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Environmental context

Emerging contaminants such as platinum (Pt) are continuously released into aquatic environments. However, due to analytical challenges related with their accurate quantification, little information exists on their geochemical cycles in coastal areas. This paper examines the potential use of Pt as a tracer of anthropogenic inputs in a model industrial/urban site (Genoa Harbor, Italy) and provides a first estimate on dissolved Pt baseline concentrations in the northern Mediterranean coast.

Abstract

Biogeochemical cycles including processes controlling platinum (Pt) distribution remain widely unknown in aquatic environments, especially in coastal systems. Dissolved Pt concentrations in coastal seawater (Pt_D) and in Suspended Particulate Matter (SPM, Pt_P) were measured, together with master variables comprising dissolved oxygen, dissolved and particulate organic carbon, chlorophyll-a, turbidity, and ammonium levels, along two longitudinal profiles in the industrial Genoa Harbor (northwest Italy). Concentrations and spatial distribution of Pt_D and Pt_P levels reflect distinct concentration gradients that were attributed to different Pt sources such as hospital, domestic and industrial wastewater, atmospheric deposition, and/or road run-off. Concentrations reaching up to 0.18 $ng.L^{-1}$ Pt_D and 14 $ng.g^{-1}$ Pt_P reflect the impact of Pt urban inputs in coastal sites. These first data highlight considerable anthropogenic contamination in the confined harbor compared to the proposed reference value for the western Mediterranean surface seawater measured at external sites. Identified correlations between Pt levels and human pollution signals suggest the potential use of Pt as a new tracer of anthropogenic inputs that can be applied in other urbanized coastal systems. Biogeochemical processes inducing changes in partitioning and fate of Pt in coastal seawater reflect spatial variability, highlighting the need for comprehensive environmental monitoring at appropriate spatial scale.

Keywords: Platinum; Technology Critical Element; emerging contaminant; seawater; suspended particulate matter; distribution coefficient; urban tracer; coastal environment

1. Introduction

Platinum (Pt) is a Technology Critical Element (TCE) and an emerging contaminant of growing concern according to evidences of anthropogenic disturbance on its global biogeochemical cycle (Rudnick and Gao, 2003; Cobelo-García et al., 2015). Among its specific properties, Pt is an excellent catalyst used in industrial processes, such as petroleum chemistry, but more importantly in vehicle catalytic converters to reduce gaseous pollutants in exhaust fumes. Strongly increasing Pt demand for this technology results in growing anthropogenic Pt inputs into the environment, leading to a global increase of Pt concentrations in all environmental compartments including soils, atmosphere and aquatic systems (e.g. Rauch et al., 2006; Rauch and Morrison, 1999; Schäfer et al., 1999). However, other anthropogenic Pt sources (potentially implying the release of different Pt species to the environment) may occur in aquatic environments including Pt-derived anti-cancer drugs (e.g. Vyas et al., 2014).

Coastal areas are facing high anthropogenic pressure due to the increasing density of human population in such attractive zones (Small and Nicholls, 2003). Monitoring of trace metal concentrations in these sites is therefore essential to detect potential contamination and prevent associated adverse consequences on the ecosystem, especially for emerging contaminants. Platinum concentration in seawater is difficult to quantify precisely, in particular in less contaminated sites, because of extremely low environmental levels (sub $ng.L^{-1}$; Mashio et al., 2017). Existing studies on marine coastal areas, including saline estuaries, report dissolved Pt concentrations ranging from 0.05 to 0.30 $ng.L^{-1}$ (Cobelo-García et al., 2013, 2014a; Goldberg et al., 1986; Mashio et al., 2016, 2017; Obata et al., 2006; Turetta et al., 2003; van den Berg and Jacinto, 1988). A small number of studies report Pt concentrations in Suspended Particulate Matter (SPM) ranging from ~ 2 to 10 $ng.g^{-1}$ in the Lérez Estuary and from ~ 0.2 to 1 $ng.g^{-1}$ in the Gironde Estuary (Cobelo-García et al., 2013, 2014a). Variations in Pt concentrations and

65 possible Pt enrichment in those coastal sites have been attributed to Pt inputs from human
66 activities, especially in systems receiving anthropogenically-impa

67 cted freshwater inputs, as observed in the Tokyo Bay (e.g. Obata et al., 2006). Several studies
68 have addressed bioaccumulation of Pt in wild marine bivalves, such as oysters and mussels
69 (Abdou et al., 2016; Neira et al., 2015). However, there is a lack of data on the comprehensive
70 characterization of the factors controlling the behavior of Pt in coastal seawater, including its
71 partitioning between suspended particles and seawater, and huge uncertainties remain
72 concerning its transport, bioavailability and fate in the coastal ocean (Cobelo-García et al.,
73 2013).

74 The Mediterranean Sea is a semi-enclosed system under ever-growing anthropogenic pressure
75 along its northwestern coast, comprising several highly populated cities with extensively
76 urbanized and industrialized areas (Martín et al., 2009). Considering the possible changes in
77 seawater chemistry due to additional anthropogenic inputs, previous studies have addressed
78 environmental quality in historical and industrial harbors such as the Toulon Bay or the Genoa
79 Harbor, reflecting intense pollution by metals, (e.g. Oursel et al., 2013; Tessier et al., 2011),
80 metal-organic components (Pougnet et al., 2014) and nutrients (Ruggieri et al., 2011). The
81 Genoa Harbor on the northwest coast of Italy (Ligurian Sea) is one of the most important ports
82 of the Mediterranean Sea, known for heavy contamination due to a variety of human activities.
83 For many years, industrial effluents were the major cause of water pollution in this site, before
84 the closure of the main heavy industries adjacent to the harbor during the 1990s. Nowadays,
85 discharges from sewage treatment plants and from creeks account for generally high levels of
86 nutrients, organic matter and faecal pollution in the harbor waters (Ruggieri et al., 2011).

87 The present work provides first information on Pt levels and spatial distribution in this major
88 Mediterranean harbor combined with physical-chemical parameters. Such findings may help to

improve our understanding on Pt sources, other than the commonly assumed influence from catalytic converter emissions, and Pt cycling in an anthropogenically impacted coastal site. The objectives are therefore: (i) to quantify Pt levels and spatial distribution in a marine system under strong anthropogenic influence, involving different Pt sources, (ii) to characterize the factors controlling Pt distribution and partitioning between seawater and suspended particles considered a prerequisite for a better understanding of its biogeochemical cycle in coastal environments, and (iii) to investigate the potential use of Pt as an innovative tracer of human inputs (traffic, wastewaters, industrial activities) in coastal environments.

2. Experimental

2.1. Study area and sampling strategy

The coastline of Genoa

The Genoa Harbor is an artificial harbor on the northwest coast of Italy (44°24'39.8"N 8°55'44.8"E). The port infrastructures extend over approximately 7 million m² along about 20 km of coastline, protected by sea defenses and artificial breakwaters. The innermost, natural part of the Genoa Harbor is the so-called Old Port hosting a ferry terminal, several marinas and receiving urban treated sewage effluents (Ruggieri et al., 2011; Fig. 1). Outside the Old Port a wide, less confined area protected by artificial breakwaters extends to the east and to the west, hosting diverse industrial activities and receiving discharges from a coal-fired power plant, treated urban wastewater and untreated surface run-off (Ruggieri et al., 2011). In addition, important dredging has affected the area in the last decade (Cutroneo et al., 2012). Two seasonally active rivers discharge freshwater and treated wastewater into the harbor area: the Polcevera River to the west and the Bisagno River to the east (Fig. 1; catchment surface area of 93 km^2 and 140 km^2, respectively; Cutroneo et al., 2017)). Both rivers, characterized by

irregular and harsh streamflow fluctuations, run through the city of Genoa and are surrounded by dense urban structures hosting a variety of commercial and industrial activities.

