig. 4. Variation of dissolved metal in Huveaune (*) and in Jarret (×) rivers, as a function of the distance until outlet, and from outlet to seawater, as a function of the salinity gradient for each sampling campaign for Cu (A), Pb (C), Cd (E), Zn (G), Co (I) and Ni (K); vertical lines at river points join maximum and minimum values. Variation of dissolved metal as a function of particulate metal for Cu (B), Pb (D), Cd (F), Zn (H), Co (J) and Ni (L); the dotted line (eq:eq) represents the same metal concentration in the dissolved and particulate phases.

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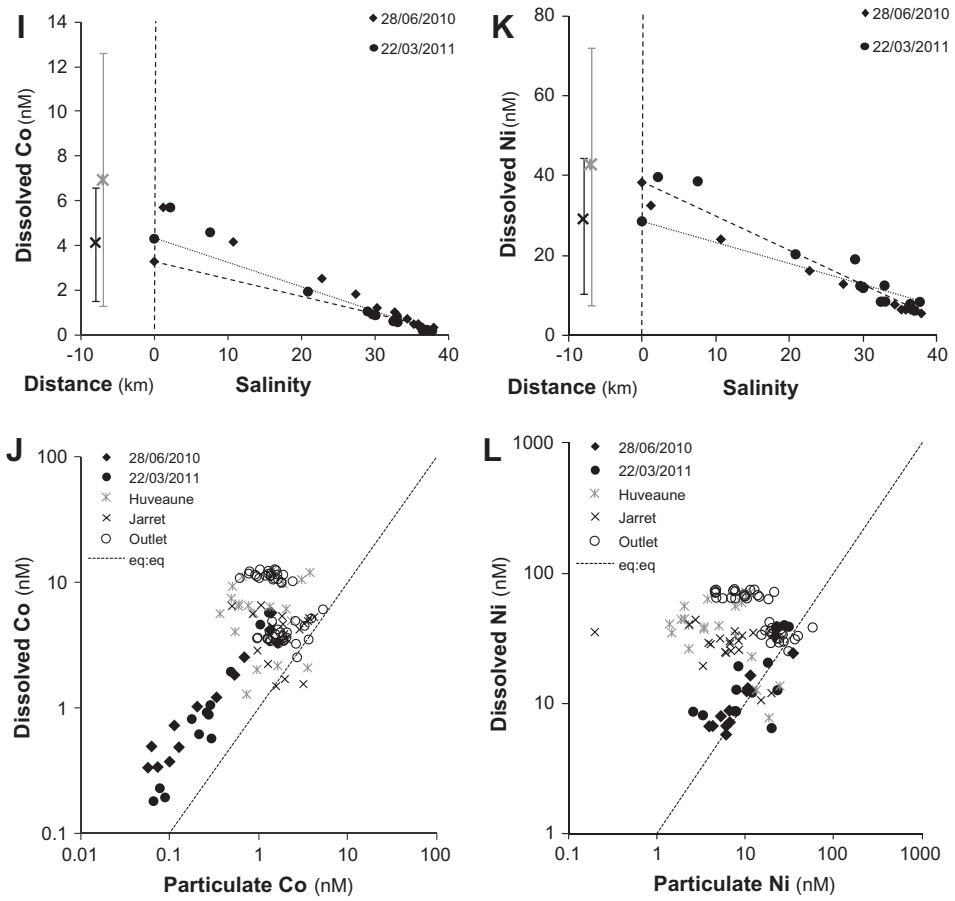


Fig. 4. (*continued*)

above the conservative mixing line until a salinity of 10 and along the conservative mixing line at higher salinities (Fig. 4I). This indicates a fast release of Co from the particles to the dissolved phase at the beginning of the plume. A non-conservative behavior was also observed for the Hudson River estuary, but there, the concentration of dissolved Co increased with increasing salinity. The main process responsible of this non-conservative behavior could be desorption from suspended particulates (Takata et al., 2010; Tovar-Sánchez et al., 2004).

