

First indication of platinum input into the southern North Sea via German Rivers

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ARTICLE INFO

Keywords:
Critical metals
Trace metals
Estuary
Environmental chemistry

ABSTRACT

Platinum (Pt) is an emerging critical metal, but the long-term environmental impacts of anthropogenic Pt remain largely unknown. We report, for the first time, Pt input from three major German rivers (Ems, Weser and Elbe) into the southern North Sea. All three rivers were a major source of Pt, with a maximum of 6.3 pmol L⁻¹ in the Elbe endmember, compared to generally <1.0 pmol L⁻¹ in the North Sea samples. All samples measured in the North Sea were elevated in Pt (mean of ~0.9 pmol L⁻¹) relative to typical open-ocean values (~0.2–0.3 pmol L⁻¹ in the Atlantic and Pacific). Across the Weser and Elbe estuarine transect, an initial sharp drawdown of Pt concentrations at low salinity ($S < 1.5$) was observed, which correlated well with Fe and Mn concentrations, indicating adsorption and co-precipitation at low salinity. At higher salinities ($S \geq 3$) Pt concentrations followed a more conservative distribution relative to salinity. In addition, we followed a 12 h tidal cycle in each of the rivers, which generally reflected an inverse correlation of Pt concentrations against salinity. This study indicates that Pt might be an emerging contaminant in the North Sea, requiring further study to define specific sources.

1. Introduction

The advent of new technologies and medical breakthroughs has led to the increased presence of rare trace elements in the ecosystem (Hatje et al., 2022; Sultan et al., 2024). The relentless and largely unregulated discharge of these metals, primarily from anthropogenic activities, presents new risks to various compartments of the environment, including aquatic ecosystems (Sultan et al., 2024). For example, the discharge of brine from desalination facilities and wastewater into rivers degrades water quality and increases the concentration of a wide variety of heavy metals and nutrients (e.g. As, Cd, Cr, Cu, Pb, Ni, Zn, Fe, Mn and more; Panagopoulos and Giannika, 2024; Rowe and Abdel-Magid, 2020).

Platinum (Pt) is an emerging critical metal with increasing industrial and medical relevance, with 80% of Pt mass transfer in the environment being anthropogenic in origin (Sen and Peucker-Ehrenbrink, 2012). The primary anthropogenic source is road runoff linked to use of catalytic converters in cars, leading to heightened Pt concentrations in some

estuary environments (Berbel et al., 2021; Cobelo-García et al., 2011). Sewage systems are another major contributor to Pt in coastal systems, particularly due to the disposal of chemotherapy agents such as cisplatin, carboplatin and oxaliplatin (Ravindra et al., 2004). Hospital waste water may contain Pt at concentrations as high as 890 pmol L⁻¹ (Abdulbur-Alfakhoury et al., 2021; Vyas et al., 2014), leading to significantly heightened Pt concentrations in riverine systems receiving these effluents, such as the Tagus estuary (Portugal) near waste water treatment plant outfall and the Zenne River (Belgium), ranging up to 66 pmol L⁻¹ (Abdulbur-Alfakhoury et al., 2021; Monteiro et al., 2021). However, the long-term environmental impacts of anthropogenic Pt entering the environment remain largely unknown.

Pt in seawater is typically present at sub-picomolar concentrations, although concentrations up to 1.6 pmol L⁻¹ have been reported in the Indian Ocean (Berezhnaya and Dubinin, 2024; Colodner et al., 1993; Jacinto and van den Berg, 1989; López-Sánchez et al., 2019). Estuaries, characterized by their dynamic chemical and biological interactions play a major role in governing trace metal fluxes into the ocean. Pt in

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ivers and estuaries is also commonly present at sub-picomolar concentrations (Soyol-Erdene and Huh, 2012; Cobelo-García et al., 2013, 2014; Padan et al., 2020; Dang et al., 2022a, 2024), but can reach much higher levels: 5–35 pmol kg⁻¹ in the Tama and Ara Rivers flowing into Tokyo Bay (Obata et al., 2006), and up to 66 pmol L⁻¹ in the aforementioned Tagus Estuary and Zenne River (Abdulbur-Alfakhoury et al., 2021; Monteiro et al., 2021), likely reflecting anthropogenic contamination from the highly-industrialized areas.

For the North Sea, which is affected by numerous industrial activities, there is a complete absence of Pt data, both in its open waters and the river systems flowing into it. Here we present first measurements of dissolved Pt concentrations in the southern North Sea and three major German rivers. The TRAM campaign (“TRAM” = TRacing geogenic and Anthropogenic critical high-technology Metals in the southern North Sea) aimed to assess the input of high-technology metals into the southern North Sea. Research cruise M169 was conducted in December 2020 aboard the research vessel (RV) Meteor in the southern North Sea (German Bight and the estuaries of three major German rivers: Elbe, Weser and Ems), which are potentially influenced by several large industrial centres including Bremen (Weser), Emden (Ems), Hamburg and Dresden (Elbe). In addition, the Thames and Rhine rivers to the southwest provide an additional source of freshwater to the southwestern North Sea. These river plumes mix with Atlantic Ocean inflow, which enters through the English Channel and travels northeast along the European coast. We observed elevated riverine concentrations of Pt compared to rivers and estuaries worldwide (up to 6.3 pmol L⁻¹), as well as elevated Pt in the North Sea (mean: 0.9 pmol L⁻¹) compared to the Atlantic Ocean (~0.2 pmol L⁻¹), filling an important gap in knowledge about this emerging critical metal.