Sampling campaigns

Two longitudinal profiles were performed to collect surface seawater and SPM samples inside and outside the Genoa Harbor on-board the Research Vessel MASO (3^{rd} – 6^{th} April 2017; Fig. 1). The first profile was carried out from the inner part of the port towards the eastern entrance (sampling sites E1 to E6; Fig. 1). This represents a supposed decreasing contamination gradient covering the strongly confined Old Port (sites E1 and E2), a less confined zone inside the breakwaters (site E3), the eastern Inlet (site E4) close to the mouth of the Bisagno River and two sites outside the Harbor, directly in contact with open Mediterranean water, i.e. the Ligurian Current (sites E5 and E6). This profile is performed along the less industrialized section of the harbor. The second profile addressed the western part of the Genoa Harbor (sampling sites W1 to W6, Fig. 1) hosting coal deposits, a terminal for oil products (no storage tanks in the harbor), and receiving power plant discharges and inputs from the Polcevera River transporting sewage treatment plant effluents (Ruggieri et al., 2011).

Eastward profile was performed on April 3^{rd} under north-northeast wind with an average speed of 16 $km.h^{-1}$ (Table 1; timeanddate.com). Westward profile was done the following day with weaker wind (~ 9 $km.h^{-1}$) originating from south-southeast. Due to complex harbor shape, station bottom depth differs according to the location. Within the Old Port, site E1 has a bottom depth of 6 m (Table 1). Other sites within the breakwaters, show average depth of 11 m while it is of 16 m for E4 at the eastern inlet. We observe average depth of 14 m for external sites E5 and E6, and 26 m for W5 and W6.

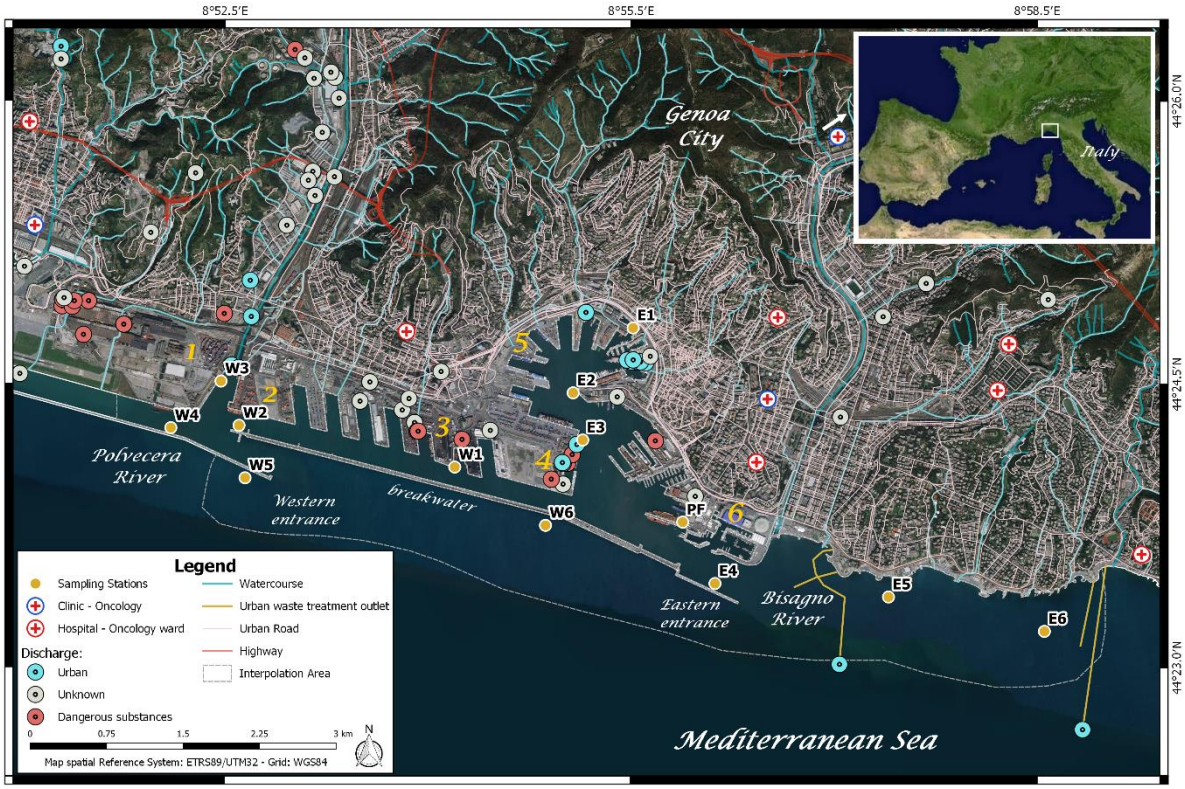

Fig. 1: Sampling sites in the Genoa Harbor. Two sampling profiles were performed with an eastward profile (sites E1 to E6) and a westward profile (sites W1 to W6). Sampling site PF (PlatForm) corresponds to the CNR Platform. Numbers correspond to main urban/industrial activities with 1: Steel mill, 2: Bulk containers, 3: Coal power plant, 4: Oil storage, 5: Ferry terminal, 6: Shipyards/marinas. Red crosses indicate hospitals with oncology ward with the Oncology Clinics highlighted in blue. Colored circles show discharges from various sources. Geospatial data provided by the Ligurian Administrative Region via own Geoportal - WFS service (https://geoportal.regiosne.liguria.it/). Satellite image provided by ESRI© (ArgGIS/Imagery)

Additional samples were taken at the CNR (National Research Council) Observation Platform (site PF, Fig. 1) on April 6th 2017 at three different times of the day (10 am, 12 pm, 2 pm). The bottom depth of this sampling site is of 6 m (Table 1). This sampling site is located at the limit of the confined area of the harbor, supporting diverse harbor activities such as navigation, ship construction and wrecking industries. Main hospitals with oncology ward of Genoa are located rather close to this area, including an Oncology Clinic (~ 3 km).

Sample collection

Seawater and SPM samples were collected at all sites (i.e. on-board the R/V MASO or from the CNR Platform) by pumping surface water (~ 5 m depth) with a purpose-built low voltage (12 V) peristaltic pump connected to Teflon tubing. The latter was rinsed with seawater, accounting for more than three times the tubing volume (seawater pumping time of 10 min) prior to sample collection. Seawater was collected into acid-washed 500 mL Teflon bottles (Nalgene®), previously rinsed with pumped water at each site. Water samples for analyses of dissolved Pt (Pt_D) were filtered immediately through 0.2 µm polycarbonate filters (Nucleopore®) with a filter-syringe (Sartorius®) into acid-washed 60 mL Teflon bottles (Nalgene®), previously rinsed with an aliquot of the filtrate, then acidified to pH = 1 (36.5–38 % HCl Baker Instra) and stored in the dark at 4 °C pending analysis. Water aliquots from the 500 mL Teflon bottle were collected to quantify ammonium (NH_4^+) and dissolved organic carbon (DOC) concentrations. The samples for NH_4^+ analysis were filtered as aforementioned into pre-cleaned 15 mL polypropylene (PP) tubes (Kartell®), and stored frozen pending analysis. Aliquots for DOC were filtered through pre-combusted (500 °C, 4 h) glass-fiber filters (0.7 µm, Whatman® GF/F) using a pre-cleaned (RBS detergent, thoroughly rinsed with ultra-pure deionised water, Milli-Q® water) and pre-combusted glass syringe. Filtrates were collected in pre-cleaned and pre-combusted glass bottles, acidified (HCl 0.3 % v/v; Baker, Analyzed) and then stored in the dark at 4 °C until analysis.

Particulate samples were collected for analyses of particulate platinum (Pt_P) and particulate organic carbon (POC). In both cases, the sampling bottle was carefully shaken and seawater was placed in a pre-rinsed filtration unit covered by a lid. For Pt_P, SPM were collected on pre-weighed Teflon filters (47 mm, 0.45 µm FHLC filter, Merck Millipore®), whereas for POC, SPM were collected on pre-combusted and pre-weighed glass-fiber filters (0.7 µm, Whatman® GF/F). Once in the laboratory, both filters were then oven-dried (48 h at 50 °C) to constant

weight, re-weighed (to determine SPM content) and kept in the dark at room temperature pending analysis. A field blank was performed for all sampled parameters and processed in the same way as seawater samples but using Milli-Q water.

