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Behaviour and fate of urban particles in coastal waters: Settling rate, size distribution and metals contamination characterization

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Abstract:

The evaluation of contaminant net fluxes from the coast to the open sea requires the study of terrigeneous particles behaviour and fate. We studied the particles issued from two small coastal rivers whose waters are mixed with treated wastewater (TWW) coming from the Marseille wastewater treatment plant (WWTP) just before discharge to the Mediterranean Sea. An experimental device was developed and used to investigate particles settling rates, size distribution and metallic contamination when mixing with seawater. The particles were sampled in flood deposits of rivers and outlets during rainy periods and in the outlet water during dry periods. The flood deposits were mainly composed of 50–200 μm-sized particles, higher metals content being observed in the finest fractions. Dry period particles showed the stronger influence of wastewater inputs. Al, Ca, Cs, Li, Rb, Ti, and Tl were mainly of terrigeneous origin, whereas Ag, Ba, Cd, Cr, Cu, Hg, Mg, Mo, Ni, Pb, POC, Sb, Sn and Zn were of anthropogenic origin, issued from non-treated sewage, TWW or industrial waste. In seafloor sediments, all metals exhibited a continuous increase of concentration from the outlet to, at least, 800 m offshore. Implementation of settling particles characteristics in a 3D hydrodynamic and sediment transport model reproduced well the observed deposition of polluted particles in the coastal zone and indicated a non-negligible offshore export of the finest particles and their accompanying pollutants.

Highlights:

► Chemical and physical characterization of river particles issued from a large urban agglomeration. ► Origin of metals in urban/river particles. ► Modelling of the behaviour and fate of urban particles in coastal zone. ► Significant metal contamination of sediments in coastal zone. ► Desorption processes control metal dissolved/particulate fractionation.

Keywords: particles contamination ; urban rivers ; coastal zone ; TWW ; hydro sedimentation modelling

1. Introduction

Trace metals are natural constituents of crustal materials. Some of them are essential to the biota, but all have the potential to be biologically toxic if their concentration exceeds certain levels. A wide range of trace metals may be generated throughout human activities, then discharged in rivers by soil erosion processes (depending on the nature of the watershed), throughout wastewaters (treated or not), throughout industrial activities (Azimi et al., 2005) and throughout agriculture (Waeles et al., 2007). Trace metals may be brought by rivers to the coastal area by continuous, diffuse inputs or during flood events, then can accumulate in

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marine sediments. Their input in the water column and in sediments may be a threat to the quality of the coastal area (Rocha et al., 2011; Weber et al., 2009). Gobeil et al. (2005) studying the Montreal (Canada) WWTP discharge in a large river, the St. Lawrence, have shown that the contribution of the treated wastewater (TWW) was not significant compared to the river metal budget, except for Ag. On the contrary, Oursel et al. (2013) have studied the Marseille (France) WWTP discharge in a small river and showed that, during baseflow periods, the river signature was hidden by the TWW input for most elements or compounds. This difference is due to the larger proportion of TWW discharge in the river stream in the case of Marseille with regard to Montreal (50% versus 1%, respectively). During flood events, significant amounts of trace metals are rapidly brought to surface aquatic system through runoff processes (Di Leonardo et al., 2009; Elbaz-Poulichet et al., 2001; Nicolau et al., 2012; Rocha et al., 2011; Weber et al., 2009). In order to evaluate the impact of such inputs to coastal zones, previous studies have quantified contaminant fluxes at river mouth (Michel et al., 2000; Nicolau et al., 2012; Ollivier et al., 2011; Statham et al., 1999), whereas others have focused on the contaminants fate in the mixing zone, identifying sorption-desorption processes or changes in chemical speciation (Dassenakis et al., 1997; Elbaz-Poulichet et al., 1996; Millward and Liu, 2003; Waeles et al., 2005; Zwolsman et al., 1997). It is therefore necessary to study the fate of particulate pollutants in the coastal zone (Millward et al., 1999), such studies requiring specific experiments.

The settling velocity of river particles in and beneath the river plume is difficult to measure because the fine material can flocculate rapidly in seawater. Indeed, during freshwater/seawater mixing the suspended matter are subjected to important changes in physicochemical properties of the water and their behaviour will depend on their nature, concentration and organic matter content (Fugate and Chant, 2006; Thill et al., 2001). At local scale, the extension and direction of the dilution plume defines where particles settle or are exported depending on the river flow, tide, wind, currents and the morphology of the study area (Alliot et al., 2003; Cugier and Le Hir, 2002; Naudin et al., 1997; Pairaud et al., 2011). Once in the water column, metals can undergo quick desorption or reversely adsorption onto particles. Particles settle directly or after flocculation and accumulate in sediments, which therefore act as a metal sink: the quantification of metal content in surface sediments is consequently a first step to assess the degree of pollution of a marine environment (Bay et al., 2003; Tessier et al., 2011). The grain size is one of the main factors that govern metals contamination in the particulate fraction, as the finest particles contain minerals (e.g. clays, oxides, sulfides, …) and particulate organic matter having strong affinity with metals. There

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is generally a marked inverse correlation between grain size and metal content in the sediment (Forstner and Wittmann., 1979; Forstner and Patchineelum., 1980). It is therefore critical to quantify the particles size distribution and to assess their settling velocity in the mixing zone. In the last four decades, numerous techniques have been developed for in situ measurement of particles size and settling velocities (Eisma et al., 1996). The Owen tube was for instance used since1971 to measure the settling velocity distribution of the suspended particulate matter (SPM). It consists in a tube sampler opened at both ends, which is lowered horizontally into the water, closed by trigger at the required depth then rotated vertically (Dyer et al., 1996). The Quisset tube, adapted from the Owen tube, has been developed to determine the settling velocity of particles in the Elbe estuary (Jones and Jago, 1996).These techniques, however, are poorly suited to a shallow plume that is not channelled through an estuary and can move quickly after wind and current changes and their use was, to our knowledge, not associated to the determination of chemical properties in relation with particle size.

Moreover, only few studies focused on the Mediterranean area despite its high population density and its climate specificities. Marseille is an example of large Mediterranean city, where the city WWTP effluents are mixed with small rivers before being rapidly discharged at sea, without passing through an estuary (Oursel et al., 2013).

In this context, through the adaptation of an instrumental laboratory device to separate particles accordingly to their settling velocity in seawater followed by the analysis of the elemental (minor, major and trace) content of each particle size fraction, the purposes of this study were (1) to investigate the physical and chemical characteristics of river/urban particles discharged to the coastal environment, (2) to relate the obtained results with the surface sediment quality in the coastal area and finally (3) to implement a 3D hydrodynamic (Pairaud et al., 2011) and sediment transport model (Verney et al., 2013) within the area to investigate the role of heavy rainfall events on the fate of contaminated particles.

2 Material and methods

2.1 Study site

The Huveaune River extends over 48.4 km long and runs through a watershed with an area of 523 km² which consists in karstic formation (60%) and detrital sediments. Land-use in the downstream part of the watershed is urban and industrial. The Jarret River extends over 21 km with a 102 km² watershed mainly urban and industrial.

In dry period, these two rivers merge in Marseille; the resulting water is mixed with the Marseille City WWTPs effluent, and then channelled by the Outlet 2 (Out2) to the sea at the Calanque of Cortiou (Fig. 1 and Fig. SI-4.1). This treatment plant, one of the largest in Europe (1.7 10^6 inhabitant eq.), uses both physical and biological treatment processes. During dry periods (~ 300 days), around 100 and 80 Mm^3 y^{-1} of TWW and river water, respectively, are discharged to the sea (Le Masson, 1997). Oursel et al. (2013) have evaluated the annual global SPM discharge to be around 3900 t, whose 840 t coming from rivers, highlighting the main contribution of the TWW in such conditions. During flood events, the Huveaune and Jarret river flows can overpass 60 and 16 m^3 s^{-1}, respectively. As the maximal outlet discharge capacity cannot overpass 30 m^3 s^{-1}, a significant part of rivers waters is channelled through the Huveaune former bed to the Prado's beach (Fig.1) during extreme events, i.e. when rainfall overpass ~40 mm h^{-1}. During rainy periods, around 4.1 and 9 Mm^3 y^{-1} of TWW and rivers waters, respectively, are discharged to the sea. Le Masson (1997) has evaluated the corresponding SPM discharge to 6500 t, 94% coming from rivers. On average, during flood events, 90% of Huveaune and Jarret waters (and SPM) are channelled through the outlet and only 10% are deviated through the Huveaune former bed. Additionally, discharge of untreated wastewater brought to the coastal zone between 456 and 1450 t y^{-1} of SPM, during the period 2001-2007 (Jany et al., 2012).