2. Materials and methods

2.1. Study site and sample collection

The sampling campaign was conducted in December 2020 during the research cruise M169 aboard RV Meteor, as a part of the TRAM campaign in the southern North Sea and north German river estuaries. The North Sea section covered the area around the island of Helgoland, the Doggerbank area in the northwest and German Bight. Samples were also collected in Weser, Elbe and Ems estuaries and endmembers (the Ems could not be sampled at salinities ~0.35–22 due to locks). Doggerbank, with relatively shallow waters, is a prominent feature of the North Sea, known for its rich fishing grounds. In this study it represented

a relatively pristine endmember, although it is potentially influenced by the Rhine and Thames to the southwest. The German Bight, an inlet of the North Sea, stretching from the Dutch coast to Denmark, experiences a high maritime traffic and is crucial for shipping, as well as for offshore wind energy. The largest freshwater source to the German Bight is Elbe River (861 m³ s⁻¹) followed by the rivers Weser (323 m³ s⁻¹) and Ems (80 m³ s⁻¹) (Speidel et al., 2024 and references therein). Passing through important industrial areas these rivers act as channels for metal transport from inland Europe to the North Sea, with significant geochemical modifications during estuarine mixing of freshwater and seawater.

Samples were collected shipboard from a range of salinities (S = 0.4–33.7) which was continuously monitored in the surface water along the cruise track (Fig. 1). In total, Pt samples were collected at 32 depth stations and 109 surface stations, including 12-h stationary tidal cycle sampling in the Elbe, Weser and Ems estuary. In addition, one sample from each river endmember was collected from a separate land-based campaign as described by Kraemer et al. (2024). Water samples at higher salinities (S ≥ 23.0) were collected near the surface (6–8 m) and at 2 or 3 additional depths (max at 50–55 m) using a Go-Flo bottle (Ocean Test Equipment) attached to a metal-free Kevlar wire. At low salinity stations (S < 23.0), a pump was used to collect seawater through acid-cleaned tubing at ~2 m depth. Seawater was then filtered through a 0.8/0.2 µm AcroPak capsule into LDPE bottles. Prior to use, the bottles were acid-cleaned using standard GEOTRACES procedure (see <http://www.geotraces.org/methods-cookbook/>) and rinsed with sample 3 times. AcroPak filters were cleaned with 0.1 M hydrochloric acid (HCl) at 45 °C for several hours, rinsed and stored in ultrapure “Milli-Q” water (Milli-Q®; 18.2 MΩ·cm) and conditioned by rinsing with seawater (several litres) and sample water (several hundred millilitres). Samples were acidified to pH 1.7 with ultrapure HCl (Roth™), stored in a cool dark area, and analysed in the home laboratory.

2.2. Tidal influences

To measure the influence of tides on metal concentrations, we collected samples from three 12-h tidal cycles while remaining in a stationary location in the Ems, Elbe and Weser estuaries. These tidal cycle stations are discussed separately (see section 3.1.2. Tidal cycles), but tidal fluctuations likely had some influence on all near-river samples. Cruise M169 began in the Ems River on 11th December after departing Emden, and the first sample was collected at ~13:45, starting at salinity ~23 during low tide. We then proceeded towards higher