2.2. Analytical methods

Platinum in seawater

Seawater samples were analyzed by Adsorptive Cathodic Stripping Voltammetry (AdCSV) as described in Cobelo-García et al. (2014b). Measurements were carried out using a μAutolab Type III potentiostat (Metrohm®) connected to a polarographic stand (Metrohm® 663 VA Stand) equipped with three electrodes: (i) a hanging mercury drop electrode (HMDE, the working electrode), (ii) a silver/silver-chloride (Ag/AgCl) reference electrode, and (iii) a glassy carbon auxiliary electrode. A polytetrafluoroethylene (PTFE) voltammetric cell served in all experiments and the potentiostat was controlled using the NOVA 2.1® software. Elimination of organic matter by UV oxidation was performed by placing sample aliquots in capped Teflon bottles with overnight irradiation using two 64 W UV lamps (NIQ 60/35 XL, Heraeus) under a fume hood. Aliquots (10 mL) of UV-digested sample were pipetted into the voltammetric cell together with 30 μL of 3.3 mM formaldehyde (37–41 % Analytical Reagent Grade, Fisher Chemical®), 30 μL of 0.45 mM hydrazine sulfate (Analytical Reagent Grade, Fisher Chemical®), and 300 μL of sulfuric acid (H_2SO_4, 93 – 98 % Trace metal grade, Fisher Chemical®). Platinum concentrations were quantified by standard internal addition method, adding a controlled amount of a Pt stock solution freshly prepared daily from a mono-elementary Pt standard solution (1000 $\mu g.mL^{-1}$ PLASMACAL, SCP Science®). We applied a deposition time of 300 s and experimental parameters as described elsewhere (Cobelo-García et al., 2014b). In the absence of Certified Reference Material (CRM) for dissolved Pt in

seawater, analytical quality of the voltammetric procedure was evaluated by means of Pt spiked CRM seawater quantification (CASS-6, NRCC) giving recoveries > 80% and precision expressed as Relative Standard Deviation (RSD) lower than 10 % (n = 5) at the 0.5 $ng.L^{-1}$ range. The detection limit (D.L.) for dissolved Pt measured by AdCSV (calculated as 3 x blank standard deviation, n = 20) was estimated to 0.03 $ng.L^{-1}$. Satisfactory results were obtained for field blank with Pt_D of 0.05 $ng.L^{-1}$.

Platinum in SPM

Particulate platinum concentrations (PtP) in Suspended Particulate Matter samples were analyzed by Triple Quadrupole-Inductively Coupled Plasma-Mass Spectrometry (TQ-ICP-MS, Thermo® iCAP TQ). Teflon filters with SPM (typical mass of ~ 3 - 5 mg) were acid digested as described in Abdou et al. (2018). Briefly, 2 mL HCl and 1 mL HNO_3 (30 % HCl and 65 % HNO_3 Suprapur, Merck®) were added to the samples in polypropylene (PP) tubes (DigiTUBEs, SCP SCIENCE®) and closed with caps. Samples were placed in a Teflon-coated heating block, and digested at 110 °C for 3 h. Cooled contents were then diluted in 10 mL Milli-Q water, centrifuged at 4000 rpm for 10 min (20 °C) and filters were discarded. Analyses were performed applying the standard internal addition method (as previously explained). After obtaining the raw signal, Hafnium-oxide (HfO^+) interferences were monitored using the ^{193}Ir signal that is highly interfered by HfO^+ (Djingova et al., 2003). Raw signal was thereafter mathematically corrected using ^{194}Pt / ^{195}Pt natural ratio and assuming that HfO^+ is the only/dominant spectral interference on those selected isotopes. Analytical quality control was performed using the BCR®-723 road dust (Institute for Reference Materials and Measurements) and Jsd-2 sedimentary rocks (indicative value from Geological Survey of Japan) as available CRMs for Pt concentrations. Analyses of these CRMs by TQ-ICP-MS gave satisfactory recovery values of 87% and 101% respectively (n = 3) and precision expressed as

RSD of ~ 5 %. The detection limit (D.L.) for Pt_P (n = 10) was estimated to 0.34 $ng.g^{-1}$ for typical sediment sample mass of 4 mg. Satisfactory results were obtained for field blank with Pt_P below detection limit.

Complementary measurements

Parallel to sampling, other master variables (i.e. temperature, dissolved oxygen, salinity, and turbidity) as well as chlorophyll-a (Chl-a) concentrations were measured *in situ* using a submersible probe (OS316*Plus*, Idronaut®), previously calibrated on-board the R/V MASO or in an on-site laboratory on the CNR Platform. Salinity was measured using the Practical Salinity Scale and Turbidity with Nephelometric Turbidity Units. Seawater pH and redox potential (Eh) were determined with a Sentix® 41 probe (PROFILINE, WTW) and a PH-25 probe (CRISON®), both previously calibrated using the manufacturer's specifications and supplied reagents (NIST pH standards).

Dissolved organic carbon (DOC) was analyzed with an automated analyzer (TOC-L, Shimadzu®) as described in Sharp et al. (1993). Accuracy of DOC measurements was tested using reference material (Deep Sea Reference, DSR, University of Miami) providing recovery results > 90 %. Analytical precision expressed as %RSD was 5 % at the 0.5 $mg.L^{-1}$ range. The D.L. (n = 10) was estimated to 0.06 $mg.L^{-1}$. Particulate organic carbon (POC) was analyzed with a LECO© CS-125 after carbonate elimination as described elsewhere (e.g. Schäfer et al., 2002). Analytical quality was checked by measuring CRMs (e.g. LECO 501–503). Accuracy was within 5 % of the certified values and the analytical error generally < 5 % (% RSD). Ammonium concentrations were determined by colorimetric procedure (visible-UV spectrophotometer, Thermo®, Genesys 20, Aminot et al., 1997). Analytical error of the method is < 5 % (% RSD), accuracy within 5 % of the reference values, and the D.L. of 18 $\mu g.L^{-1}$.

Satisfactory results were obtained for field blank values of DOC, POC and NH_4^+ (~ 0.2 $mg.L^{-1}$, 0.04 %, and ~ 30 $\mu g.L^{-1}$ respectively).

2.3. Data treatment

The correlation matrix for the different parameters was produced using the software PAST® applying the linear r (Pearson) parametric correlation coefficient. The statistical significance (p-value) was set to 0.05. Surfer® software (Golden Software Inc., ver. 13) was used to produce the distribution maps of the analytical results and the data interpolation was performed using Minimum Curvature algorithm. Due to the complexity of the port area, a fault traces file of the port shape (Fig. 1) and a spatial resolution of 5 m were used to perform the calculation gridding. The interpolated variable limits were fixed to minimum/maximum of the measured data for the Pt_D map; and from 0 until the maximum of the measured data for the Pt_P map. For each interpolation map, the software returns the coefficient of multiple determination (R^2), which represents the goodness of fit of the model. When the regression equation fits well to the data, R^2 is large and close to 1.

Particle–water distribution coefficients, K_D, defining the concentration ratios of Pt_P over Pt_D were calculated according to the equation (1)

$$K_D = [Pt_P] / [Pt_D] \times 10^3 \quad (1)$$

3. Results

The results obtained for major physical-chemical parameters and complementary measurements are represented for two distinct longitudinal profiles, both starting from inside the Genoa harbor and going towards the open Mediterranean Sea along the east and west part of the coastline (Table 1). A clear decreasing gradient occurred for turbidity values from inside towards the open sea eastward while westward profile featured no clear trend. Temperature values varied between 14.5 °C and 15.0 °C with a trend for higher temperature for sampling sites located inside the breakwaters. For both profiles, lowest temperatures occurred for external sites being E6 and W6. For the eastern profile, salinity (S) of ~ 37.7 in the inner harbor, compared to S = 38.0 in the outmost sites, suggested a ~ 1 % mixing of freshwater. Westward, only the site W1 showed lower salinity (37.8), whereas other sites showed average salinity of ~ 38. Redox potential (Eh) showed an increasing trend for eastward inner sites with highest value of 211 mV for site E4, while at external sites E5 and E6, lower values (~ 190 mV) occurred. Westward, Eh values did not show any particular trend (~ 180 mV), yet slightly higher values at external sites W5 and W6 (~ 204 mV). Measurements of pH varied between 8.14 and 8.24, with highest values for external sites in both profiles (Table 1). Oxygen saturation levels, DOC, and POC ranged between ~ 70 % and 98 %; 0.7 and 2.0 $mg.L^{-1}$; and 1 % to 5 % respectively. An increasing gradient occurred for O_2 saturation eastward from inner to outer sites while levels of DOC, POC%, Chl-a and NH_4^+ decreased (except for one higher POC% value at site E5). Chlorophyll-a and NH_4^+ values at sites E5 and E6 were of ~ 0.3 $\mu g.L^{-1}$ and below the D.L. (18 $\mu g.L^{-1}$), respectively. In contrast, the westward profile showed relatively constant values for O_2 saturation (~ 90 %). Elevated Chl-a, DOC, and POC % levels tended to occur for stations inside the breakwaters, while most NH_4^+ concentrations were below the D.L.