Statistics on the 01/01/2009 to 31/08/2011 studied period (Météo-France) showed an average of 609 mm y^{-1} of rain distributed as follow: 304, 41, 12, 5and 3 d y^{-1} where rain was <1, 1-10, 10-20, 20-40 and >40 mm d^{-1}, respectively, which are typical values for a Mediterranean coastal area.

2.2 Sampling and sample conditioning

Two types of samples were considered: (1) flood deposits sampled after a rain with the aim of characterizing most of the particles discharged to the sea during flood events and (2) suspended matter collected using a sediment sampler placed in the river flow (Phillips et al., 2000) in order to characterize the particles brought to the sea during base-flow periods.

2.2.1 Rainy periods sampling

In order to characterise particle inputs to the Calanque of Cortiou, flood deposits were sampled after a rainy event on the 11/05/2009 at Outlet 1 (FDOut1) and on the 14/04/2011 at Outlet 2 (FDOut2). Outlet 1 is only active when the WWTP is by-passed (Fig. SI-4.1) due to

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an overflow of sewage/rain waters mixture due to the fact that the old Marseille centre has a non-separated sewage network which collects both wastewaters and runoff. The FDOut1 sample is thus likely to contain non-treated sewage particles, as also occurs in many southern Mediterranean coastal cities. In order to characterise particle inputs upstream the WWTP, flood deposits were sampled on 14/04/2011 after a rainy event in the Huveaune (FDHuv) and Jarret rivers (FDJar). The flood deposits were sampled manually, frozen at -18°C in the laboratory, subsequently freeze-dried and 2-mm sieved.

2.2.2 Base-flow period sampling

Suspended particles during dry period corresponding to the river baseflow mixed with TWW were sampled in Outlet 2 (SPOut2) using a sediment sampler built by IFREMER according to Phillips et al. (2000). This 1 m long inox tube was installed in Outlet 2. Phillips et al. (2000) have shown that such device collects ~71 % of the total river particles, taking into account that the faster the river flow, the more fine particles pass throughout the system. After 1 month, the sampler water and SPM were collected in 10 L HDPE (high density polyethylene) bottles. Bottles were placed in the fridge at +4°C during one day for particles sedimentation. Then supernatant water was siphoned using a pump and wet particles were stored in 120 mL HDPE bottles, frozen at -18°C and subsequently freeze-dried. The maximal diameter of collected particles was 4 mm, corresponding to the diameter of the inlet hole.

In this study, the SPOut2 sample used corresponds to the sampling period from 11/04/2011 to 11/05/2011. During this month, only 30 mm of cumulative rainfall (Météo-France) were brought to rivers, which represented around 2% and 12% of the month total water and SPM discharge, respectively, accordingly to the recorded outlet flow and average SPM concentration during dry and rainy periods (data not shown). In such conditions, the SPOut2 sample can be considered as mainly representative of dry period particle inputs.

2.2.3 Sediment sampling

Twelve surface sediments were sampled along a transect from the coast to the open sea at the Calanque of Cortiou (Fig.1) by divers. Sampled sediments were treated using the same protocol developed previously for flood deposits.

2.3 Settling rates experiment

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The experimental device was composed by a vertical Plexiglas tube (1 m long and 10 cm diameter), open on the top and equipped with a valve on the bottom to collect water samples. The tube was filled with 7 L of "clean" seawater sampled at 2 km offshore and 4 m depth (Oursel et al., 2013) and equilibrated during one day to obtain a homogeneous temperature of the water column (20°C). During flood conditions, SPM can exceed 1 g L^{-1} in tributaries (Jany et al., 2012). Accordingly, the experiments were performed using 7 g of dried particles (flood deposit or dry period particles) pre-wetted with few mL of milliQ water (Millipore 18.2 MΩ). Such mass also allowed to collect enough material to perform chemical analysis. After one day of wetting, particles were injected on the top of the system and the bottom 500 mL were successively sampled at 14 times (in log scale) ranging from 30 s to 5 days, so covering a large domain of settling rates and particles diameters (Dyer et al., 1996). The 14 samples were immediately filtered (see part 2.4) and particles which had remained on the walls of the tube were collected in a 15th class corresponding to the fraction which cannot settle in the defined conditions.

Accordingly, settling velocity and particle diameter were calculated for the 14 classes (supplementary information SI-1).

2.4 Filtration protocols and filters treatment

A part of the collecting samples was filtered through 25 mm glass filters (Whatman GFF, 0.7 µm) for particulate organic carbon (POC) analysis. The filter treatment protocol for POC analysis is described in Oursel et al. (2013).

The remaining water was then filtered through 47 mm cellulose nitrate filters (Sartorius, 0.45 µm) for particulate elements analysis. Half of each filter was used to quantify major/minor/trace elements after microwave digestion (AntonPaar Multiwave 3000) in aqua regia (trace metal grade acids, Fisher Scientific) accordingly to a procedure previously validated (Tessier et al., 2011). The second half of the filter was used to quantify particulate mercury.

2.5 Mineralogical characterization

Mineralogical identification of dried sieved (2 mm) samples was done by X-ray diffraction (XRD) spectroscopy with Cu Kα radiation (Phillips, PW1200) on powder samples

finely crushed in a tungsten carbide mill. Because of the low quantity of particles collected in the tube during dry period, the XRD analyse was not realized on SPOut2 sample.

2.6 Batch experiments

As dissolved metals were not analysed from the settling rate experiment (due to the non-homogeneity of the water column inside the settling tube), an additional batch experiments were undertaken to study metal release from particles in seawater. Flood deposits and baseflow period particles samples were mixed to seawater in FEP bottles (SPM = 1 g L^{-1}). FEP bottles were placed on head-over-head agitation system (Reax 20, Heidolph) and aliquots were sampled at 15 min, 1, 6, 24 h and 5 days of mixing time using pre-cleaned syringe, then filtered through pre-cleaned 0.22 µm on-line filters (Sartorius). A first aliquot of filtrate (dissolved fraction) was stored in 60mL FEP bottles, acidified with 60 µL HNO_3 (supra pure 65%, Merck) and digested 2 h under UV-irradiation (Metrohm 705, 500 W) for further analysis of total dissolved metal concentrations (Louis et al., 2009). A second aliquot of filtrate was stored in 24 mL glass tube (Wheaton, equipped with Teflon/silicone septum) pre-calcinated 4h at 450°C, azidified with 25 µL 1 M NaN_3 (NaN_3> 99%, Aldrich) and kept at 4°C for further analysis of dissolved organic carbon (DOC).

2.7 Sample chemical analysis

2.7.1 Particulate phase characterization

2.7.1.1Particulate carbon forms

Total carbon (TC) contents were quantified from flood deposits, suspended particles and sediments using a TOC-V_{CSH} analyzer (Shimadzu), coupled with a SSM-5000A module. The total and organic carbon contents were 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 mgC. For POC analyse, GFF filters were dried to constant weight at 60 °C, and then exposed to HCl fumes for 4 h to remove all the inorganic carbon (Lorrain et al., 2003).

Particulate inorganic carbon (PIC) contents were quantified from flood deposits, suspended particles and sediments using the same analytical equipment after addition of H_3PO_4 (Analytical Reagent grade 85%, Fisher Scientific) at 200°C followed by CO_2 IR

detection, calibrated using $NaHCO_3/Na_2CO_3$ (Shimadzu) with an accuracy of 0.1 mgC. Then, POC content was calculated by difference between total and inorganic carbon contents.

2.7.1.2 Major elements

Major elements (Ca, K, Mg and Na) were analysed by a flame atomic absorption spectroscopy (VARIAN SpectrAA 800). The instrument was calibrated using standard solutions and flame was supplied with a mixing of acetylene (99.99%) and air. Major elements analysis was validated using certified reference material (MISSIPPI-03, Canada); obtained values remained within the certified limits.

2.7.1.3 Minor and trace elements analysis

Particulate elements (Ag, Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, Ti, Tl, U, V and Zn) were quantified from the acid-digested filters by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP-MS Element 2, Thermo Finnigan). The instrument was calibrated using standard solutions and an In was added as internal standard in each sample (Lenoble et al., 2013). Quality control of HR ICP-MS measurements was checked by the determination of elements concentration on Certified Reference Material (SLRS-4 river water, LGC6187 river sediment, National Research Council Canada). All results presented good agreement with the certified data. Results obtained for LGC6187 (triplicate) are provided in Table SI-2, showing that the values obtained for most of the studied elements fall in 90-110 % of yield an/or in the required range of certified contents at the exception of V having slightly higher value.

2.7.1.4 Particulate mercury

Mercury analysis was carried out using an automatic AMA-254 (ALTEC) analyzer. Filters were divided in few small pieces placed in a nickel nacelle and introduced into the system. The principle of the method is described in Heimbürger et al. (2012) and the detection limit of the method was 0.007 µg g^{-1}. To validate the method, mercury in a certified reference material (CRM) MESS-3 was daily quantified and results were in the range of the certified value (0.091 ± 0.009 µg g^{-1}).