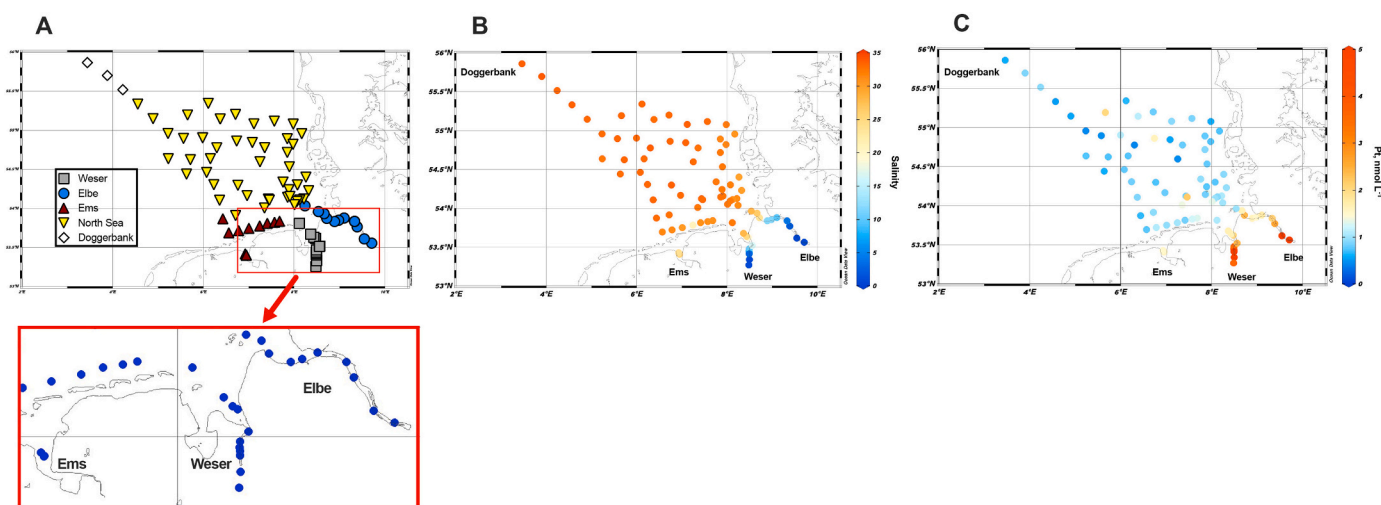


Fig. 1. Map of cruise M169 transect (A), surface water salinity (B) and dissolved (< 0.2 µm) Pt concentrations (C) for sampling stations in southern North Sea, estuaries and lower courses of rivers Ems, Weser and Elbe. The red box in A shows a magnified area of the rivers to show higher-resolution of these sampling stations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

salinity stations in the direction of the North Sea. We returned to the Ems on 14th December at ~08:30 to sample a 12-h tidal cycle starting at high tide, before returning to the North Sea. We entered the Elbe River on 19th December, starting at Hamburg during low tide and sampling downstream along the transect towards Brokdorf during high tide. At Brokdorf, we sampled a 12-h tidal cycle starting at low tide. On 20th December at ~19:30, we sampled along the salinity transect from Brokdorf downstream towards Cuxhaven, mostly with ebb tide. At Cuxhaven we sampled almost at low tide, and further out we sampled with high tide. We then returned to sampling North Sea stations and Helgoland. We entered the Weser River on 25th December, taking the river endmember near Elsfleth at ~15:00 at low tide. We then headed towards Brake, and then Bremerhaven, with rising tide. In Bremerhaven, we collected our final 12-h tidal cycle, starting with high tide around midnight on 26th December.

2.3. Voltammetric analysis of Pt

Dissolved (< 0.2 μm) Pt was analysed in the home laboratories using catalytic adsorptive cathodic stripping voltammetry method following the procedure optimized and detailed in [Padan et al. \(2020\)](#). Briefly, the water samples were UV-irradiated for 24 h in transparent Teflon bottles using a home-built system with 250 W high-pressure mercury vapor lamp. Voltammetric analysis of Pt was conducted using an Metrohm-Autolab potentiostat. The three-electrode system consisted of a hanging mercury drop (HMDE) working electrode, an Ag/AgCl reference electrode, and a glassy carbon rod auxiliary electrode. A 10 mL sample aliquot was added in a home-made quartz cell, then sulfuric acid (Trace Select, Fluka), hydrazine sulphate solution (Riedel-Haen) and formaldehyde (Fluka) were added to a final concentration of 0.7 mol L⁻¹, 0.4 mmol L⁻¹ and 3.0 mmol L⁻¹, respectively. Platinum was measured via standard addition (concentration range adjusted to each sample). Each sample was purged with nitrogen gas for 200 s prior to the first measurement and for 20 s between repetitions and standard addition measurements in the same sample. After 5 s equilibration time, the deposition potential was set to -0.65 V with the deposition time of 60–300 s, depending on the Pt concentration in the sample. In riverine and estuarine samples, an additional desorption step was applied (at -1.3 V for 1 s) to avoid interferences from surface active substances ([Padan et al., 2020](#)). Other parameters of the differential pulse cathodic stripping voltammetry technique used for Pt detection were as follows: step of 0.002 V, modulation amplitude of 0.040 V, modulation time of 0.025 s and interval time of 0.1 s. Finally, the stripping potential was scanned from -0.5 V to -1 V, with a Pt peak forming at about -0.9 V. For quality control purposes, a blank of Milli-Q water and the chemicals involved was assessed prior to each set of measurements and gave a value of 0.015 \pm 0.011 pmol L⁻¹. In the absence of certified reference material for Pt in natural waters, the accuracy of the analysis was verified using known nominal Pt concentrations, yielding recoveries of ~100%. Evaluating the method's reproducibility indicated an experimental uncertainty margin of \pm 10%. Analytical error for each sample was determined based on the curve fit for the standard addition, expressed as 95% confidence interval. For other method specifics readers are referred to [Padan et al. \(2020\)](#).