Dissolved Pt concentrations ranged from 0.08 ng.L^{-1} to 0.18 ng.L^{-1} (Table 1) and showed clear concentration differences between sites inside the harbor and sites outside the breakwaters (Fig. 2A). Despite the distance from the stations, a coefficient of multiple determination of 0.51 was obtained for Pt_D map that clearly confirms the observed gradient (Fig. 2A). Westward profile showed somewhat similar Pt_D concentrations at the sites W1 to W3, all inside the breakwaters, and a decrease towards the most distant site of this profile (~ 0.10 ng.L^{-1} at W6). The eastward profile displayed an increasing Pt_D gradient from ~ 0.10 ng.L^{-1}at E1 to 0.18 ng.L^{-1} at E4 and a sharp drop towards lower values at sites E5 and E6 (0.08 ng.L^{-1}; Table 1).

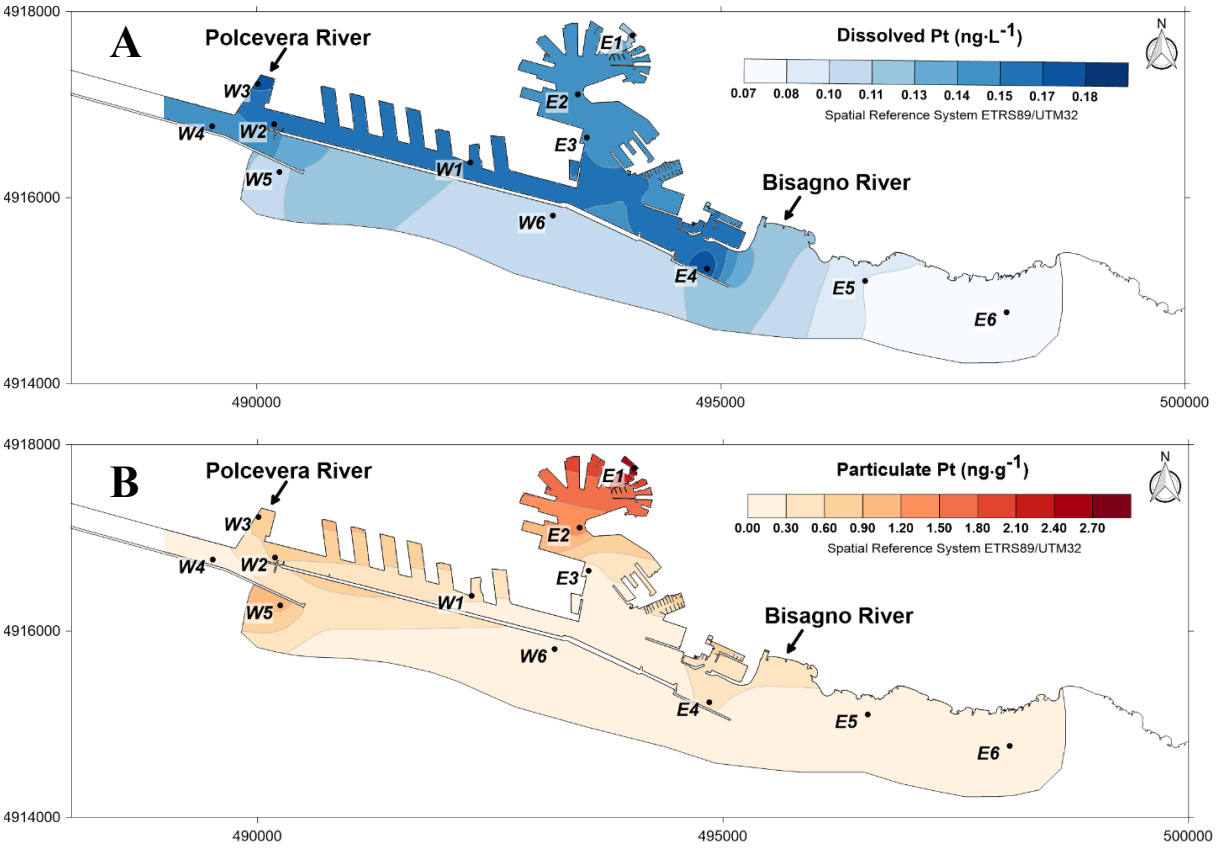

Fig. 2: Dissolved and particulate Pt concentrations along the two longitudinal profiles in the Genoa Harbor. A: spatial distribution of dissolved Pt concentrations (Pt_D; ng.L^{-1}); and B: spatial distribution of particulate Pt concentrations (Pt_P; ng.g^{-1}).

The observed Pt_P concentrations ranged from below D.L. (< 0.34 $ng.g^{-1}$) up to ~ 3 $ng.g^{-1}$ (Table 1). A coefficient of multiple determination of 0.61 was obtained for the Pt_P map. Along the westward profile, Pt_P concentrations were relatively constant and low (< 1 $ng.g^{-1}$; Fig. 2C) with values below D.L. in sites W4 and W6. In the eastward profile, Pt_P were highest in the Old Port (site E1), and showed an overall decreasing trend towards the outer sites reaching values below D.L. at sites E5 and E6 (Pt_P level at site E3 was also below the D.L.).

Calculated particle–water distribution coefficients varied from 2 x 10^3 to 23 x 10^3 and showed eastward and westward gradients similar to those observed for Pt_P concentration variations (Table 1).

The relationships between spatial variations of Pt_D and Pt_P concentrations and the other parameters measured are displayed separately for each profile only for the sites within the breakwaters (Table 2). Despite the low number of samples, results of the correlation matrix suggest that linear correlations exist between selected master variables and Pt levels in both the dissolved and particulate phases along the profiles (Table 2). Eastward, Pt_D concentrations seemed to be slightly positively correlated ($r \sim 0.6$) with wind speed and pH, and significantly positively correlated ($r > 0.9$) with Eh and O_2. These concentrations were significantly negatively correlated with turbidity, DOC, POC Chl-a, and with NH_4^+ levels ($r < -0.9$). Opposite behavior occurred for Pt_P concentrations. In the westward profile, Pt_D concentrations which were weakly positively correlated with turbidity, Eh, ($r > 0.8$) and pH ($r \sim 0.6$) and negatively correlated with O_2% ($r \sim -0.6$). Again Pt_P concentrations showed opposite behavior with significant correlations (Table 2). .

Platinum concentrations at the CNR Platform (fixed site PF; Fig. 1) measured at three different times of the day showed variations for both Pt_D (0.09 to 0.15 $ng.L^{-1}$) and Pt_P (3.1 to 14 $ng.g^{-1}$; Table 3), with highest concentrations at 12 pm. Dissolved Pt concentrations were in the same

range as those measured along the profiles, whereas relatively higher Pt_P levels occurred, leading to higher K_D values. During the measurements at the CNR Platform, wind direction changed from north to south with relatively weak wind speed, similar to those during the sampling of the westward profile. The master variables at the CNR Platform were in the same range as levels observed at other internal sites (Tables 1 and 3). Only dissolved O_2 saturation values were somewhat lower than those measured along the longitudinal profiles and were close to those in the Old Port site (E1; Table 1). Dissolved Organic Carbon was also in the lower range compared to longitudinal profiles, with values similar to those observed at site E4. Ammonium values were close to those quantified during the westward profile.