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2.7.2 Dissolved phase characterization

2.7.2.1 Dissolved Organic Carbon (DOC)

DOC concentrations were determined using the same TOC-V$_{CSH}$ analyzer, calibrated using potassium hydrogenophtalate (Shimadzu) standard solutions, with an accuracy of 0.02 mgC L^{-1} (Louis et al., 2009). DOC analysis was validated using certified reference material (MISSIPPI-03, Canada); obtained values remained within the certified limits.

2.7.2.2 Dissolved trace metals

Total dissolved metal concentrations were determined by Differential Pulse Anodic Stripping Voltammetry (Cd, Cu, Pb and Zn) and Differential Pulse Adsorptive Cathodic Stripping Voltammetry (Co and Ni) using fully automated analytical procedures previously described (Louis et al., 2009; Omanović et al., 2006; Oursel et al., 2013).

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

2.8 Modeling of the fate of particulate pollutant released at Cortiou during a flood event

A 3D hydrodynamic (Pairaud et al., 2011) and sediment transport model (Verney et al., 2013) was implemented within the area to investigate the role of heavy rainfall events on the fate of contaminated particles, focusing on particulate Pb dynamics. Model functioning and input parameters are described in supplementary information SI-3. Briefly, the hydrodynamic part is based on the RHOMA configuration of the MARS3D ocean model developed by Ifremer (Pairaud et al., 2011) implemented from Rhone River to Cap Sicié (Fig. SI-3.1) with a 200m horizontal resolution orthogonal grid and 30 vertical sigma levels. The sedimentary transport part was implemented from the SiAM3D model (Le Hir et al., 2011), with the sediment discretized in thin layers which are created or deleted based on net erosion/sedimentation at each time step. The model takes into account the various water sources from the city of Marseille: small urban rivers, storm water overflows and WWTP (Fig. 1 and SI-3.1). The flow from each input is defined using measured data provided by local authorities. Associated SPM concentrations were evaluated, depending on weather conditions, according to field measurements (Jany et al., 2012). Characteristics (proportion, settling velocity, pollutant content: Table SI-3.1) of 4 classes of particles were implemented

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in the model based on the results obtained in the present study (see part 3.3.1). Modelling of particulate pollutant inputs and fate to the coastal zone was performed from the 12th of September to the 28th of October 2008, a period which included a strong rain event the8[th] of October 2008 with a cumulated rainfall of 41 mm (at "MARSEILLE-OBS" Météo-France rain gauge) inducing an outflow increase from 3 to 45 m^3 s^{-1} at Cortiou (Fig. SI-3.2). The particulate Pb budget in the area was assessed for the Cortiou box (43.18N 5.35E / 43.22N 5.45E).

3 Results and discussion

3.1 Mineralogical and elemental characteristics of flood deposits and baseflow suspended particles

The mineral proportions determined by XRD in the 4 flood deposits varied from 6 to 11% for clay minerals, from 15 to 31% for quartz and from 50 to 69% for carbonates (calcite and dolomite). The calcareous pattern of these flood deposits are due to the nature of the river watersheds and so mainly composed of particles carried in rivers by rainwater after soil weathering.

Elemental composition of the samples used for the settling rate experiment are summarised in Table 1. Elemental compositions are here after compared (1) to the particles discharged by the Rhône River during flood events (flow>1500 m^3 s^{-1}), considering that the Rhône River provides the most important discharge of particulate matter to the Mediterranean Sea (Cathalot et al., 2013; Ollivier et al., 2011), (2) to the Montreal effluents, as an example of large city effluent with high WWTP contribution (Gobeil et al., 2005), (3) to values obtained during baseflow periods at the Outlet2 (Oursel et al., 2013) and (4) to the upper continental crust (UCC) average values (Wedepohl, 1995).

Compositions of FDHuv, FDJar and FDOut2 samples were quite comparable, within a factor ranging from 0.5 to 2, for most of the elements excepting Pb that was more than 10-fold higher in the FDJar sample. The similar values between the two rivers reflect the similarities between their catchment areas. The similar values found between FDOut2 and rivers samples are likely due to the predominance at Outlet 2 of the river particles accordingly to higher river flow compared to WWTP effluent flow during flood events (cf. part 2.1.).

When compared to rivers values, the values obtained for the FDOut1 sample indicated a contamination with regard to most trace metals and metalloids. Bi, Hg, Pb and Zn values were

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for instance 16- to 30-fold higher when crustal elements (e.g. Al, Li, Rb, Ti) fell in the same range of value than on rivers. This contamination can be related to bypassing of non-treated wastewater in Outlet 1 during flood events (Fig. SI-4.1), permitting deposit of contaminant-rich particles that would have normally been removed during the WWTP process by particles sedimentation (Buzier et al., 2011).

The POC content in the Huveaune and Jarret rivers (1.5-2.5%) was in the same range of concentrations as in the Rhone River (Cathalot et al., 2013), but low when compared to FDOut2, FDOut1 and SPOut2 samples (2-, 7.4- and 7.9-fold less respectively), signature of high organic matter inputs by TWW, noticeable even in flood conditions.

Considering other elements, most values obtained for the Huveaune and Jarret rivers were slightly lower (in average 0.6 times lower) than in the Rhône River. The Al content, however, was around 6-fold lower than in the Rhône particles, indicating a lower proportion of the fine fraction that impacts most of trace metal contents (Roussiez et al., 2005). To better compare contamination status between rivers, it is therefore convenient to perform a normalization to Al content or other elements such as Fe, Ti, Th… (Larrose et al., 2010; Reimann and de Caritat, 2005; Vystavna et al., 2012). Here, Al-normalized values (data not shown) showed that Ba, Bi, Co, Cs, Fe, K, Mn, Na, Rb, Ti and V contents in the FDHuv, FDJar and FDOut2 samples presented levels comparable to the Rhône River particles and to the UCC values, indicating a likely crustal origin. The Sb Al-normalized value was 2-foldhigher than the Rhône River particles value and 12-fold higher than the UCC value, indicating a significant contamination of the Huveaune and Jarret rivers. The Ca, Cd, Cr, Cu, Mg, Ni, Pb, Sr and Zn Al-normalized values were 4- to 10-fold higher than the Rhône River particles values. These high values reflect the calcareous signature of Huveaune and Jarret watersheds for Ca, Mg and Sr and a significant anthropogenic contamination for the other considered elements.

Regarding the FDOut1 samples, Ba, Co, Cr, Fe, Hg, Sb values were from 4- to 15-fold higher and Bi, Cd, Pb, Zn values respectively 47-, 24-, 240-, 126-fold higher than for the Rhône River particles, confirming the high contamination status of these samples likely due to a WWTP bypass.

Suspended particles collected during baseflow periods at Outlet 2 (SPOut2) were slightly less contaminated, but remaining in the range of variability of the baseflow periods values measured at Outlet 2 by Oursel et al. (2013). Consequently, elements content values of SPOut2 were close to those of FDOut2 excepting the POC and Cu contents which were respectively 4- and 3-fold higher. For most of elements, the SPOut2 values were in the same range of concentration than those observed in the Montreal WWTP effluent particles (Table

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1). Ag was considered as typical of urban input by Gobeil et al. (2005), recording 56 µg g^{-1} in the Montreal effluent. In the present study, Ag ranged from 0.62 to 32 µg g^{-1} at Outlet 2, where the WWTP signature is roughly divided by 2 during baseflow due to river inputs (Oursel et al.,2013), which confirms the significant input of this element by urban TWW.

Finally, for each sample the sum of Ca, Mg and PIC contents was consistently close to the calcite and dolomite content obtained by XRD analysis.

3.2 Data statistical analysis

A statistical analysis (PCA, Principal Component Analysis) was applied to 116 samples issued from the present study (collected particles, settling experiment, marine sediments) and from Oursel et al. (2013) (baseflow suspended particles from Outlet 2). The two first factorial axes explained 50.60% of the total variance (PC1: 36.95%; PC2: 13.65%) (Fig.SI-4.2). Additionally, as Al can be considered as a reference for terrigeneous particles, elements contents were plotted as a function of Al content (Fig. 2). These visualizations allowed identification of 4 groups of elements having similar behaviours.

The 1st group was composed of Al and Cs, Li, Rb, Sr, Ti, elements typically terrigeneous having a good correlation with Al (R^2>0.41); Rb is given in Fig. 2A as an example. Suspended particles from baseflow periods had higher content for these elements than marine sediments; flood deposits were in between. Such patterns can be explained by a higher proportion of Al-rich particles in baseflow samples than in flood samples, while low values in marine sediments reflect dilution by calcitic autochthonous particles, as currently observed in coastal areas (Tessier et al., 2011). Cs, Ti and Rb were in the same order of concentrations than in UCC (Table 1), higher values for Li and Sr being related to the calcareous watersheds and soils (De Vos et al., 2006).