Dissolved Ni was slightly higher in the Huveaune river than in the Jarret river and 2–3-fold higher than the world river average (Table 1). The TWW input brought both dissolved and particulate Ni, but the higher particulate/dissolved Ni ratio at the outlet compared to the rivers indicates a higher particulate input by the TWW (Fig. 4L). Dissolved Ni decreased from 50 nM, on average, at the outlet to 8.4 nM at the marine end-member, this latter value being high when compared to the 2.30 nM value given for surface western Mediterranean waters by (Morley et al., 1997), but in the same range of concentration as in eastern Mediterranean waters ((2.22–18.5 nM) (Zeri and Voutsinou-Taliadouri, 2003)). The proportion of dissolved Ni within the total increased along the salinity gradient from 60% to 80%. For the June 2010 campaign, the data points were below the theoretical mixing line, which signifies adsorption of Ni onto particles (Fig. 4K). For March 2011, the data points were above the theoretical mixing line, which implies a release of Ni into the dissolved phase. These behaviors differ from the conservative behavior observed in the Ob Estuary (Dai and Martin, 1995) and in the Rhône Estuary (Elbaz-Poulichet et al., 1996).

3.2. Daily estimated fluxes and specific fluxes during the dry period

Considering our data set of recorded carbon and metal levels, daily element fluxes during the dry period were estimated by dividing the average concentrations (Table 1) by the average flow (see Section 2.1) for each element studied in both the rivers and the outlet. Additionally, specific element fluxes were calculated by dividing the obtained element fluxes according to river watershed (see Section 2.1). For the outlet, the watershed was estimated as the sum of the Huveaune and Jarret watersheds, which then comprise the main part of Marseille city. To evaluate the TWW contribution to the global discharge to the coastal zone, the element flux ratio (F) was calculated as the outlet flux divided by the sum of the river fluxes. The values obtained are summarized in Table 2 and compared to those calculated for the Eygoutier and the Rhone Rivers, used as examples of small and large coastal Mediterranean rivers, respectively. Concerning the Eygoutier, fluxes were calculated using the element concentrations reported by Nicolau et al. (2012) using the average flow during the dry period (15 L s^{-1}). Concerning the Rhone, fluxes were estimated by averaging the measured concentrations (Ollivier et al., 2011) at low flow periods, i.e., below the Rhone average flow of 1600 m^3 s^{-1}. The results obtained for the rivers showed that the total specific fluxes of carbon and metals were higher for the Jarret than for the Huveaune, meaning that the watershed of the Jarret river is more contaminated compared with that of the Huveaune (Table 2). The total specific fluxes of the Eygoutier River were lower than those observed for the Huveaune and Jarret Rivers, which implied a higher level of contamination for the Huveaune and Jarret watersheds compared with that of the Eygoutier. In contrast, the total specific

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Table 2
Daily dissolved (D), particulate (P) and total element fluxes (in kg d^{-1} and g d^{-1} for SPM/OC and metals respectively) and specific fluxes (in kg d^{-1} km^{-2} and g d^{-1} km^{-2} for SPM/OC and metals respectively) for rivers, outlet, Eygoutier river (Nicolau et al., 2012) and Rhone river (Ollivier et al., 2011) and fluxes ratio (*F*) (see text for more details).