2.4. Experimental hindrances

We aim to caution readers about the issues that could appear in Pt analysis. One of them is the significant contamination risk associated with commonly used laboratory equipment, such as filtration system. In addition to previously reported contamination risks ([Padan et al., 2020](#)), we experienced Pt contamination due to the use of 0.015 μm filters and ultrafiltration towers, as well as an ultrafiltration unit (1–10 kDa), which prevented the analysis of size fractions smaller than 0.2 μm . Following initial AcroPak filtration, these samples were filtered through 0.015 μm nucleopore (Whatman) filter membranes, after rinsing the

filter tower with 0.1 M HCl (ultrapure, Roth), Milli-Q water, and sample. The release of Pt from the filtration system generated a Pt concentration in the sample that exceeded the 0.2 μm -filtered sample (up to ~20 pmol L⁻¹ in station 13) We hypothesize this was caused by a Pt catalyst used in manufacturing the silicone o-rings (Sartorius) for the filter towers. In addition, a subset of samples was treated using ultrafiltration: following initial AcroPack filtration, seawater was filtered through a Millipore Pellicon 2 tangential flow ultrafiltration unit using either a 10 kDa (~3 nm) or 1 kDa membrane. Unfortunately, we also observed heavy Pt contamination in these samples (up to ~34 pmol L⁻¹). Therefore, we only report AcroPak-filtered (0.2 μm) data here, which was not subject to these contamination sources.

Another concern to consider during experiment planning is the nitrate interference which can significantly reduce the sensitivity of the method for Pt measurement. This hindered the analysis of particulate Pt in this work because the filters were digested and taken up in nitric acid, subsequently disrupting the analytical method.

2.5. Fe and Mn analysis

Concentrations of Fe and Mn were determined with a tandem inductively-coupled plasma mass spectrometer (ICP-MS/MS; Thermo Fisher Scientific iCAP-TQ), that was coupled with the automated online pre-concentration and matrix separation system seaFAST SP2 (Elemental Scientific Inc). To enhance sensitivity, an Apex 2Q desolvating nebulizer (Elemental Scientific Inc.) was used prior to sample introduction into the ICPMS/MS.

The seaFAST SP2 system utilises two Nobias PA1 resin columns (200 μL) and automatically loads, washes and elutes the analytes with automated syringes in a high-purity PFA environment. The preconcentration factor during the online seaFAST application is roughly 15. All seaFAST reagents used for this study were of ultra-high purity and were prepared using ultra-pure deionised (DI) water (18.2 M Ω cm⁻¹ resistivity) from a Sartorius water purification system. We used a 4 mol L⁻¹ ammonium acetate buffer with a pH adjusted to 6.20 \pm 0.05, a 5% HNO₃ eluting acid, a HCl pH 1.7 carrier/diluent solution for autocalibration and autodilution, and a 10% (v/v) NaCl stock solution for matrix matching of all blank, calibration and sample solutions to 3% NaCl (except for seawater reference material). Indium (10 μg L⁻¹) was used as an internal standard (IS) during analysis and prepared in 5% HNO₃. The ICP-MS/MS system was operated in oxygen mode and was tuned to CeO/Ce ratios of around 1%.

2.6. Quality control

Concentrations were quantified by external standard calibration, and for analytical quality control we used the certified reference materials (CRMs) SLRS-6 and NASS-7 (river water and seawater, respectively; both from National Research Council of Canada). The CRMs were measured as triplicates after the calibration, in between the measurement sequence and at the end of the sequence, with a run precision of < 5%. The analytical accuracy is within 2% of certified Fe and within 8% of certified Mn in the SLRS-6, and within 5% of Fe and within 9% of Mn in the NASS-7 ([Table 1](#)). The method precision using the average concentrations of CRM measurements from all measurement sequences is better than 9% for Fe and better than 4% for Mn. Duplicate measurements of selected samples covering the full salinity range revealed general agreement of the obtained concentrations within 10%.

3. Results and discussion

This study investigated the input of dissolved Pt (< 0.2 μm), from three major rivers in northern Germany, the Elbe, Weser, and Ems, into the southern North Sea ([Fig. 1A](#)). The surface salinity and Pt distribution is detailed in [Fig. 1B-C](#).

Table 1

Limit of detection (LOD) and CRM values for Fe and Mn.

	LOD		SLRS-6 this study (n = 7)		SLRS-6 certified		NASS-7 this study (n = 7)		NASS-7 certified	
	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	SD	nmol kg ⁻¹	U _{CRM}	nmol kg ⁻¹	SD	nmol kg ⁻¹	U _{CRM}
Mn	0.05	3	2290	75	2120	100	810	38	740	60
Fe	0.71	40	86,200	5940	84,500	360	360	31	344	26

U_{CRM}: expanded uncertainty.

3.1. Platinum in rivers Elbe, Weser, Ems and their estuaries

Dissolved Pt concentrations displayed large variation across different salinities, ranging from 3.4 to 6.3 pmol L⁻¹ in the river endmembers (S < 0.5) to 0.4–2.2 pmol L⁻¹ in the high-salinity North Sea stations (S ≥ 33.0) (Fig. 1C, 2A, Table 2). Notably, Pt levels were elevated in the Weser River stations, with a maximum concentration of 5.4 pmol L⁻¹. Although the Elbe endmember recorded the highest Pt concentration at 6.3 pmol L⁻¹, Pt levels in the Elbe estuary were generally lower than those in the Weser across all other salinities. This suggests a more rapid removal of Pt, possibly through scavenging at lower salinity conditions.