The 2nd group was composed of As, Ba, Fe, Mo, Pb, Sb, Zn, all uncorrelated with Al (R^2<0.06). Among these elements, Ba and Fe, Pb and Zn presented a good correlation one with each other (R^2>0.69). This group is likely to reflect the affinity of elements for Fe-oxides, regardless of terrigeneous origin because Fe (mainly as $FeCl_3$) is currently used as flocculent in the WWTP process (Buzier et al., 2006; Buzier et al., 2011; Poon and Chu, 1999). As an example, points corresponding to low Al content associated to high Fe content in Fig. 2B correspond to FDOut1 and SPOut2 samples. Regarding As, Cancès et al. (2005) and Lenoble et al. (2012) shown that As^V (the main fraction in oxic conditions) is dominantly

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sorbed/coprecipitated on/with Fe oxides, a minor fraction of As^V remaining associated with clay minerals and/or Al hydroxides.

The 3rd group, composed of Ag, Be, Bi, Cr, Cu, Co, Cr, Hg, Mn, Ni, Sn and V represents elements or compounds having a weak or moderate correlation with Al ($0.07 < R^2 < 0.39$). Among these elements, Cr, Co and Ni presented high correlations one with each other ($R^2 > 0.87$), possible signature of common behaviour or origin, as cements manufacturing, (Frias and Sanchez de Rojas, 2002).

These two last groups can correspond to both contamination of river watershed and contamination by TWW and can be related to differential affinity with carrying phases.

A 4th group was composed of Ca and PIC which had no correlation with Al but a good correlation one to each other. These elements signed the calcareous river watersheds or the marine calcitic particles (Fig.2C).

Cd, located close to the center of the correlation circle, exhibited no significant correlation ($R^2 < 0.04$) with any other elements.

3.3 Settling rates experiments

3.3.1 Settling rates and element distribution between particles

The distribution of particles as a function of the settling rate is given in Fig.3. Additionally an experiment was done using FDOut2 sample sieved at 63 µm and the same distribution of particles was obtained as a function of the settling rate (data not shown). For the 5 samples, 75 to 85% of the sample weight was comprised of particles whose settling rate was higher than 4 mm s^{-1}, corresponding to particles which had an estimated diameter higher than 70 µm, and 0.2 to 7.6% of the sample weight was comprised of particles with settling rate was lower than 4 µm s^{-1}, corresponding to particles which had an estimated diameter below 2.2 µm. Part of the large particles can result from flocculation processes in seawater (Manning et al., 2010).

The element contents in particles as a function of the settling rate showed four types of pattern. The Ca content was highest in high settling rate particles and decreased with decreasing settling rate (data not shown), Ca was thus mainly contained in large calcitic particles issued from erosion within the calcareous catchment area. The distribution of elements identified as typically terrigeneous (Al, Cs, Li, Rb, Sr, Ti, Tl) exhibited sigmoidal curves; Al is given as an example in Fig. 4A. Most metals (Ag, As, Bi, Cd, Cr, Cu, Fe, Hg, Mo, Ni, Pb, V, Zn) showed increasing contents with decreasing settling rates; Cu is given as

an example in Fig. 4B. The fine fraction, mainly composed of clay minerals and oxi-hydroxides, is effectively known to concentrate metals by adsorption on high specific surface particles (Villaescusa-Celaya et al., 2000). Ba, Be, Co, K, Mg, Mn, Sb, Sn and U content distributions were roughly constant over the whole range of settling rates; Sb is given as an example in Fig. 4C. The POC distribution increased from large to fine particles for the SPOut2 sample but exhibited bell-shaped curve for other samples.

The element distribution asa function of the settling rate at 20°C was calculated for each element by multiplying the element content by the SPM concentration for each fraction; Cu is given as an example in Fig.SI-4.3. For a better understanding of the results, element distributions were reduced to between 4 size classes of particles based on the Udden-Wentworth sediment grain size scale, according to Leeder (1982) and Bainbridge et al. (2012): (1) sand particles (S), whose settling rate and diameter were higher than 3.3×10^{-1} cm s^{-1} and 63 µm, respectively; (2) coarse silt particles (CS),whose settling rate were between 2.0×10^{-2} and 3.3×10^{-1} cm s^{-1} and diameter between 15.6 and 63 µm, respectively; (3) fine silt particles (FS), whose settling rate were between 1.3×10^{-3} and 2.0×10^{-2} cm s^{-1} and diameter between 3.9 and 15.6 µm, respectively; (4) fine fraction particles (FF), whose settling rate and diameter were lower than 1.3×10^{-3} cm s^{-1} and 3.9 µm, respectively. Settling rate, SPM proportion and elements content of each fraction for the 5 studied samples are summarized in Table SI-5.1. The element distributions between each fraction are given in Fig.5 and Fig. SI-4.4, and classed by increasing contamination of the fine fraction.

FDJar, FDHuv, FDOut2 and SPOut2 samples exhibited similar distributions; FDOut2 is given as an example in Fig. 5A and for FDJar, FDHuv and SPOut2 samples graphs are plotted in Fig. SI-4.4A, B and C, respectively. Although the fine fraction was the most concentrated for most elements – and for all metals – the contribution of S and CS to the total contamination was the highest for all analysed elements because of the high contribution of the sand fraction to the sample weight. For all elements, more than 80% of the total load was contained in S plus CS. Contrarily, Bainbridge et al. (2012) observed in an Australian river flood plume that more than 70% of the total load was contained in FF plus FS. Here the relatively high metal load in coarse fractions could be due to flocculation of fine particles in seawater. The Pb, Cr, Mo, Bi, Zn and Ni FF contributions were higher in FDHuv than in FDJar although lower total contents in FDHuv than in FDJar (Table 1), which indicates different sources of contamination for the two rivers.

The FDOut1 experiment exhibited a different distribution, with all elements a higher proportion of FF (Fig. 5B). 7.4% of the total SPM had not yet sedimented after 5 days, most

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probably because of a higher proportion of organic particles issued from sewage bypassing. Such particles are likely to remain in the surface layer of the plume and to be exported to the open sea with their contaminants load (more than 60% of the total Pb for instance). Under normal conditions, such particles would have probably been partly eliminated in the WWTP by flocculation after $FeCl_3$ addition (Buzier et al., 2006).

3.3.2 Settling rates and sedimentation at sea

The fate of particles at sea was addressed by characterizing the marine surface sediments in front of Cortiou. Distribution of element contents in these sediments as a function of the distance from the outlet presented three main patterns (Fig. 6). (1) Ca and PIC contents decreased from the outlet to 400 m offshore then increased from 400 to 800 m offshore. This confirmed that the large calcitic particles were sedimented within 400 m from the outlet. The Ca content increase after 400 m is likely due to marine autochthonous calcite. (2) Mg and Mn exhibited constant values from 0 to 800 m, which indicates a negligible or similar input from the suspended matter brought at the outlet and the marine organisms. (3) All other elements exhibited a significant increase from the outlet to at least 800 m offshore; Pb is plotted in Fig. 6 as an example. Such pattern is related to the fact that these elements are mainly contained in finer fractions that settle slowly with regard to the plume and seawater 3-D velocity field.

Additionally, trace elements concentrations in seafloor sediments were compared to the French action levels (N1 and N2) concerning dredged marine and estuarine sediment (JORF No. 184, 10-08-2000). Below the N1 level, the potential environmental impact of dredged sediment deposited onshore is considered neutral or negligible. Between levels N1 and N2, further investigation may be necessary. Above the N2 level, an impact on the environment is demonstrated. For trace metals, As and Cr, were between the N1 and N2 levels and Hg, Cu, Cd, Pb and Zn over-passed the N2 level by a factor 7, 2, 1.4, 1.2 and 1.4, respectively, in sediments sampled between 400 and 800 m from the outlet. Such urban impact on estuarine sediments was evidenced in other studies (Feng et al., 1998; Radakovitch et al., 2008).