	SPM	OC			Cu			Pb			Cd			Zn			Co			Ni		
	P	D	P	Total	D	P	Total	D	P	Total	D	P	Total	D	P	Total	D	P	Total	D	P	Total
HUVEAUNE																						
Fluxes	1700	240	180	420	310	170	480	24	200	220	1.4	1.4	2.9	620	560	1200	74	15	89	460	78	540
Specific fluxes	*3.2*	*0.45*	*0.35*	*0.80*	*0.60*	*0.33*	*0.93*	*0.05*	*0.38*	*0.42*	*0.0027*	*0.0027*	*0.0055*	*1.2*	*1.07*	*2.3*	*0.14*	*0.03*	*0.17*	*0.88*	*0.15*	*1.03*
JARRET																						
Fluxes	1100	150	260	410	150	150	300	6.6	48	55	0.68	0.68	1.4	410	490	900	21	11	31	450	38	18
Specific fluxes	*11*	*1.5*	*2.5*	*4.03*	*1.5*	*1.5*	*2.9*	*0.065*	*0.47*	*0.54*	*0.0066*	*0.0066*	*0.013*	*4.02*	*4.8*	*8.8*	*0.20*	*0.10*	*0.31*	*1.4*	*0.37*	*1.8*
OUTLET																						
Fluxes	13000	3600	3200	6800	1200	5600	6800	106	1000	1100	8.0	19	27	7600	11000	19000	250	59	300	1700	580	2300
Specific fluxes	*21*	*5.8*	*5.1*	*11*	*1.9*	*9.0*	*11*	*0.17*	*1.6*	*1.8*	*0.013*	*0.030*	*0.043*	*12*	*18*	*30*	*0.40*	*0.094*	*0.48*	*2.7*	*0.93*	*3.7*
FLUXES RATIO (F)	4.6	9.2	7.3	8.2	2.6	18	8.7	3.5	4.0	4.0	3.8	9.2	6.3	7.4	11	9.0	2.6	2.3	2.5	1.9	5.0	4.1
EYGOUTIER																						
Fluxes	17	5.5	4.2	9.6	4.6	5.1	9.7	0.80	2.8	3.6	0.054	0.21	0.26	24	30	55						
Specific fluxes	*0.69*	*0.22*	*0.17*	*0.38*	*0.19*	*0.21*	*0.39*	*0.032*	*0.11*	*0.14*	*0.00022*	*0.00084*	*0.011*	*0.97*	*1.2*	*2.2*						
RHONE																						
Fluxes	1600000				220000	120000	340000	6200	91000	98000		1400		340000	420000	760000		27000		71000	94000	160000
Specific fluxes	*16*				*2.2*	*1.2*	*3.5*	*0.063*	*0.92*	*0.99*		*0.014*		*3.5*	*4.2*	*7.7*		*0.28*		*0.72*	*0.95*	*1.7*

fluxes of the Rhone River were comparable to those of the Huveaune and Jarret Rivers, which indicates the same range of contamination for the three corresponding watersheds.

At the outlet, the carbon- and metal-specific fluxes were between 2- and 4-fold higher than the total specific fluxes of the rivers, which implies high carbon and metal inputs by the WWTP. For instance, the Zn daily flux was estimated as 19 kg (40% as dissolved), which means approximately 5.7 t of Zn were discharged each year in this coastal zone during the dry period (considering 300 days a year). This value appeared to be significantly higher than the "background input" estimated at 0.2 t calculated using the upper continental crust Zn content of 52 $\mu g\, g^{-1}$ (Wedepohl, 1995) and the SPM daily discharge (Table 2). The specific fluxes at the outlet were also between 2- and 4-fold higher than specific fluxes of the Rhone river. Moreover, the element flux ratio (*F*) varied from 2 (for dissolved Ni) to 18 (for particulate Cu), which demonstrated the high impact of the WWTP on the river quality and, finally, on the coastal zone.

3.3. Remobilization experiment

Results from the remobilization experiment were compared to the measurements performed on samples from the 28 June 2010 campaign, allowing a direct comparison between real and batch mixing of the effluent with the seawater. DOC results showed conservative behavior with salinity (data not shown). Conversely, dissolved metal concentrations showed significant discrepancies with theoretical mixing lines (Fig. 5); these discrepancies were time-, element- and salinity-dependent.

Regarding Cu, the field campaign results indicated a slight release of dissolved Cu from the SPM in the plume (Fig. 5A). The same behavior was observed during the batch experiment, but with a higher amplitude at low salinity (<10), especially for the shorter mixing time. This indicates a fast release of Cu from SPM during the first minutes after mixing, up to 38% of the outlet particulate Cu content, followed by a progressive re-adsorption until reaching the field level at approximately 1 h after mixing. These results signify that the dissolved Cu measured from field samples at salinities below 10 was presumably under-estimated compared to the actual values because filtration was performed a few hours after sampling.