A significant inverse correlation ($R > 0.7$; $p < 0.05$) was observed between Pt concentrations and salinity across all three estuarine transects, underscoring the role of rivers as sources of Pt to the marine environment. At low salinity levels however, deviations from conservative pattern were noted, suggesting that other processes are affecting Pt concentrations. In the Elbe estuary, a sharp decrease in Pt concentration was observed, dropping from 6.3 pmol L⁻¹ (S = 0.4) to 1.9 pmol L⁻¹ (S = 1.5), and in Weser an initial dropdown of Pt from 5.4 pmol L⁻¹ to 3.8 pmol L⁻¹ was observed (Fig. 2A; Supplemental Table S1). Such non-conservative drawdown has been observed in other estuaries at low salinity (e.g. Cobelo-García et al., 2013) and may reflect processes such as colloidal flocculation or particle reactivity.

Interestingly, in the Weser transect, an increase in Pt concentrations was observed at salinity of ~3, suggesting the phenomenon of de-adsorption from particles. Similar trends of mid-estuary dissolved Pt peaks have been documented in Tokyo Bay, Lérez River estuary and Krka River estuary (Cobelo-García et al., 2013; Obata et al., 2006; Padan et al., 2020). Such patterns may result from a shift in Pt redox state from Pt(II) in freshwater to Pt(IV) in seawater, enhancing Pt release from particles (Cobelo-García et al., 2014; Padan et al., 2020). Namely, while Pt(II) readily binds to particulates in freshwater conditions, Pt(IV) demonstrates reduced particle affinity at increasing salinity due to the formation of hydroxy chloride complexes and diminished electrostatic interactions with negatively charged suspended matter (Turner, 2007). Indeed, experimental findings of Turner (2007) showed enhanced

Table 2

Concentrations of Pt, Fe and Mn in the river endmembers (Elbe, Weser and Ems), maxima (if different than endmember) and North Sea averages. The Elbe and Weser endmembers are based on the shipboard sampling campaign, and the Ems endmember is based on the land sampling campaign due to shipboard sampling limitations.

Sampling region	salinity	Fe (nmol L ⁻¹)	Mn (nmol L ⁻¹)	Pt (pmol L ⁻¹)
Endmembers (± analytical error)				
Elbe	0.40	112 ± 11 (max: 1045 ± 105)	971 ± 97	6.3 ± 0.7
Weser	0.50	616 ± 62 (max: 2060 ± 206)	1225 ± 123 (max: 1669 ± 167)	5.4 ± 0.3
Ems	0.34	1048 ± 105	2673 ± 267	3.4 ± 0.1
North Sea average (± standard deviation)	32.39	3.6 ± 1.5	20 ± 12	0.9 ± 0.3

particle partitioning of Pt in riverine water compared to saline or chloride-amended river water. Particle-water distribution coefficient for Pt decreases from freshwater to seawater, aligning closely with behaviour of metals like nickel (Ni), zinc (Zn), and cadmium (Cd), all affected by the interplay of divalent cations and chloride (Cobelo-García et al., 2008, 2013; Turner, 2007). Being increasingly complexed by chloride ions, these metals become increasingly unavailable for sorption as salinity increases (Turner, 1996). Similarly, Cobelo-García et al., (2008) found Pt behaviour to mirror that of Cd, with reducing tendency to interact with particles across the estuarine gradient, thus facilitating Pt release if loosely bound to particle surfaces.

At salinity > 2.2, Pt concentrations decreased in both the Weser and Elbe, and followed a mostly conservative distribution, excluding an increase in the Elbe at S = 23.4. Except for one endmember sample collected on land, we were unable to sample the Ems at low salinity (S

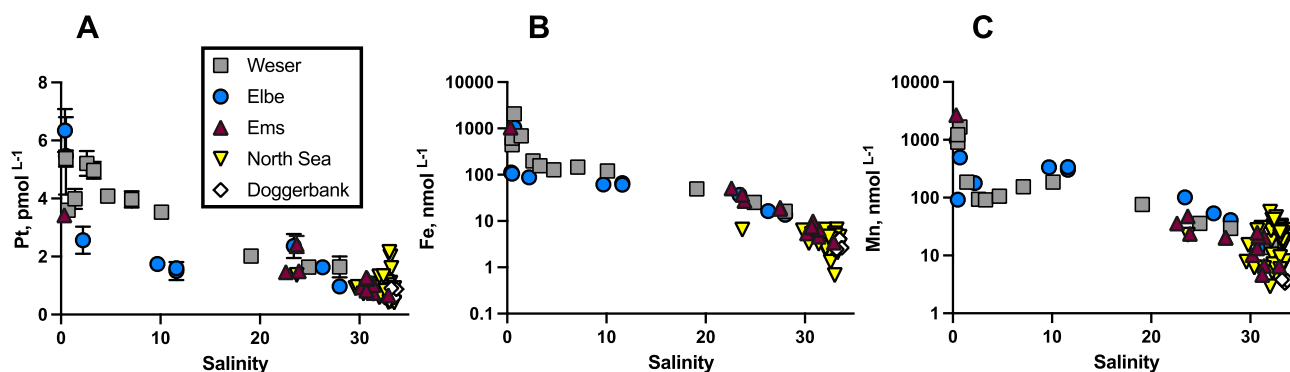


Fig. 2. Dissolved (< 0.2 μm) concentrations of Pt, Fe and Mn plotted against salinity in the Weser (grey squares), Elbe (blue circles) and Ems (red triangles) rivers and estuary mixing zones, as well as the North Sea (S ≥ 32.0, yellow triangles) and Doggerbank (“pristine” northwesternmost point of our transect, white diamonds). Note the logarithmic scales of the Fe and Mn concentration axes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

~0.35–22) due to locks, however Pt levels in available samples from the Ems estuary fell within a similar range to those observed in the Weser and Elbe estuaries for comparable salinity levels.