3.4 Evaluation of the fate of particulate Pb input to the coastal zone during a flood event by modeling

The studied rain event (8th of October 2008) discharged to the coastal zone ~1.9 Mm^3 of water (accordingly to the measured flows), ~650 t of SPM and ~170 kg of particulate Pb (values evaluated from the SPM vs. flow relationships (Table SI-3.1) and considering the

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proportion of the 4 fractions of particles and their Pb content (Table SI-5.1)). This last value, compared to the ~300 kg y^{-1} of particulate Pb discharged during dry weather at Cortiou (Jany et al., 2012; Oursel et al., 2013), confirmed the importance of pollutant inputs to the coastal zone from strong rain events in Mediterranean areas (Nicolau et al., 2012). Results on the fate of particulate Pb in the Cortiou box (Fig. SI-3.1) obtained with the 3D coupled RHOMA model are summarized in Table 2 and illustrated on Fig. 7 for deposition on seabed sediment of particulate Pb in CS, FS and FF fractions 4 days after the studied rain event. In comparison, similar maps simulated 1 day after the rain event are provided in Fig. SI-4.5 and clearly show the importance of local hydrodynamic, governed by offshore current and wind, on the fate of particles and associated pollutants. The S and CS fractions constituted 83% of the total SPM discharge which brought to the coastal zone 49% of the total Pb, S being totally deposited on seabed sediment in vicinity of the outlet and CS in the Cortiou box after 4 days (Fig. 7A). FS particles (Fig. 7B) are partly trapped in sediments (23%) or in the water column (11.5%) and mainly exported offshore (65.5%). Finally, FF represented only 14% of the total SPM but 47% of the total Pb brought by this rain event. Accordingly to their weak settling rate both lowering their settling efficiency and enhancing influence of resuspension events (waves, hydrodynamic), these particles were totally exported offshore (99.5%), only a small fraction remaining on seabed sediment (Fig. 7C). Results from this modelling also confirmed the observed Pb content distribution in surface sediments sampled from Cortiou outlet to 800m offshore (Fig. 6). Indeed, considering the average Pb content of each of the 4 particles fraction and their respective fate in the studied area (Table 2), increases of measured Pb content (from 28 to 250 µg g^{-1}) in surface sediments is most probably due to the deposition of S and CS, whereas the highest Pb content determined for FS and FF were not observed in surface sediments as they remained in the water column or were exported to the open sea. Consequently, if such urban inputs clearly affect the sediment quality locally, they also have a non-negligible influence on the water column due to the exportation of polluted particles offshore.

3.5 Element release in seawater

The percentage of metal released from the initial sample after 15 min, 1 h, 6 h, 24 h and 5 days of contact time with "clean" seawater was calculated. An example is plotted for Cu on Fig. SI-4.6, the percentages represent the Cu concentration in the solution divided by the Cu concentration in the corresponding initial sample (determined after acid and UV digestion).

The metal release resulted from the balance between two opposite processes: (1) metal mobilization due to ionic exchange or degradation of organic complexes and (2) metal re-adsorption on existing or newly formed solid phase (Shulkin and Bogdanova, 2003), both processes depending on the nature of the solids, the particles size, the pH of the solution, the solid/liquid ratio (S/L) and the considered metal (Cantwell et al., 2008; Hatje et al., 2003).

Cu, Co, Ni and Zn exhibited similar release patterns, with a maximal release between 4 and 30%, whereas Cd exhibited a higher release, between 11 and 100%, and Pb a release lower than 1.1%. Shulkin and Bogdanova (2003) observed similar Cd and Pb behavior when studying mobilization of riverine SPM in seawater. High release of Cd, however, is well documented and corresponds to the formation of stable and soluble chlorocomplexes from particle-desorbed Cd (Dai and Martin, 1995; Waeles et al., 2008; Wang and Liu, 2003).

For all samples the metal release increased with contact time. Metal release was still occurring between 1 and 5 days, though with slower kinetics, indicating that the plume particles are able to release dissolved metals in the water column more than 24 h after discharge at sea. Particles can thus continue to release metals after their sedimentation or may release metals after surface sediment resuspension, e.g. during storms events. Similar kinetics were observed by Hatje et al. (2003) studying metal desorption in seawater from an estuarine sediment.

Samples FDHuv, FDJar and FDOut2 had similar behavior one to each other. The FDOut1 sample, although having higher metal concentrations than other samples, exhibited the lowest total release (11% for Cd and less than 5% for other metals). As this sample was likely contaminated after WWTP by-passing, this would indicate a low metal lability from non-treated sewage particles. Compared to the present results, results of the 18/04/2012 campaign (by-pass of WWTP) published in Oursel et al. (2013) showed a higher metal released in the dissolved phase especially when samples were directly filtered on field. To the contrary, the SPOut2 samples that have a characteristic TWW signature exhibited the highest release for all metals, up to 100% for Cd. This indicates a higher metal lability from particles issued from the WWTP, likely due to changes in particles nature and reactivity through the treatment processes (Buzier et al., 2006). Oursel el al. (2013) published results of remobilization experiment designed to simulate mixing of outlet effluent with seawater during dry period. In the salinity gradient, the release of Cd was up to 100% after 6h of mixing as it is found here. However, Oursel et al. (2013) observed that dissolved Co and Ni were adsorbed onto particles in the salinity gradient, showing a non-conservative behaviour. These differences are most

probably related to the different S/L ratio, as the lower is the ratio the more released is the metal.

4 Concluding remarks

Most studies dedicated to Mediterranean rivers input to the sea focused, on the one hand, on metal content in SPM and, on the other hand, on physical properties of suspended particles in estuaries. Here we investigated both chemical properties – metal content and metal release in the mixing zone – and physical properties – particles settling rate.

Metal and POC contents in river sediments were comparable to the values observed in other small coastal Mediterranean rivers and, at the TWW impacted outlet, comparable to the values observed in effluents of other large cities such as Montreal.

Al, Ca, Cs, Li, Rb, Sn, Ti and V were mainly of terrigenous origin while Ag, Ba, Cd, Cr, Cu, Hg, Mg, Mo, Ni, Pb, POC, Sb and Zn were of anthropogenic origin as non-treated sewage, TWW or industrial waste. Many elements showed concentrations over the N2 French action level.

Although the fine fraction was the most concentrated for most elements (and for all metals) the contribution of the sand and the coarse silt fractions to the total contamination was the highest for all analysed elements.

A non-negligible part of metals could be exported to the open sea (e.g. more than 60% of total Pb) due to non-settable contaminated particles (FDOut1 sample). This type of behaviour, due to non-treated urban particles, could also be observed along the Mediterranean coast especially in countries where WWTP are not set up.

Metal desorption kinetics in the mixing zone depended on the metal type and on the particles origin. Particles issued from the WWTP exhibited higher desorption and desorption rates than particles issued from non-treated sewage. Metal desorption still occur more than 24 h after mixing, indicating that the transfer of polluted fine particles to the open sea is most probably accompanied by a non-negligible pollutant release to the dissolved compartment, amplifying potential harmful effects to marine organisms.

In seafloor sediments, all metals exhibited a significant increase from the outlet to, at least, 800 m offshore indicating that the considered elements were partly contained in fractions that settles slowly with regard to the plume and seawater 3-D velocity field.

Implementation of settling particles characteristics in a 3D hydrodynamic and sediment transport model allowed evaluating the fate of particulate Pb in the studied area during a flood

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event, which confirmed the observed deposition of polluted particles in the coastal zone but also indicated a non-negligible export offshore of the finest particles.

Acknowledgments

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Figure caption

Table 1: Elemental composition of the samples used for the settling rate experiment compared to the Rhône River (flow>1500 m^3 s^{-1}, Cossa and Coquery, 2005; Ollivier et al., 2011; Cathalot et al., 2013), to the Montreal effluents (Gobeil et al., 2003), to the Marseille outlet under dry conditions (Oursel et al., 2013) and to the Upper Crust Continent (UCC, Wedepohl K.H., 1995).

Table 2: Calculated Pb fate in the coastal zone for the 4 particle fractions from 3D hydrodynamic and sediment transport modeling after a flood event (8th of October 2008 5:00 AM to the 11th of October 2008 5:00 PM)

Figure 1: Map of the studied site: the dotted area represents the urbanized zone of Marseille, (inset) position of the sediment sampling sites. Sampling points: O: outlet; Jar: Jarret River; Huv: Huveaune River; S1 to S12: surface sediment sampling points.

Figure 2: Variation of Rb (A), Fe (B) and Ca (C) contents as a function of Al content for dry period samples (open symbols), wet period samples (full symbols) and sediments (＋).

Figure 3: Variation of the percentage of particles for each class as a function of their settling rate and calculated diameter.

Figure 4: Distribution of Al (A), Cu (B) and Sb (C) contents for each class as a function of their settling rate.

Figure 5: Distribution of the percentage of element contents in each fraction for FDOut2 (A), and FDOut1 (B) samples.

Figure 6: Distribution of Pb, Ca and Mg contents in surface marine sediments as a function of the distance from the Cortiou outlets. The dotted lines represent the mean values of Pb contents in the 4 particles fractions from 3D hydrodynamic and sediment transport modeling (Table 2).