Ni had an opposite behavior to Cu in both the plume and the batch experiments, with a strong and fast adsorption (up to 55% of the outlet dissolved Ni) onto particles at low salinity, followed by increasing desorption with mixing time (Fig. 5B). This behavior was, however, most pronounced during the first minutes after mixing, the field campaign values being reached at approximately 1 h after mixing. Therefore, in contrast to Cu, dissolved Ni measurements from the field samples at salinities below 10 were presumably over-estimated compared to the actual values.

Regarding Cd, both the field and batch values indicated strong release from particles to the dissolved phase, but in contrast to Cu, the dissolved Cd concentrations continuously increased with the mixing time (Fig. 5C). The maximum, close to 0.15 nM, was observed at the lowest salinity ($S = 1$) after 6 h of mixing and corresponded to desorption of ~100% of the particulate Cd. Finally, as observed for Cu and Ni, the field points were in the same range of concentration as the 1 h-mixing batch points.

Co, Pb and Zn (data not shown) presented non-conservative behaviors in both the plume and the batch experiments, with maximal desorptions at the lowest salinity for Co and Pb and at salinity 10 for Zn. No clear trend was observed with the mixing time. For these three metals, the field points showed similar values to the 15 min-mixing batch points.

Finally, this remobilization experiment showed that release of at least Cu in the salinity gradient is achieved with fast kinetics,

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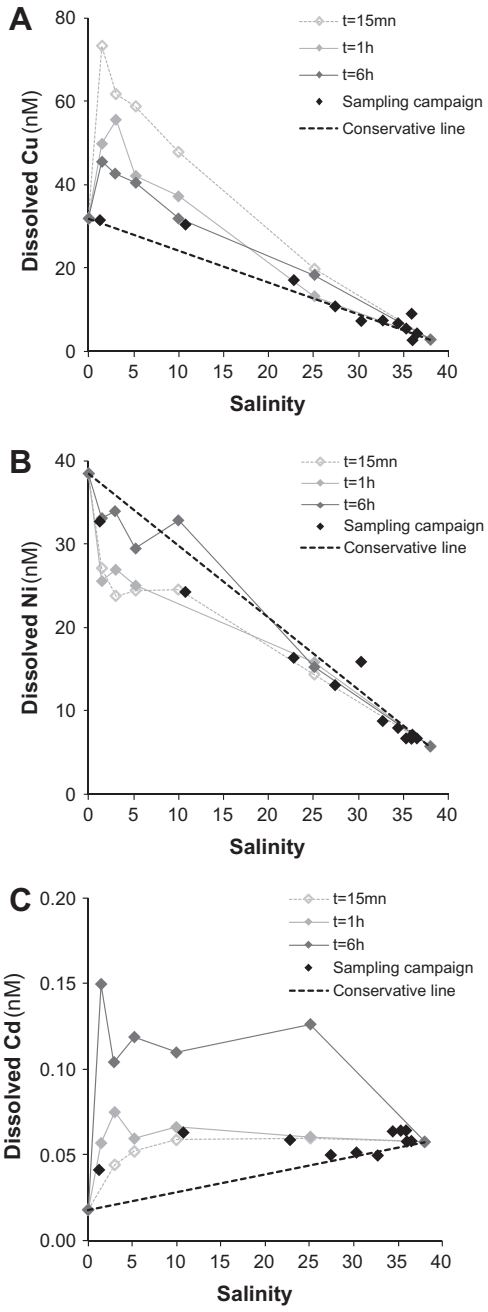


Fig. 5. Dissolved Cu (A), Ni (B) and Cd (C) as a function of salinity after different mixing time during the remobilization experiment and comparison with field level.