The different efficiency of Pt removal along the estuarine gradient between the Elbe and Weser estuaries, marked by a more pronounced decrease of Pt concentrations at initial salinity increase, as well as further non-conservative behaviour in the Elbe, could stem from the presence of distinct species of Pt introduced by human activities (for instance, organic Pt complexes from chemotherapy treatments as opposed to inorganic Pt from catalytic converters) which may interact differently with the entrained seawater. Both Weser and Elbe Rivers are influenced by traffic emissions: the Weser by maritime traffic due to its significant port activities, especially in Bremen, and the Elbe by both heavy road and maritime traffic, particularly in the Hamburg area. Furthermore, the Elbe passes through several urban areas that contribute to road traffic emissions. The Elbe, due to its flow through more and larger urban centres (e.g., major cities such as Dresden, Hamburg, and Magdeburg) with their large populations and numerous medical facilities, would also be more exposed to hospital effluents. Platinum emissions from catalytic converters would be in the form of colloidal nanoparticles (metallic or oxides), which gradually transform into dissolved complexes in natural waters. In the effluents from wastewater treatment plants (WWTP), Pt predominantly exists in the form of organoplatinum compounds, including aquation and hydrolysis products of anticancer drugs (Abdulbur-Alfakhoury et al., 2021). Platinum in these forms exhibits a reduction in its tendency to adsorb to suspended particles along the estuarine gradient since they become progressively less reactive as the chloride concentration increases (Cobelo-García et al., 2014). Differences in Pt behaviour might be due not only to the distinct Pt sources but also to the unique environmental conditions and dynamics in each river system. For example, the concentration and nature (e.g., greater surface reactivity) of colloidal particles in the Elbe may promote more effective Pt removal, or the differences in natural organic matter could affect Pt behaviour by forming complexes with organoplatinum compounds, contrasting with the reactions of inorganic Pt from catalytic converters. The presence of other pollutants and chemicals or the distinct microbial communities in each river could also modify particle aggregation and settling behaviour, indirectly affecting the flocculation and removal of Pt from the water column.

Moreover, the differences in hydrodynamics, including flow rate, turbulence, water column depth and formation of salinity gradient, along with variations in sediment properties may also play a crucial role in Pt trajectory. River flow rate data (www.pegeonline.wsv.de) showed relatively low fluctuation for the dates and times that each river was sampled: $36 \pm 2 \text{ m}^3\text{s}^{-1}$ for the Ems (11–14 December), $302 \pm 1 \text{ m}^3\text{s}^{-1}$ for the Elbe (19–20 December), and $171 \pm 12 \text{ m}^3\text{s}^{-1}$ for the Weser (25–26, 28 December). However, the flow rate for the Weser was notably high at sampling compared to December 2020 average ($115 \pm 39 \text{ m}^3\text{s}^{-1}$), while the Elbe and Ems had low flow during sampling compared to the month's averages ($336 \pm 26 \text{ m}^3\text{s}^{-1}$ and $59 \pm 33 \text{ m}^3\text{s}^{-1}$, respectively). All rivers experienced a notable increase in flow rate starting on ~22 December, resulting in the comparatively high outflow during Weser sampling, so it is possible that this variability also contributed to the observed differences in Pt concentration between the rivers.

3.1.1. Relationship with Fe and Mn

Iron (Fe) and manganese (Mn) oxides in aquatic environments form colloidal particles, which can effectively scavenge platinum group elements from the water column through surface adsorption or incorporation into the oxide structure (see e.g. Liu and Gao, 2019). Mashio et al. (2017) identified Pt contents in Fe and Mn oxide components of sediment, indicating that Fe and Mn colloids have played a role in its removal from the water column. Understanding the significant role of Fe and Mn oxides in adsorbing and co-precipitating trace metals due to

their high surface reactivity, we recognized the importance of assessing their concentrations in our samples.