Figure 7: Maps of particulate Pb deposition on seabed sediment for (A) coarse silt, (B) fine silt and (C) fine fraction (as percentage of the total particulate Pb discharged to the coastal zone for each fraction, expressed in log$_{10}$) 4 days after the rain event of the 8th of October 2008.

Site	POC	PIC	Ca	K	Mg	Na	Ag	Al	As	Ba	Be	Bi	Cd	Co	Cr	Cs	Cu
	mg g⁻¹	mg g⁻¹	mg g⁻¹	mg g⁻¹	mg g⁻¹	mg g⁻¹	µg g⁻¹	mg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹
FDHuv	15	69	180	1.7	21	0.21	1.2	11	6.8	110	0.57	0.17	0.30	2.6	26	1.2	54
FDJar	25	71	200	1.5	17	0.24	0.23	9.6	3.1	180	0.54	0.19	0.34	2.8	47	1.0	43
FDOut2	37	60	170	2.2	22	0.24	0.78	15	7.8	140	1.1	0.31	0.68	4.2	48	1.7	58
FDOut1	140	30	160	2.2	20	0.30	3.6	8.8	9.0	800	0.47	6.5	2.1	7.9	74	1.2	240
SPOut2	150	55	76	3.6	13	0.64	1.3	16	4.6	110	0.72	3.0	0.72	3.1	32	2.1	130
Rhône River (Ollivier et al., 2011; Cathalot et al., 2013*)	19*		130	17	8.7	3.6		57		370		0.89	0.57	13	88	8.9	43
sd or (min-max)	5		(57-160)	(13-21)	(6.8-12)	(1.7-5.8)		(45-69)		(290-600)		(0.36-3.2)	(0.28-0.88)	(9.5-18)	(63-120)	(6.3-15)	(26-69)
Montreal Effluents (Gobeil et al., 2005)							56	30	5.5	350		2.9	5.4	2.8	160	0.21	670
sd							15	22	3.1	240		1.5	2.7	1.7	41	0.19	190
Out2 baseflow period (Oursel et al., 2013)	240	54	100	5.2	11	0.7	4.9	15	7.3	220	0.51	9.8	1.5	7.4	99	2.9	420
(min-max)	(78-420)	(34-65)	(50-170)	(4.3-6.0)	(5.8-16)	(0.30-1.4)	(0.62-32)	(3.2-66)	(3.8-19)	(100-540)	(0.038-2.1)	(1.3-18)	(0.37-5.1)	(1.5-130)	(15-1200)	(1.3-5.9)	(58-1600)
UCC (Wedepohl K.H., 1995)			29	29	13	26	0.055	77	2	670	3.1	0.12	0.10	12	35	5.8	14

Site	Fe	Hg	Li	Mn	Mo	Ni	Pb	Rb	Sb	Sn	Sr	Ti	Tl	U	V	Zn
	mg g⁻¹	ng g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	mg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹	µg g⁻¹
FDHuv	9.5	180	14	240	0.81	16	60	13	0.8	18	300	0.62	0.06	1.1	22	160
FDJar	7.2	86	13	180	3.0	23	740	12	0.8	4.4	370	0.51	0.07	0.92	20	210
FDOut2	13	370	18	250	2.3	31	79	18	0.8	9.3	310	0.67	0.09	1.2	27	260
FDOut1	40	3500	14	350	46	65	1700	11	4.3	24	220	0.32	0.17	1.1	23	3300
SPOut2	12	360	19	150	3.2	21	48	20	1.8	13	290	0.18	0.11	1.0	28	300
Rhône River (Ollivier et al., 2011; Cossa and Coquery, 2005**)	27	480**		690		45	45	100	1.9		390	2.9		10	97	170
sd or (min-max)	(21-36)			(410-1200)		(36-62)	(22-110)	(75-140)	(0.82-5.0)		(270-490)	(1.7-3.5)		(1.9-20)	(78-140)	(107-310)
Montreal Effluents (Gobeil et al., 2005)	47			108	7.8	21	42	0.86			140			1.2	14	480
sd	46			40	4.2	7.4	16	0.52			48			0.33	8.8	14
Out2 baseflow period (Oursel et al., 2013)	31	1500	20	320	12	160	83	28	1.5	21	350	0.41	0.15	1.1	25	1000
(min-max)	(8.5-56)	(250-3200)	(5.0-86)	(130-830)	(1.5-170)	(10-3800)	(38-340)	(12-68)	(0.47-5.01)	(6.0-53)	(150-890)	(0.10-1.2)	(0.07-0.27)	(0.50-2.1)	(2.5-73)	(240-3600)
UCC (Wedepohl K.H., 1995)	31	56	22	530	1.4	19	17	110	0.31	2.5	320	3.2	0.75	2.5	53	52