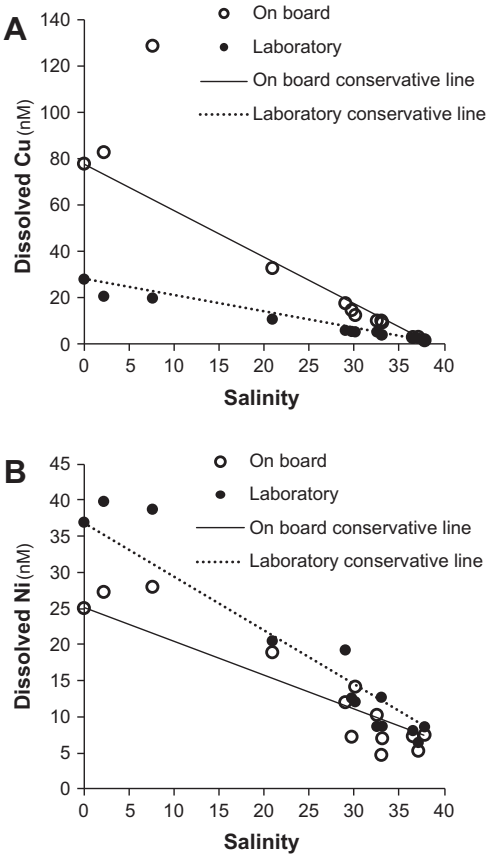


Fig. 6. Comparison between on board (open circles) and laboratory (full circles) filtrations for dissolved Cu (A) and Ni (B) as a function of salinity for the 22/03/2011 sampling.

which raises questions about sample stability between sampling and filtration in the laboratory.

3.4. Comparison between on-board and in-laboratory filtration

Concentrations of dissolved Cu and Ni using the two protocols for filtration (see Sections 2.2 and 2.3) are given in Fig. 6.

Regarding dissolved Cu, the on-board filtration gave much higher values than did the laboratory filtration (Fig. 6A). Moreover, while the laboratory filtration suggested a conservative trend, the on-board filtration revealed (1) a 2.6-fold higher dissolved Cu concentration at the outlet and (2) a significant additional Cu desorption from the SPM at low salinities, as was observed during the remobilization experiment. Similar results were observed for Pb, Zn and Cd. Regarding dissolved Co and Ni, the on-board filtration gave lower values than did the laboratory filtration (Fig. 6B). Both protocols revealed metal desorption from the SPM at low salinity, followed by re-adsorption at salinities higher than 25. Concerning DOC (data not shown), no significant difference was observed between the on-board and in-laboratory filtrations, which means that the dissolved/particulate organic carbon fractionation was at equilibrium.

These results are consistent with the remobilization experiment and show that, at the outlet, the mixing of the river water with the TWW was not at equilibrium and that fast desorption/adsorption kinetics in the plume necessitates rapid processing of the samples. Moreover, these results suggest that the dissolved fraction of the metal fluxes from the outlet was most likely significantly underestimated, except for Cd.

3.5. Identification of an abnormal event

The 18/04/2012 campaign showed unexpectedly high SPM, DOC, POC and metal concentrations compared with the previous ones. The DOC in the rivers was similar to that observed during the other campaigns (1.3 mg C L^{-1} for the Huveaune and 2.3 mg C L^{-1} for the Jarret), but at the outlet, the DOC was approximately 30 and 55 mg C L^{-1} using laboratory and on-board filtration, respectively (Fig. 7), these values being, respectively, 5- and 9-fold higher than the average value at the outlet (Table 1). The difference between the laboratory and on-board filtration values indicates that the outlet sample was not at equilibrium at the sampling moment. In the salinity gradient and for both filtrations, data points were below the conservative mixing lines,