4. Discussion

4.1. Water masses in the harbor and Pt distribution

Inside the harbor, water mass characteristics are supposedly strongly influenced by the wind/wave conditions, the freshwater supply by the two main water courses (the Polcevera and Bisagno Rivers), and run-off in the port area (Capello et al., 2010). Such physical parameters may influence Pt distribution in the Genoa Harbor. Cutroneo et al. (2012) report the formation of eddies in the current formed by wind in the Genoa area. The relative shallowness of the port area (Table 1) further accentuates the influence of the wind on the entire water column (Capello et al., 2010). Higher wind speed as recorded during the first day (Table 1) was correlated with O_2 saturation and turbidity ($r \sim 0.8$ and -0.8 respectively; data not shown). This result suggests an influence of wind speed on water mixing along the eastward profile. Along the westward profile, weaker winds (coming from the south and probably stopped by breakwaters) showed no correlation with O_2 saturation levels. Considering only the eastward profile, increasing wind and subsequent water mixing is correlated with increasing Pt_D and decreasing Pt_P levels ($r \sim 0.6$

and -0.9 respectively). In the inner harbor, strong wind could lead to vertical and horizontal seawater mixing, sediment resuspension, and redistribution of dissolved and especially particulate components throughout the water column as observed in other studies (e.g. El Sayed et al., 1994; see *Section 4.3.*).

The two profiles sampled westward and eastward from the Old Port show elevated Pt_D concentrations within the whole harbor area, compared to the external sites (E5, E6 and W5, W6). The lowest Pt_D values occurred at the sites E5 and E6 (Fig. 2A) mainly influenced by open Mediterranean water transported with the east-west oriented northern Ligurian Current. Therefore, the Pt_D concentrations in seawater from these sites (~ 0.08 $ng.L^{-1}$) may be considered as representative of surface water in the northwestern Mediterranean Sea. This assumption is supported by identical Pt_D levels of 0.08 $ng.L^{-1}$ in surface waters from an open-sea site, south from the Balearic Islands (Abdou, 2018). Open Mediterranean surface water Pt_D concentrations appear somewhat higher than average Pt_D in the North Atlantic seawater reported in the early nineties (~ 0.05 $ng.L^{-1}$; Colodner, 1991) and recently confirmed by López-Sánchez et al. (2019) for North, Central and South West Atlantic Ocean. Values are also higher than those reported in the northwest Pacific Ocean (~ 0.04 $ng.L^{-1}$; Suzuki et al., 2014). However, the supposed Mediterranean surface water Pt_D is similar to values in the coastal North Atlantic Ocean off the slightly Pt-contaminated Gironde Estuary (0.08 $ng.L^{-1}$; Cobelo-García et al., 2014a) and lies within the range of values reported for the Lérez Estuary seawater end-member (from 0.08 to 0.10 $g.L^{-1}$; Cobelo-García et al., 2013). These observations are consistent with expected relatively higher Pt inputs into the semi-enclosed Mediterranean Sea due to the strong urbanization of its coastline. Similarly, the western profile shows the lowest Pt_D values (i.e. ~ 0.10 $ng.L^{-1}$; Fig. 2A) at the sites located outside the breakwaters (W5 and W6). These concentrations are slightly higher than open Mediterranean Pt_D, suggesting minor local contamination off the harbor and 'downstream' from the sites E5 and E6 (with respect to the

dominant westward Ligurian Current). Conversely, inside the breakwaters, contamination is consistently higher with Pt_D concentrations up to more than 2-fold the open Mediterranean value (Fig. 2A).

Particulate Pt concentrations in suspended particles partly reflect the general concentration gradient from inside the harbor towards the open sea. They were measurable (~ 0.4 to 3 $ng.g^{-1}$) at all internal sites and behind the breakwaters (except site E3), whereas for the external sites from outside the breakwaters Pt_P were below D.L. (< 0.34 $ng.g^{-1}$; Fig. 2B). The Pt_P levels inside the Genoa Harbor were similar to those reported for the Lérez Estuary (~ 1 to 15 $ng.g^{-1}$), interpreted as anthropogenic Pt enrichment (Cobelo-García et al., 2013). Such enrichment may partly originate from small watercourses flowing into the harbor (Fig. 1), even though salinity measurements show little influence of freshwater inputs. Since sampling took place at ~ 5 m depth i.e. below the main influence of freshwater torrents (Capello et al., 2016) and no strong rainfall occurred the previous days (only 3.8 mm on April 2nd), our salinity records mainly reflect seawater influence. In the inner part of the Old Port, the semi closed shape and shallow bottom (< 10 m depth; Table 1) of the harbor make the water exchange times rather long, in particular close to the bottom depth (corresponding to E1 sampling point). Povero et al. (2005) calculated a mean of 20 days for a complete water exchange in this inner part and 7 days in the outer system (central basin and eastern entrance), which is wider and ~ 10 m deeper. Although both calculated water residence times are not representative of the whole area (because they do not consider its irregular shape) and refer mainly to the eastward transect, they can help explaining the Pt enrichment in the inner part of the harbor. They may also explain the decreasing gradient towards the outer basin and the open sea, together with dilution affecting the generally stagnant harbor waters when flowing outside. Moreover, inside the harbor, important dredging activities were undertaken from 2009 to 2014 and are, to a lesser extent, still carried out in the recent years. Since then, turbid plumes, influenced by wind/wave

403 conditions, have been recorded (Cutroneo et al., 2012). Intensification of big ships and ferry
404 transit and berthing increase the presence of turbid plumes (Capello et al., 2010), suggesting
405 that sediment resuspension may represent a source of trace metals, including Pt, in the system.

406

407 4.2. Anthropogenic Pt sources

408 *Industrial activities*

409 Along the eastern profile, from the inner to the outer part of the harbor, Pt_D concentrations
410 tended to increase with a maximum at site E4, close to the mouth of the Bisagno River (Fig. 2A),
411 while the highest Pt_D in the westward profile occurred inside the breakwaters, including site
412 W3 (0.17 $ng.L^{-1}$), i.e. near the Polcevera River mouth. The western part of the harbor hosts coal
413 deposits and a terminal for oil products (Fig. 1). Indeed, westward the Polcevera River mouth,
414 the Multedo oil terminal is one of the most important in Italy and Europe. It handles crude oil,
415 final products (petrol, gasoline, fuel oil) semi-manufactured, and basic petrochemical products,
416 for a maximum total capacity of 30 million tons per year (Recchia et al., 1999). Platinum is
417 commonly used as a catalytic agent in oil industry (e.g. catalytic cracking of crude petroleum;
418 Peavy, 1958) and such activities could therefore be a source of Pt inputs into the coastal system.
419 Built in 1952, the coal power plant of Genoa is also located on the west side of the harbor. Coal
420 industry may contribute to local Pt concentrations, since high Pt concentrations have been
421 reported for coal samples (~ 5 $ng.g^{-1}$, Finkelman and Aruscavage, 1981; up to 70 $ng.g^{-1}$, Dai et
422 al., 2003). The bulk terminal of the harbor containing coal (dry bulk) and oil (liquid bulk) is
423 also located in the western area (Cutroneo et al., 2017). Historical intense oil and coal-based
424 industrial activities in the Genoa Harbor and erosion/leaching of such deposits stored uncovered
425 against wind and/or rain might lead to the presence of industrial coal particles in the suspended
426 particulate matter around the Polcevera River mouth and in the Sampierdarena channel that

connects the outer basin of the Old Port and Polcevera River mouth. Although the Pt concentrations in this oil or coal are unknown, one cannot exclude that oil inputs, industrial coal and/or fly ashes could contribute to the Pt enrichment at this sampling site given the range of values reported in the literature. Since 1953, a steel mill has also been present in the western area and related activities cause the release of particulate matter of different sizes (Mazzei et al., 2006). Metallurgic activities can be a source of Pt release into aquatic environments as recorded in other systems (e.g. Gironde fluvial estuarine continuum; Abdou et al., 2016). Furthermore, in urban systems, other possible Pt sources may arise from direct inputs of dental laboratories, electronic industries, glass manufacturing, Pt-containing pharmaceuticals or industrial catalyst productions (Kümmerer et al., 1999).