Table 2

fraction	µg g^{-1} Pb content of sedimented particles	% deposited on seabed sediment	% trapped in the water column	% exported from the box
Sand	140	100	0	0
Coarse Silt	210	99.7	0	0.3
Fine Silt	310	23	11.5	65.5
Fine Fraction	5900	0.4	0.1	99.5
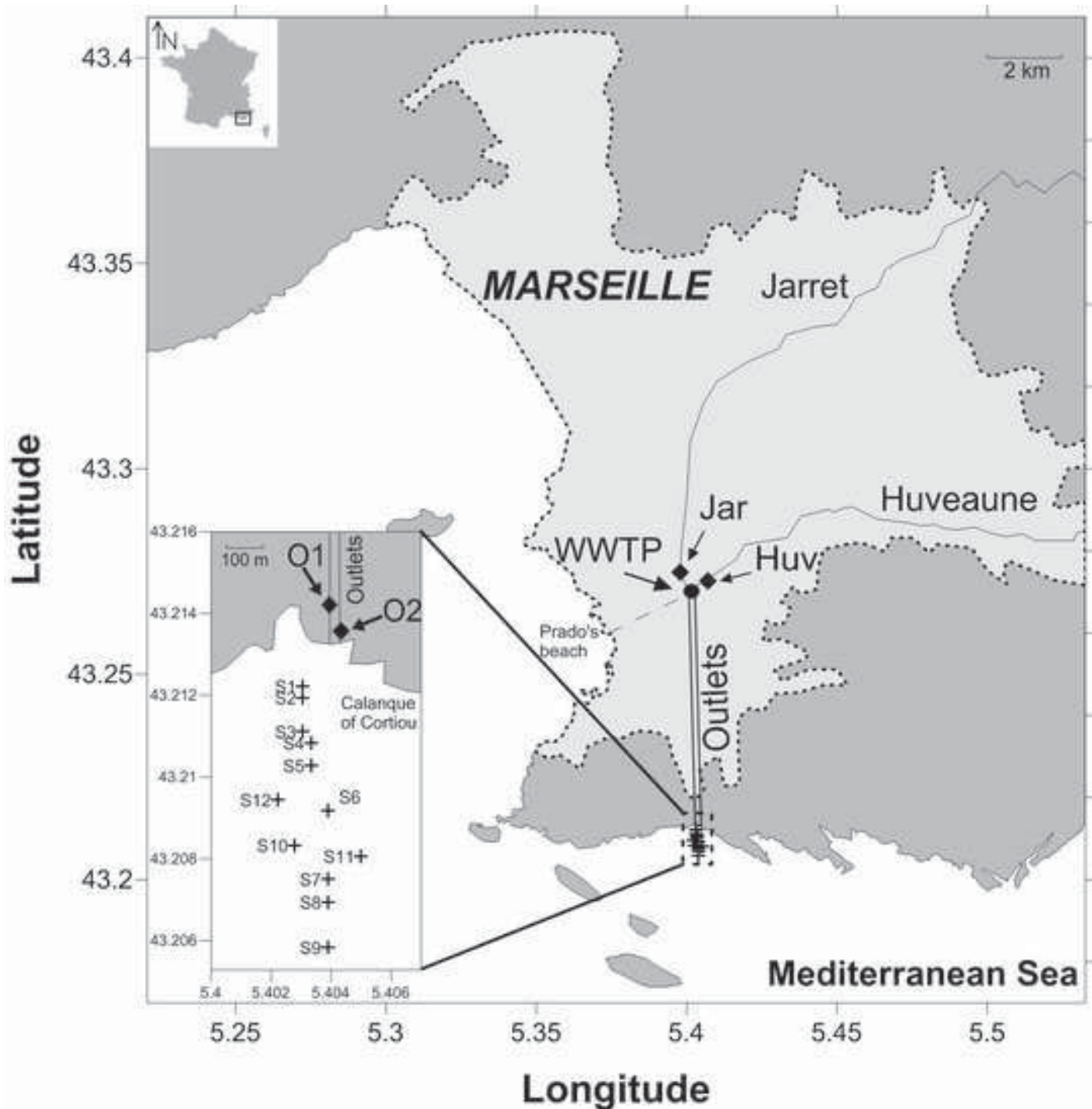
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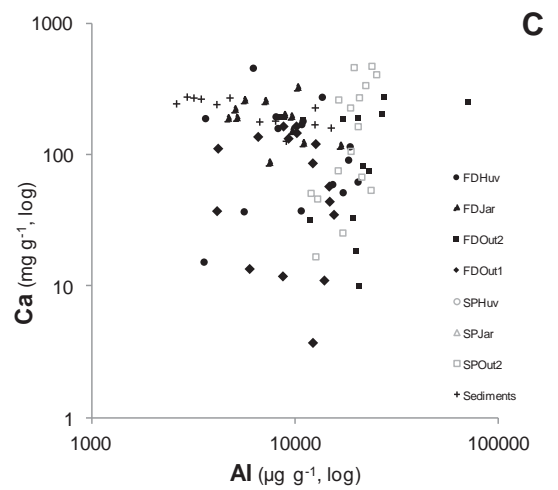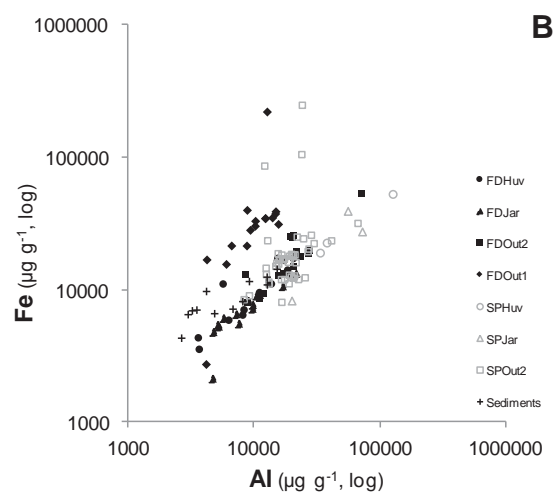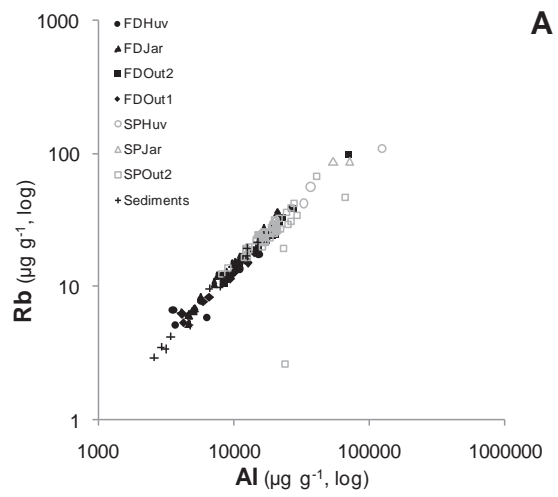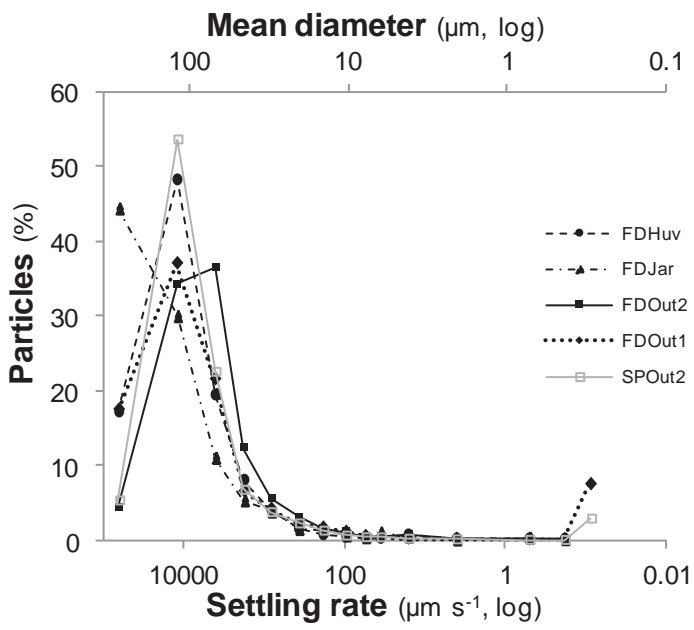