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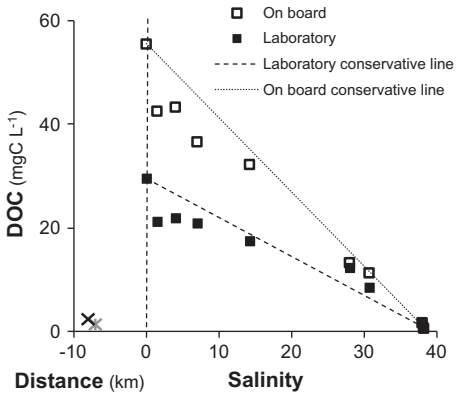


Fig. 7. Comparison between on board (open square) and laboratory (full square) filtrations for DOC as a function of salinity for the 18/04/2012 sampling.

indicating a transfer from the dissolved to the particulate fraction, most likely corresponding to OM agglomeration/flocculation processes.

Dissolved metals at the outlet were in the same range of concentration as was found during the other campaigns after laboratory filtration, but were 2-fold higher than the 22/03/2011 campaign after on-board filtration. The behavior of the dissolved metals in the plume was the same as during other campaigns.

The higher DOC and metal values observed at the outlet during this event was likely due to a malfunction of the WWTP or a bypass of the WWTP. Even if the occurrence of such phenomena is likely infrequent, their local impact on the coastal zone is most likely not negligible.

3.6. One-day outlet monitoring: impact of the TWW on the elements discharged to the coastal zone

Interpretation of results obtained from the outlet effluent day monitoring (see Section 2.5) will allow evaluation of hourly changes in the TWW and quantification of the TWW's overall impact on elements discharged to the coastal zone. The results obtained for dissolved Pb and DOC are plotted in Fig. 8.

The river flows during the sampling day remained roughly constant (~3.5 and 1 $m^3 s^{-1}$ for the Huveaune and Jarret, respectively), therefore the observed flow variation at the outlet can be attributed mostly to TWW input fluctuation. The average daily flow at the outlet was 6.4 $m^3 s^{-1}$; 2 minima (4.9 $m^3 s^{-1}$ at 6:30 am and 5.4 $m^3 s^{-1}$ at 5:30 pm) and 2 maxima (9 $m^3 s^{-1}$ at 10:00 pm and 9.5 $m^3 s^{-1}$ at 11:15 am) were observed. During the night, the flow decreased due to the diminution of wastewater brought to the WWTP. From 6:30 to 11:15 am, the flow increased due to the increase of anthropogenic inputs to the WWTP. It should be noted that the wastewater residence time in the WWTP being 1 h, the TWW flow peaks correspond roughly to wastewater input peaks that occurred 1 h before.

The contribution (in%) of the rivers and the TWW to the outlet water was calculated for the whole sampling day period for each element or compound (X) using the 4 following equations, where Q_{Huv}, Q_{Jar}, Q_{Out} and Q_{WWTP} are the fluxes of the Huveaune River, the Jarret River, at the outlet and from the WWTP, respectively, and $[X]_{Huv}$, $[X]_{Jar}$, $[X]_{Out}$ and $[X]_{WWTP}$ are the corresponding concentrations of the given element or compound.

$$Q^i_{out} = Q^i_{WWTP} + \overline{Q}_{Huv} + \overline{Q}_{Jar} \quad (1)$$

$$Q^i_{out} \times [X]^i_{out} = Q^i_{WWTP} \times [X]^i_{WWTP} + \overline{Q}_{Huv} \times [\overline{X}]_{Huv} + \overline{Q}_{Jar} \times [\overline{X}]_{Jar} \quad (2)$$