Hospital and sewage effluents

Platinum-based compounds have been successfully applied in anti-cancer chemotherapy for decades (e.g. Lenz et al., 2007). Surface waters draining effluents from hospital with oncology ward contain patient excretion of Pt-based anticancer drugs and display Pt concentrations that could exceed natural inputs (Vyas et al., 2014). Monteiro et al. (2017) evaluated Pt_D concentrations in the inflow and outflow of a wastewater treatment plant (WWTP) in Lisbon to ~ 5 and 15 $ng.L^{-1}$ respectively after a dry weather period and ~ 10 and 25 $ng.L^{-1}$ after a raining event. In the western part of the Genoa Harbor, Pt inputs from sewage treatment plants reach the Polcevera river mouth (Fig. 1). Despite probable dilution in natural waters compared to levels previously reported, such inputs may add to Pt sources affecting the sampling site W3 (Pt_D ~ 0.18 $ng.L^{-1}$). Small sewage effluents also occur directly in the Old Port (Fig. 1). Considering only the sites E1 to E4 located inside the relatively stagnant harbor waterbody (due to confinement and low tidal amplitudes; Cutroneo et al., 2017, 2012), the eastward gradients of Pt concentrations have been correlated with parameters reflecting sewage effluent signature.

Inside the harbor, Pt_D concentrations were positively correlated with dissolved oxygen ($r > 0.9$) and pH ($r > 0.6$), and negatively correlated with turbidity, Chl-a, % POC, DOC, and NH_4^+ ($r < -0.9$). The opposite trends occurred for Pt_P concentrations, which were positively correlated with Chl-a, % POC, DOC, and NH_4^+. Assuming that these major variables serve as proxies for wastewater inputs and degradation (Ruggieri et al., 2011), this could explain Pt distribution inside the Old Port. Accordingly, supply of discharged sewage rich in organic matter and poor in oxygen content typically occur into the harbor basins (Ruggieri et al., 2011). The CNR platform (site PF) and surrounding waters are close to the urban area hosting a relevant center for Medical Oncology (red cross/blue circle). Highest levels of Pt_P (14 $ng.g^{-1}$) are recorded at this sampling site and relatively higher levels of Pt_D (0.15 $ng.L^{-1}$) both at 12 pm. For the same sample, sewage-related signals are recorded, with clearly lower O_2 saturation and highest POC levels compared to the other sites. Sites E1 and PF are also characterized by a more confined area with shallower bottom depth (~ 6 m depth). High levels of Pt_P and relatively low levels of Pt_D, where sewage inputs are at maximum (site E1) might be related to: (i) the presence of originally high Pt_P concentrations in wastewaters or run-off, and/or (ii) the adsorption of Pt_D on organic-rich ligands present in wastewaters (high concentrations of dissolved and particulate organic carbon in the turbid sewage plume). The effect of sediment resuspension in these shallower sampling sites is not discarded. Kinetics of suspected adsorption/desorption processes may explain the observed differences in Pt_D and Pt_P distributions between sites (see *Section 4.3.*).

Traffic-related emissions

The Genoa Harbor is in direct vicinity (< 5 km distance) from the urban highway and very close to urban heavy traffic roads, a likely source for Pt bearing particles. Automobile catalysts, which are thought to be the principal Pt anthropogenic source, have atmospheric residence times

ranging from hours to days depending on particle size and density and can be transported from regional to longer distances (Rauch et al., 2006, 2004). Dust and suspended matter with Pt particles are thereafter removed from the atmosphere by wet (rainfall) or dry (gravitation) deposition (Pawlak et al., 2014). For other trace metals such as copper (Cu), enhanced atmospheric input of Cu-rich urban particles showing great water solubility may result in the predominance of the atmospheric input of Cu over the river input (El Sayed et al., 1994). Therefore, in addition to causing water mixing, wind can be a vector of Pt into aquatic systems. The two wind situations observed during our study are typical of the Genoa area. Winds from the N–NE (0–30° N) and SE (135–150° N) are two of the most frequent wind situations in winter and summer, respectively (Cutroneo et al., 2012). Our field campaign took place in spring, a period of the year generally featuring the two situations. The eastward profile was sampled under relatively strong N-NE winds causing the currents in the entire harbor to flow outwards (Cutroneo et al., 2012). Relatively clear gradients of all monitored parameters can be explained by such conditions. Recent data confirm the importance of atmospheric deposition in Pt enrichment of oceanic surface waters (López-Sánchez et al., 2019). Automobile catalyst exhaust Pt inputs come from the land and Pt-bearing particles can be transported by the wind causing a gradient of Pt_P concentrations eastward. In the Genoa Harbor system, such particles could originate from catalyst exhaust fumes and/or industrial fly ashes. On the reverse, the westward profile was carried out under weaker, SE winds and showed less clear parameter variations. The E and SE winds generate a westward current forcing the surface harbor waters inside, while only in the bottom layer a weak outflow can occur (Cutroneo et al. 2017, 2012). However, due to the morphological complexity and the port structures jutting out in all directions, there is an extreme variability in the current direction in the port (Capello et al., 2010) and more data would be needed covering longer time-scales to confirm the present assumptions. If such source types influence Pt partitioning and its spatial distribution, they also

may affect Pt levels both in historical records (e.g. Abdou et al., 2019, 2016) and at short temporal scales as observed in site PF.

4.3. Platinum reactivity and partitioning

Platinum seawater speciation

Platinum concentrations in both dissolved and particulate phases are controlled by several factors implying various biogeochemical processes. Assuming that Pt originates from multiple potential point sources prevailing at different sites it is likely that Pt speciation differs from site to site. Organic forms might be represented by the three Pt-based drugs mainly used in the hospital: cisplatin, carboplatin and oxaliplatin along with their metabolites, while Pt emitted from vehicles or industrial activities may be under inorganic forms. Hospital effluents transport dissolved Pt ranging from < 10 ng.L^{-1} to 250 µg.L^{-1} (Rauch and Peucker-Ehrenbrink, 2015; Vyas et al., 2014), mainly excreted from these anticancer drugs and/or derived metabolites. Such excretion also continues outside the hospital, as more and more patients go home directly after the treatment to the extent that the majority of Pt is emitted from outpatients at home (Lenz et al., 2007; Vyas et., 2014). The phase in which Pt species are released as well as the dissolved/particulate partitioning in sewage and the related removal efficiency in WWTPs remain widely unknown. Previous studies suppose that municipal and hospital effluents contain carboplatin (the most stable drug) as well as degradation products being the monoaquacisplatin and the diaquacisplatin, from anti-cancer drug administration (Lenz et al., 2007; Vyas et al., 2014). Recent work reports that the behavior of organic Pt species in recipient waters is governed by chloride (Cl^-) concentrations with, for cisplatin, decreasing proportion of reactive species with increasing salinity (Curtis et al., 2010; Turner and Mascorda, 2015). Curtis et al. (2010) proved that environmental conditions favoring cisplatin retention and its adsorption on

526 particles are turbid waters of low chlorinity and long residence time. Dispersal is likely to occur
527 in rapidly flushed waters under low turbidity conditions and high chlorinity. Our study site is
528 characterized by high salinities that may limit cisplatin adsorption, but turbid plumes arriving
529 from sewage effluents and long water and particle residence times inside the breakwaters may
530 in turn favor such process. More investigation is needed under similar environmental
531 conditions.

532 Both run-off and sewage also contain PGE-bearing catalytic converter fragments with intact
533 PGE-load (Prichard and Fisher, 2012), which may undergo partial dissolution in contact with
534 seawater. The few data on Pt speciation in seawater suggest that Pt(IV) is the most important
535 oxidation state (Cobelo-García et al., 2013). Laboratory works showed that its inorganic
536 equilibrium speciation is dominated by the stable $PtCl_5(OH)^{2-}$ complex (Gammons, 1996;
537 Cobelo-García et al., 2014a). Laboratory and field observations report decreasing particulate-
538 aqueous distribution coefficient for inorganic forms with increasing salinity (Cobelo-García et
539 al., 2014, 2008; Turner, 2007), suggesting increasing Pt levels in the dissolved phase as Cl^-
540 concentrations increase. The observed eastward particulate/dissolved gradients suggest Pt
541 dissolution from solid carrier phases, either road dust (Sebek et al., 2011) or small sewage
542 particles, and subsequent dilution of Pt_D by seawater that would be favored by Pt-Cl complex
543 formation.