The Weser River showed generally the highest levels of Fe at low salinity ($S < 1$; $0.6\text{--}2.10 \mu\text{mol L}^{-1}$). The Elbe and Ems also had a near-endmember concentration of $\sim 1.0 \mu\text{mol L}^{-1}$, although the rest of the Elbe datapoints were comparatively lower ($0.1 \mu\text{mol L}^{-1}$) (Fig. 2B, Table 2). For both the Weser and Elbe, the maximum concentration was observed at $S \sim 0.7$, rather than at the lowest salinity endmember. The low salinity concentrations for Mn were more similar between the transects, with the Ems endmember being the highest ($2.7 \mu\text{mol L}^{-1}$; Fig. 2C). For both Mn and Fe, unpaired *t*-tests showed no significant difference between the Elbe and Weser transects overall ($p > 0.05$). Following the confluence of the rivers with saline waters in the Weser and Elbe estuaries, there was a substantial reduction in the concentrations of both elements, dropping to below $0.10 \mu\text{mol L}^{-1}$ ($S \geq 19$). Manganese concentrations displayed a mid-salinity increase in the Weser and Elbe, with a maximum (excluding the tidal cycle station) at $S \sim 10\text{--}12$ ($0.33 \mu\text{mol L}^{-1}$). This increase could be attributed to resuspension of Mn from sediments or reduction of Mn oxides to more soluble Mn(II) under suboxic conditions. Speidel et al. (2024) suggested pore-water outwelling is a significant contributor of Mn to researched North Sea area, aside from riverine inputs. Their research, albeit using a lower-resolution salinity scale, also recorded a mid-salinity Mn peak in Elbe, and reported similar Mn concentration ($\sim 0.09 \mu\text{mol L}^{-1}$) as we observed in Elbe estuary at salinity ~ 1.0 (Speidel et al., 2024). Weser endmember data were not reported, but at comparable salinity ($S = 5.0$) in the Weser estuary their findings indicated a higher Mn concentration; around $0.45 \mu\text{mol L}^{-1}$, compared to the $\sim 0.10 \mu\text{mol L}^{-1}$ we observed. We note however, that seasonality plays a major role in the geochemical behaviours in the Wadden Sea (Beck et al., 2020), so the differences in sampling time by Speidel et al. (March 2019), may contribute to some of the observed differences from our study.

In all the samples in this study, there was a trend of increasing Pt concentration with increasing Mn and Fe concentrations, particularly evident at higher Pt ranges (Fig. 3), which implies considerable physical or chemical association between these metals, such as co-precipitation or adsorption processes, in addition to being derived from the same riverine sources and dilution effects. This association appeared to be stronger at higher metal concentrations i.e. at lower salinities. The correlation between Pt and Mn ($R = 0.50$; $p < 0.0001$), and Fe ($R = 0.47$; $p < 0.0001$) (Fig. 3) both indicate a moderate positive relationship. At lower concentrations (e.g., $\leq 2 \text{ pmol L}^{-1}$ Pt) the relationship was less pronounced. However this is the area of higher salinity where Pt affinity to particles is highly diminished (Cobelo-García et al., 2014; Turner, 2007).

There is limited comparative data of Pt with Mn and Fe in estuaries, but where it exists, the relationship between dissolved Pt, Fe and Mn is variable. In the estuary and Gulf of St. Lawrence (Canada), Pt, Fe and Mn (as well as Cd) all displayed uncharacteristically conservative mixing behaviour with respect to salinity during the winter season (Dang et al., 2022a, 2022b). This was explained by the lack of colloidal and organic matter under winter ice conditions, resulting in relatively little removal of these metals from colloidal flocculation. In the Krka River estuary (Croatia), Pt also displayed near conservative mixing behaviour, although a slight non-conservative deviation at $S < 10$ was attributed to a change in Pt redox speciation, favouring desorption from particles (Pađan et al., 2020). On the other hand, dissolved ($< 0.1 \mu\text{m}$) Fe and Mn in the same estuary displayed highly non-conservative behaviour, with significant partitioning to larger size fractions (Marcinek et al., 2022). In the Lérez River estuary (Spain), dissolved Pt and Fe both displayed non-conservative behaviour, but in different ways (Cobelo-García et al., 2013). Dissolved Pt had an initial drawdown at low salinity ($S < 2$), followed by an increase at higher salinity. As salinity increased, Pt showed decreased particle reactivity, attributed to changes in its redox state. Fe followed a general decrease until $S \sim 15$, and then increased due to additional inputs in that region of the estuary. In all cases, the riverine