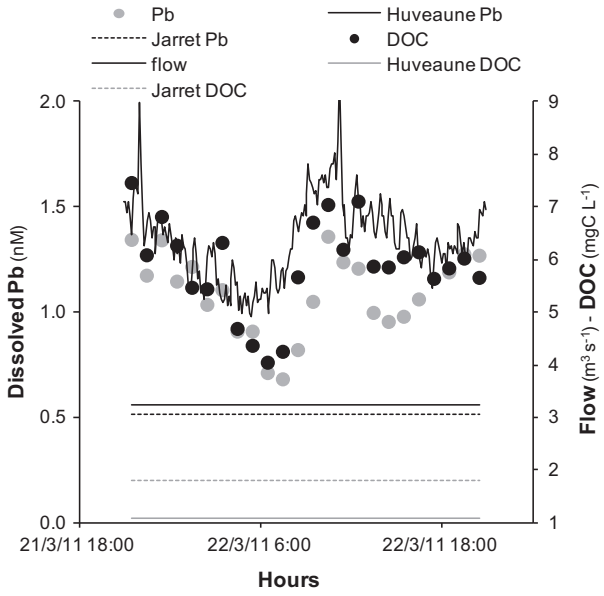


Fig. 8. Variations of dissolved Pb and DOC concentrations and flow as a function of time.

$$\%X_{river} = \left(\frac{\overline{Q}_{Huv} \times [\overline{X}]_{Huv} + \overline{Q}_{Jar} \times [\overline{X}]_{Jar}}{\left(\sum_{24}^{i=1} Q^i_{out} \times [X]^i_{out}\right)/24} \right) \times 100 \quad (3)$$

$$\%X_{WWTP} = \left(\frac{\left(\sum_{24}^{i=1} Q^i_{WWTP} \times [X]^i_{WWTP}/24\right)}{\left(\sum_{24}^{i=1} Q^i_{out} \times [X]^i_{out}/24\right)} \right) \times 100 = 100 - \%X_{river} \quad (4)$$

TWW temporal flow (Q^i_{WWTP}) was calculated using Eq. (1). Resolution of Eq. (2) for each dissolved/particulate element studied (organic/inorganic carbon, major ions and trace elements) enabled the calculation of their temporal concentrations ($[X]^i_{WWTP}$) in the TWW. Eq.3 and Eq.4 enabled evaluation of the respective contributions of the rivers vs. the WWTP to the outlet. The results obtained, ranked by increasing contributions of the rivers, are depicted in Fig. 9.

In the rivers, dissolved Pb was approximately 0.5 nM, whereas at the outlet, it varied from 0.7 to 2 nM (1.13 nM on average) during the day. The variation in dissolved Pb at the outlet followed the variation of the outlet flow, which indicates that the dissolved Pb at the outlet was significantly influenced by the TWW input. The dissolved Pb in the TWW was calculated from the flows and concentrations in the rivers and at the outlet, and it varied from 1.3 to 7.4 nM (3 nM on average) during the sampling day.

In the Huveaune and Jarret Rivers, the DOC was approximately 1 and 1.8 mg C L^{-1}, respectively. At the outlet, it varied from 4 to 7.5 mg C L^{-1} (5.9 mg C L^{-1} on average). Therefore, as was observed for the dissolved Pb, the DOC at the outlet was mainly controlled by the TWW inputs. Calculated DOC in the TWW varied from 15 to 40 mg C L^{-1}, 21 mg C L^{-1} on average.

The contribution of the rivers was higher for dissolved Mg^{2+}, Ca^{2+}, SO_4^{2-}, F^- and DIC; these species are characteristic of karstic systems and are naturally present in river systems (Nicolau et al., 2012). In contrast, the contribution of the WWTP was higher for most of the dissolved and particulate metals, TOC, N species and SPM. For instance, WWTP is responsible for more than 90% of the particulate Cd, Pb and Cu inputs to the coastal zone. The presence