Potential carrier phases of Pt in sites with anthropogenic influence

Given the above, one would expect inputs of different co-existing Pt forms from different overlapping sources into the marine environment with wastewater, run-off of the surrounding area and atmospheric deposition. Numerous discharges occur in the Genoa Harbor area, comprising release of unknown and potentially dangerous substances (Fig. 1) that may contribute to Pt contamination. A rough mass balance ($Pt_D = Pt_P \times SPM \times 10^{-3}$) for the eastern profile inside the harbor suggests that Pt release from suspended particles would account for a Pt_D addition of ~ 0.02 $ng.L^{-1}$, whereas the observed Pt_D values increased by ~ 0.06 $ng.L^{-1}$. The amount of Pt presumably transferred from the particulate to the dissolved phase is not contradictory to the field data but does not explain all the Pt_D addition observed, supporting the idea of additional Pt_D inputs through the different discharges (Fig. 1). Outside the breakwaters, biogeochemical equilibration processes and the resulting higher Pt_D would be masked by massive dilution with open Mediterranean water. Biogeochemical processes, inherent to anthropogenic discharges and the mixing of environmental waters can widely modify the original Pt phase. Previous work has shown that relatively high dissolved metal loads in wastewater inputs equilibrate in the recipient waters. Efficient adsorption on high complexation site particles induces profound changes in element partitioning between the dissolved and particulate phases (e.g. Deycard et al., 2014). Indeed, the residual POC in effluent wastewater mainly consists of reactive (degradable) organic matter, once exposed to natural microorganism communities in the receiving waterbody (Deycard et al., 2017). Such organic matter and especially that containing thiols and reduced sulfur groups, may strongly bind soft metals and potentially compete with inorganic ligands such as Cl^- from the recipient waters (Levard et al., 2013; Wood et al., 1990). Literature suggests that, considering cisplatin flocculation in natural water, complexation with specific organic ligands containing nitrogen or sulphur is likely (e.g. Curtis et al., 2010; Turner and Mascorda, 2015). This means that Pt partitioning between the

two phases might be partly influenced by interactions with POC from wastewater discharges when mixing with coastal waters, although the degree of surface complexation with organic matter remains unknown (Couceiro et al., 2007). Natural sediments may also contain POC and laboratory experiments have proven that Pt adsorption kinetics onto estuarine sediments is greatest for cohesive sediments with relatively high total carbon contents (Couceiro et al., 2007). Another experimental study showed that complexation with organic ligands can be critical to particle-water fractionation of Pt discharged into aquatic systems, removal from the dissolved phase being most favorable when entering a turbid watercourse (Turner et al., 2006). All of these observations seem in line with the reported highest Pt_P levels co-occurring with high turbidity sewage inputs in the Genoa Harbor (Tables 1 and 3; Fig. 2B). Depth profiles of Pt_D concentrations in the Atlantic Ocean also showed a higher particle-reactivity or lower solubility of Pt_D with decreasing oxygen levels (López-Sánchez et al., 2019).

The related daily variations in K_D values at site PF (Table 3) suggest that the observed K_D might not describe equilibrium conditions. However, the average K_D values obtained for the Genoa Harbor (~ 8×10^3) are consistent with values obtained for the seawater end-member of the Gironde Estuary (~ 4×10^3, Cobelo-García et al., 2014a), and the maximum K_D value recorded at the CNR Platform (~ 1×10^5) is similar to those found in the seawater end-member of the Lérez Estuary (Cobelo-García et al., 2013). Outside the Old Port, but still inside the harbor, the growing influence of open seawater with a decrease in turbidity, as well as change in the nature of SPM surfaces (decrease in %POC) could explain low Pt_P concentrations (below detection limit), going along with increasing Pt_D. Considering possible wind effect and water column mixing, remobilization of Pt from particles through the degradation of organic matter and redox reactions (correlation of Pt levels with pH and Eh parameters; Table 2) seems to contribute to Pt_D enrichment at those sampling sites, as observed elsewhere for Pt and other trace metals (Almécija et al., 2016; El Sayed et al., 1994). However, multiple solid phases other than solely

POC can also decrease Pt_D concentrations. Inorganic mineral phases such as iron and manganese oxides may also be important Pt carrier phases (Colodner et al., 1992). In fact, those phases could be more important than organic material for the removal of cisplatin degradation products (Turner and Mascorda, 2015).

Whatever the dissolved or particulate phase transporting Pt, this element has proven to be bioavailable to marine organisms (e.g. Rauch et al., 1999). It is crucial to better understand Pt speciation and distribution, since the physical and chemical forms of this emerging contaminant are expected to considerably influence its biological availability. In fact, previous work on Pt toxicity in marine bivalves has shown strong accumulation and the onset of defense mechanisms, for exposure levels that might be reached in case of acute pollution, especially in semi-closed coastal systems (Abdou et al., 2018).

4.4. Coastal anthropogenic contamination – Pt as a novel urban tracer

Although the geochemical cycles of Pt in coastal environments under high urban/industrial pressure are far from being fully understood (due to the limited number of data), our study, combined to already existing works, allows to draw perspectives for future research in this field. Assuming the dominance of Pt organic forms released by hospital effluents, monitoring of Pt concentrations may serve as a tracer for these effluents release and spreading in the environment together with other proxies commonly used such as POC% or nutrient levels. Main substances expected in effluents are the most stable anti-cancer compounds (including carboplatin) and degradation products from the different drugs (Lenz et al., 2007; Vyas et al., 2014). However, important behavior differences (reactivity, phase affinity, removal…) are observed among Pt-based drugs and their various degradation products (Turner and Mascorda, 2015). Such organic Pt sources need monitoring and characterization, especially considering the increasing cancer

incidence and the related increasing demand for chemotherapy treatment in developed countries (Johnson et al., 2008). Inorganic forms of Pt are assumed to dominate in catalytic converters emissions. High resolution monitoring of concentrations of those forms could therefore reflect atmospheric particle deposition and traffic-related urban contamination in coastal areas. Inorganic Pt forms may also reflect atmospheric contamination related to industrial activities including oil and coal-based industries. The lack of knowledge regarding Pt speciation is directly related to analytical challenges inherent to the ultra-trace environmental levels of this emerging metallic contaminant. Future work should focus on developing analytical techniques for routine Pt quantification in seawater for both dissolved and particulate phases including speciation analyses.

Spatial distribution of Pt concentrations in the Genoa Harbor showed disparities partly depending on urban source proximity, yet, temporal aspects also may be crucial. Dredging activities, daily cycles in traffic intensity, industrial emissions, and/or wastewater composition (Deycard et al., 2014; Mazzei et al., 2006; Kümmerer and Helmers, 1997), as well as wind conditions could lead to variable fluxes of Pt into the harbor waters explaining why Pt_P varied by a factor of ~ 5 (i.e. from 3 to 14 $ng.g^{-1}$ at site PF) within few hours. Spatial and temporal variations in Pt levels inside the Genoa Harbor may therefore reflect both distance from the source and release dynamics of a wide range of different potential sources.

Platinum distribution therefore appears to vary according to urban pollution type, source and intensity, suggesting that this element can serve as an innovative and sensitive tracer of anthropogenic impact from multiple urban sources (traffic, sewage, hospital effluents). The present dataset suggests that such anthropogenic inputs supplied to rivers or directly in the harbor by urban and/or industrial wastewater discharges and by atmospheric deposition may represent important local Pt point sources to coastal waters. Platinum levels observed in the Genoa Harbor waters are far lower than concentrations measured in highly contaminated waters

including polluted rivers (up to ~ 7 ng.L^{-1} in Tokyo Bay urban rivers; Obata et al., 2006) or even hospital effluents (up to 250 µg.L^{-1}; Lenz et al., 2007; Vyas et al., 2014). It remains unclear to what extent dilution of Pt concentrations by recipient seawater or the absence of rainy events during our sample collection could have resulted in relatively low Pt levels. Future research and field sampling should therefore consider sample collection both near pollution sources (i.e. rivers, urban discharges, sewage effluents) and in recipient coastal waters in order to perform relevant mass balance calculations. This should be done at high spatial as well as high temporal resolutions in order to fully understand Pt cycles in urban coastal environments.