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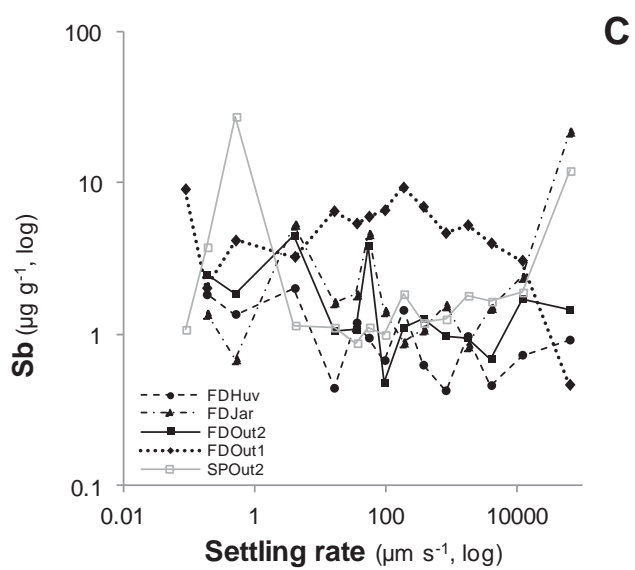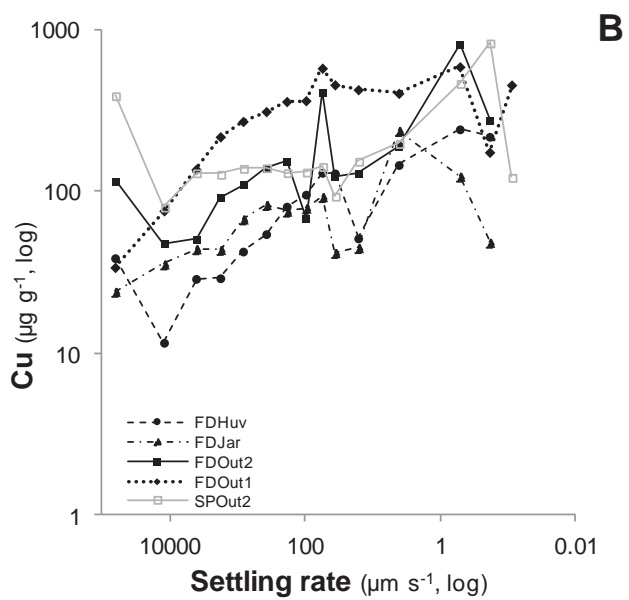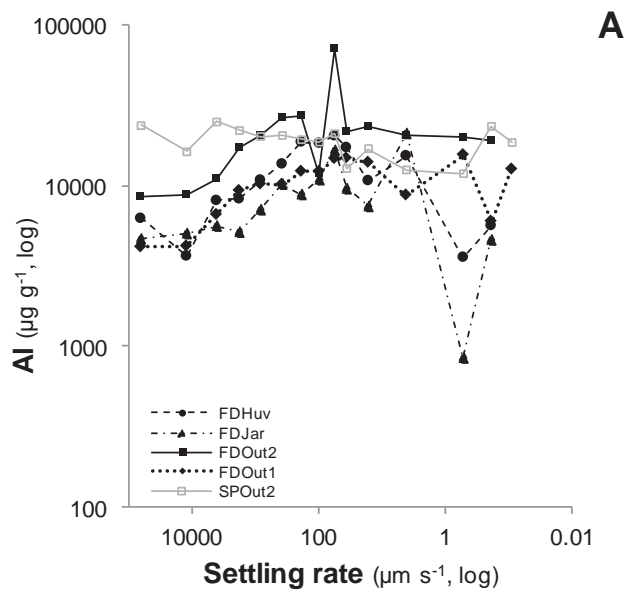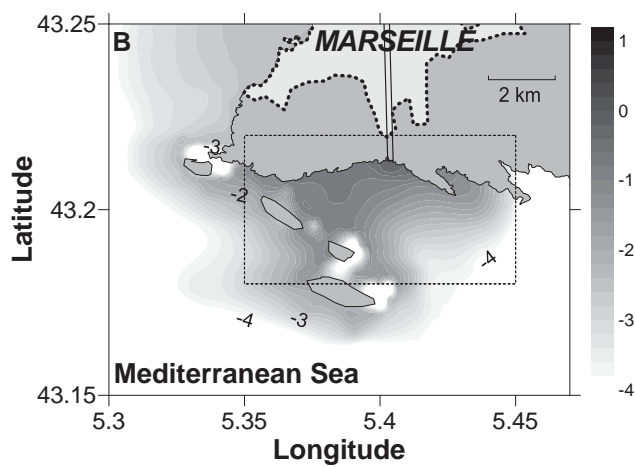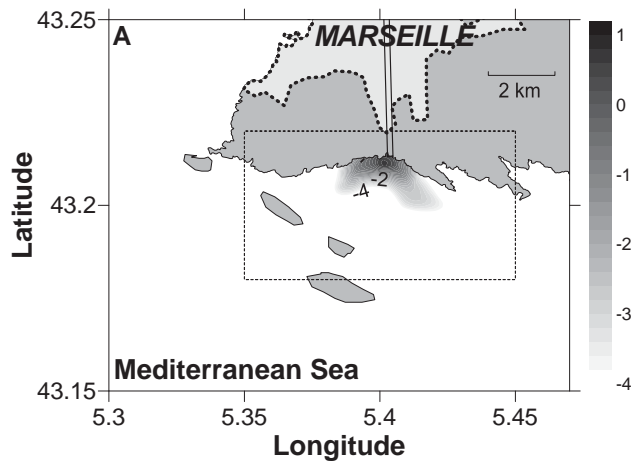
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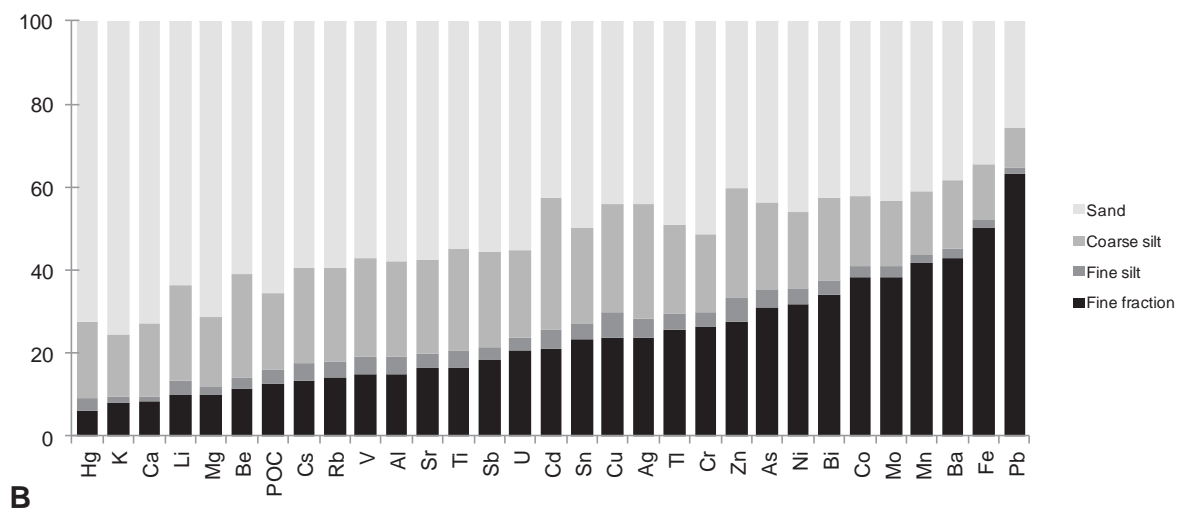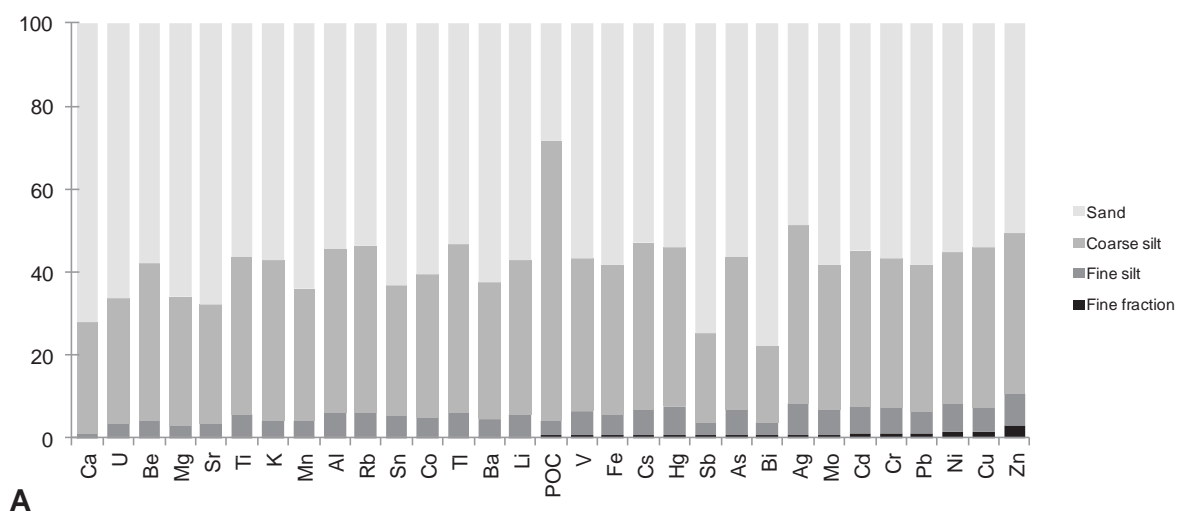
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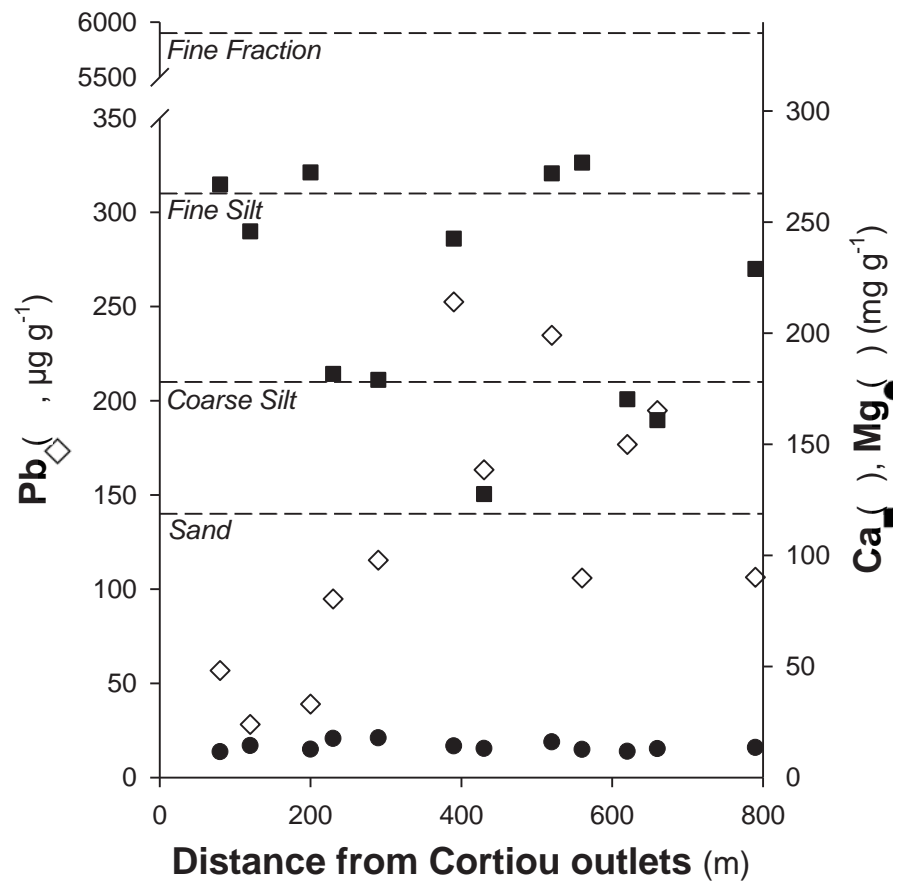
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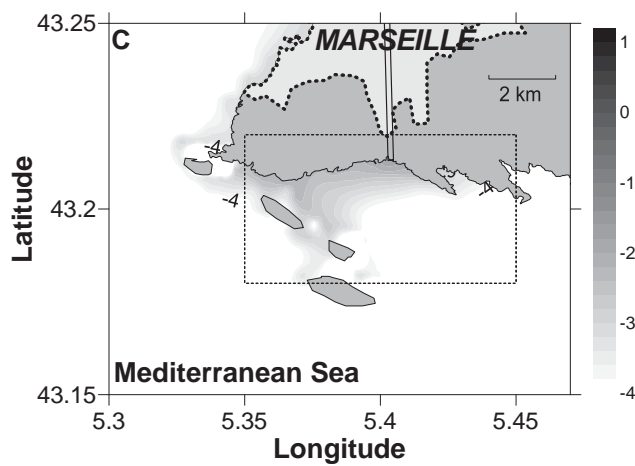
Supplementary Information corrected

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