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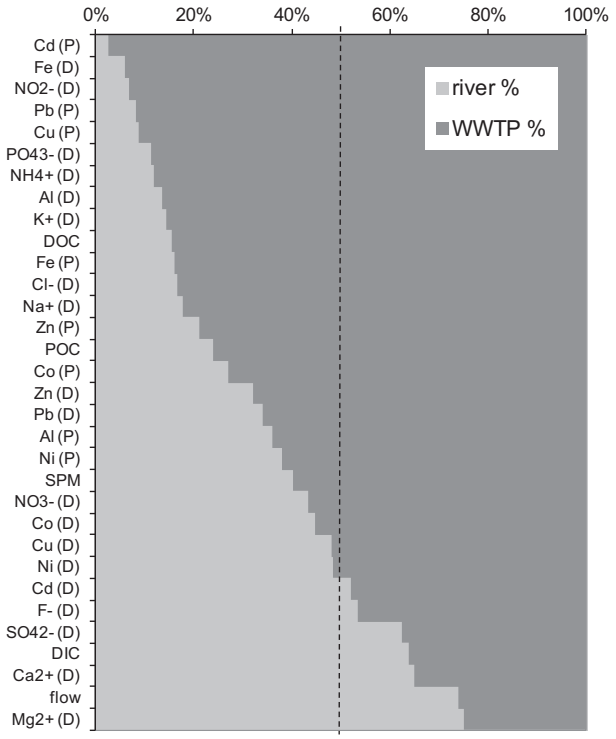


Fig. 9. Contribution of river vs. WWTP at the outlet. The dotted line represents equal contribution of rivers and WWTP; the letter in brackets indicates particulate (P) or dissolved (D) fraction.

of reduced N forms (NO_2^-, NH_4^+) in the outlet water is also a clear signature of bacterial degradation of the WWTP organic matter inputs, and confirms the dissolved O_2 consumption previously observed (see Section 3.1.1). In summary, river signatures at the outlet were hidden by anthropogenic inputs for most elements and compounds, which demonstrates the influence of TWW inputs to the coastal zone despite physical/biological treatments used in the WWTP. Some elements could be used as tracers (ex: K^+, Na^+, Cl^-) to quantify the influence of TWW in outlet waters.

4. Concluding remarks

Most studies dedicated to Mediterranean river inputs to the sea have focused on flood events because storm flows in such areas are responsible for most of the annual inputs to the sea of SPM, organic matter and potentially toxic metal. Herein, the dynamic of contaminants during dry periods (which represent more than 300 days per year in such systems) was investigated, during which slow chronic contamination can occur in the plume of a Mediterranean stratified urban estuary receiving effluents from a large sewage treatment plant (Marseille agglomeration).

Dissolved and total organic carbon and metal concentrations in the rivers considered were comparable to values observed for other small coastal Mediterranean rivers, surpassing the world average river values. Concerning the trace metal dynamics in the plume salinity gradient, Cu, Cd, Co, Pb and Zn are desorbed from the SPM, increasing the potentially bioavailable fraction of these metals. This study has clearly demonstrated that the release of metal ions can occur at low salinity with fast kinetics followed by partial re-adsorption onto SPM; this behavior was especially observed for Cu. Other metals, such as Ni, can undergo a fast adsorption onto SPM followed by slower desorption. Such unusual behaviors make mandatory the practice of filtration immediately after sampling to avoid under- or over-estimation of dissolved metal concentrations.

The second important point of this study is that, at the outlet, the river signatures were hidden by the WWTP anthropogenic input for most elements or compounds. The anthropogenic input was higher than 90% of the total input to the sea for particulate Cd, Pb and Cu and higher than 65% for particulate Zn, Co and dissolved Zn and Pb. The daily variation of these inputs followed the fluctuations of the TWW issued from WWTP. Although most likely not frequent, the observed abnormal event linked to a WWTP malfunction or by-pass can temporally strongly enhance the impact of an urbanized area on the coastal zone. Similar phenomena all around the Mediterranean are more than probable, especially in countries without wastewater treatment plants. This underlines the need for such treatment facilities for an improvement of local coastal water quality, but most likely also at a more global scale. Such chronic fluxes of pollutants require better study in comparison to other main sources (large rivers, aerosols, etc.). Considering the high anthropogenic organic matter and trace element contents of the output to the sea, a detailed study of their chemical speciations, which are known to be strongly influenced by dissolved organic ligands, must be performed to evaluate their bioavailability for marine biota.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.marpolbul.2013.01.023.

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