5. Conclusions

With TCE increasing environmental release being a global concern, this work provides knowledge on the extent of Pt contamination and biogeochemical processes occurring in a representative urban coastal site. The first information on Pt distribution and reactivity of both dissolved and particulate phases in an industrialized and urbanized Mediterranean harbor is given. Measured concentrations for Pt_D (~ 0.08 to 0.18 $ng.L^{-1}$) and Pt_P (< 0.34 to 14 $ng.g^{-1}$) allowed proposing Pt_D ~ 0.08 $ng.L^{-1}$ (as measured in the Ligurian Current and south from the Balearic Islands) as a first reference value for western Mediterranean surface seawater. There is a clear evidence of anthropogenic Pt contamination at all sites studied within the Genoa Harbor showing distinct concentration gradients. They are attributed to different overlapping local sources such as industry, run-off, hospital effluents, domestic wastewater as well as physical parameters such as wind and dust / catalyst particles atmospheric deposition. Gradients in both Pt_D and Pt_P as well as major variables attributed to input and degradation of urban sewage inside the relatively stagnant harbor waters reflect biogeochemical processes modifying the nature, surface properties and abundance of suspended particles, leading to profound changes in Pt partitioning and carrier phases. While quantification of Pt emitted from vehicle exhaust, supposedly under inorganic form, rise attention, organic forms may also be of major concern in urbanized coastal systems. Such mobilization of anthropogenic Pt can enhance its bioavailability, bio-uptake and induce adverse effects on marine organisms. The role of biogeochemical processes and responses from marine wildlife to contamination, including potential Pt complexation to biologically-derived organic ligands such as algae exudates, are still unknown and need further investigation. On the other hand, this study opens the perspective of using Pt as an innovative tracer of urban inputs that should be applied in other urbanized coastal areas of the Mediterranean Sea and worldwide.

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682

683 **Conflicts of interest**

684 The authors declare no conflicts of interest.

685

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Tables

Table 1: Dissolved and particulate Pt concentrations, Pt distribution coefficients, and master variables monitored along two longitudinal profiles in the Genoa Harbor. The eastward profile corresponds to sites E1 to E6, with E1 being located in the Old Port, while the westward profile corresponds to sites W1 to W6. With: Dissolved Pt concentration (Pt_D; $ng.L^{-1}$), Particulate Pt concentration (Pt_P; $ng.g^{-1}$), Particle-water distribution coefficient (K_D), Wind direction (Wind dir.), Wind speed (Wind sp.; $km.h^{-1}$), Bottom depth (m), Turbidity (Turb.; NTU), Temperature (Temp; °C), Salinity, Redox potential (Eh; mV), pH, dissolved oxygen saturation (O_2%), Dissolved Organic Carbon (DOC; mg/L), Particulate Organic Carbon (POC%), Chlorophyll-a (Chl-a; µg/L), ammonium (NH_4^+; µg/L), d.l.: detection limits, n.d.: not determined.

Param./Site	W6	W5	W4	W3	W2	W1	E1	E2	E3	E4	E5	E6
Pt_D	0.10	0.11	0.14	0.17	0.16	0.17	0.12	0.15	0.15	0.18	0.08	0.08
Pt_P	<d.l.	0.99	<d.l.	0.65	0.65	0.37	2.6	1.4	<d.l.	0.50	<d.l.	<d.l.
K_D ($x10^3$)	n.d.	9.1	n.d.	3.7	4.1	2.2	23	9.9	n.d.	2.8	n.d.	n.d.
Wind dir.	ESE	SSE	SSE	SE	S	SSE	N	NNE	N	NE	N	N
Wind sp.	15	9	7	9	6	6	7	17	22	15	22	15
Bottom depth	24.3	27.6	11.0	13.0	11.0	9.6	6.0	9.7	10.7	16.0	12.5	15.0
Turb.	2.23	7.38	2.89	5.17	2.51	4.17	6.47	4.85	3.88	3.52	2.10	2.13
Temp.	14.61	14.82	14.88	14.80	14.84	15.02	14.94	14.84	14.85	14.96	14.50	14.88
Salinity	38.0	37.9	38.0	38.0	38.0	37.8	37.8	37.7	37.8	37.8	38.1	38.0
Eh	204	203	168	187	187	179	173	182	196	211	181	196
pH	8.24	8.21	8.17	8.22	8.22	8.18	8.14	8.14	8.19	8.17	8.21	8.20
O_2%	94.5	92.5	93.9	90.4	96.0	92.6	69.1	87.9	91.4	94.0	97.9	96.8
DOC	1.05	1.17	1.16	0.98	0.84	1.14	2.05	1.28	1.10	0.68	0.91	1.04
POC%	3.75	2.81	2.60	4.87	2.32	0.89	4.81	2.73	3.11	2.47	4.35	1.94
Chl-a	0.37	1.02	1.12	1.48	0.59	0.95	1.16	0.98	0.82	0.82	0.25	0.35
NH_4^+	<d.l.	25.1	<d.l.	41.5	<d.l.	<d.l.	137	113	111	102	<d.l.	<d.l.

Table 2: Correlation table of Pt_D and Pt_P concentrations with master variables. Values correspond to Pearson's r coefficient. n.d.: not determined. Stars correspond to a significant level of 0.05 (p-value<0.05). Note that only the sites inside the breakwaters are considered.

	Eastward profile (E1 to E4)		**Westward profile (W1 to W4)**	
	Pt_D	**Pt_P**	**Pt_D**	**Pt_P**
Wind sp.	0.59	-0.90	0.43	0.52
Turb.	-0.95*	1.00*	0.80	-0.12
Temp.	0.15	-0.14	-0.07	-0.99*
Salinity	0.43	-0.34	-0.39	0.99*
Eh	0.96*	-0.93	0.83	1.00*
pH	0.63	-0.86	0.63	1.00*
O_2%	0.92*	-0.98*	-0.62	0.10
DOC	-0.99*	1.00*	-0.35	-0.87
POC%	-0.90*	0.94	0.36	0.79
Chl-a	-0.91*	1.00*	0.33	0.12
NH_4^+	-0.97*	0.99*	n.d.	n.d.

Table 3: Dissolved and particulate Pt concentrations, particle-water distribution coefficients, and master variables at the CNR Platform (site PF) at 10 am, 12 pm, and 2 pm. Units of the various parameters are as reported in Table 1.

Param./Time	**10 am**	**12 pm**	**2 pm**
Pt_D	0.09	0.15	0.11
Pt_P	7.7	14	3.1
K_D ($x10^3$)	82	94	27
Wind dir.	N	SSE	S
Wind sp.	4	9	7
Bottom depth	6	6	6
Turb.	4.00	2.60	4.60
Temp.	14.76	14.66	14.73
Salinity	38.0	38.0	38.0
Eh	190	182	191
pH	8.20	8.20	8.21
O_2%	81.9	82.8	87.1
DOC	1.01	0.68	0.63
POC%	2.50	5.15	2.02
Chl-a	1.00	1.40	1.60
NH_4^+	47.0	48.1	44.8

Figure captions

Fig. 1: Sampling sites in the Genoa Harbor. Two sampling profiles were performed with an eastward profile (sites E1 to E6) and a westward profile (sites W1 to W6). Sampling site PF (PlatForm) corresponds to the CNR Platform. White arrows indicate river mouths. WWTPs: Wastewater Treatment Plants.

Fig. 2: Dissolved and particulate Pt concentrations along the two longitudinal profiles in the Genoa Harbor. A: spatial distribution of dissolved Pt concentrations (Pt_D; $ng.L^{-1}$); and B: spatial distribution of particulate Pt concentrations (Pt_P; $ng.g^{-1}$).

List of tables:

Table 1: Dissolved and particulate Pt concentrations, Pt distribution coefficients, and master variables monitored along two longitudinal profiles in the Genoa Harbor. The eastward profile corresponds to sites E1 to E6, with E1 being located in the Old Port, while the westward profile corresponds to sites W1 to W6. With: Dissolved Pt concentration (Pt_D; $ng.L^{-1}$), Particulate Pt concentration (Pt_P; $ng.g^{-1}$), Particle-water distribution coefficient (K_D), Wind direction (Wind dir.), Wind speed (Wind sp.; $km.h^{-1}$), Bottom depth (m), Turbidity (Turb.; NTU), Temperature (Temp; °C), Salinity, Redox potential (Eh; mV), pH, dissolved oxygen saturation (O_2%), Dissolved Organic Carbon (DOC; mg/L), Particulate Organic Carbon (POC%), Chlorophyll-a (Chl-a; µg/L), ammonium (NH_4^+; µg/L), d.l.: detection limits, n.d.: not determined.

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