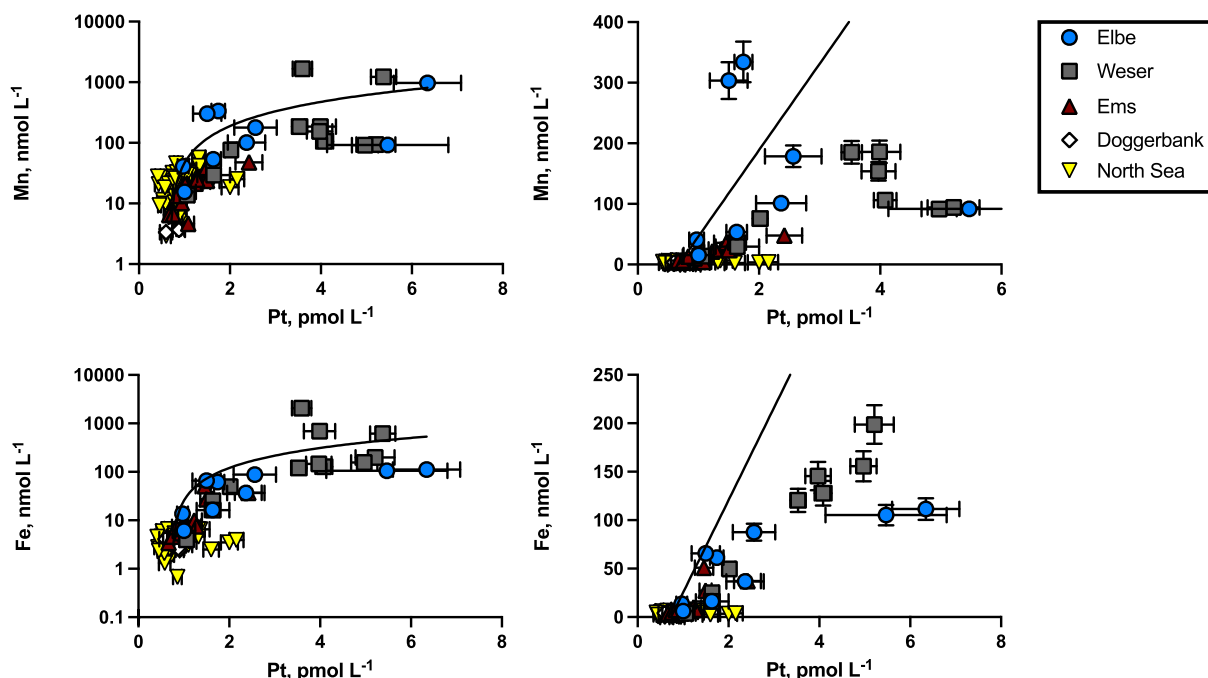


Fig. 3. Dissolved (< 0.2) Pt relationship with Mn (top) and Fe (bottom) in the Weser (grey squares), Elbe (blue circles) and Ems (red triangles) rivers and estuary mixing zones, as well as the North Sea ($S \geq 32.0$, yellow triangles) and Doggerbank (“pristine” northwesternmost point of our transect, white diamonds). Linear regression is shown with black lines. On the left, all datapoints are shown in log scale. On the right, magnified views focusing on lower concentrations of Mn and Fe, are shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

endmember concentrations for Fe, Mn and Pt were lower than measured in our study: $< 20 \text{ nmol L}^{-1}$ for Mn and $< 15 \text{ nmol L}^{-1}$ for Fe and in the Krka estuary, $< 500 \text{ nmol L}^{-1}$ for Fe in the Lérez and St. Lawrence estuaries, and sub-picomolar Pt in all three (Table 3). Therefore, the relationship between Pt, Fe and Mn is complex, depending on the estuary environment, and not always directly correlated.

3.1.2. Tidal cycles

The Elbe, Weser, and Ems estuaries experience semi-diurnal tides with similar tidal ranges. Despite their proximity and being influenced by the same tidal and atmospheric forces, these estuaries, located about 100 km apart, exhibit distinct water stratification and tidal dynamics due to different river runoff conditions (Stanev et al., 2019): at intra-tidal time scales, the relationship between water level and salinity varies considerably among the estuaries, with the Elbe showing the largest differences between flood and ebb tides, and the Ems the smallest due to smallest river runoff. Both tidal gauges and simulations reveal distinct changes in tidal range along each estuary (Stanev et al., 2019). In the Weser Estuary, the tidal range increases from the northern part of the outer estuary to Bremen. The Ems Estuary’s tidal range is similar to the outer Weser but decreases landward south of Emden, resembling the pattern seen in the Elbe River.

To delve into Pt dynamics during these tidal cycles, surface samples were also collected in the estuary zone from the three rivers at stationary sampling points over the course of ~ 12 h, in order to capture a complete tidal cycle (Fig. 4). Among these, the Weser exhibited the highest salinity range ($S = 7.0\text{--}17.0$) revealing pronounced inverse correlation with Pt ($R = 0.92$; $p = 0.001$) (Supplemental Fig. S1A), which was expected from conservative mixing observed in its estuarine transect. In the Elbe and Ems (with salinity ranges 1.5–6.6 and 22.0–25.0, respectively), the link between Pt concentrations and salinity was less straightforward, lacking significant correlation ($p > 0.05$), thereby suggesting that factors beyond simple dilution were modulating Pt concentrations, perhaps including chemical speciation changes, particle

interactions (e.g., with Fe and/or Mn colloids), biological influences, or hydrological factors (e.g., tidal currents promoting sediment resuspension).

Further Fe and Mn analysis within these tidal cycles revealed distinct behaviours between these elements. Iron concentrations were consistently higher at low tides across all three estuaries and showed a significant inverse correlation ($p < 0.05$) with salinity in the Elbe and Ems but not the Weser (Supplemental Fig. S1B), indicating that additional factors (e.g., sediment resuspension) control dissolved Fe concentrations in Elbe and Ems. Total suspended solids (TSS) also correlated inversely with salinity in the Elbe as well as the Weser (no data for the Ems; Supplemental Fig. S2), indicating that particle scavenging likely plays a role in Fe concentrations. Conversely, Mn displayed a positive correlation with salinity (significant in all except Ems; Supplemental Fig. S1C) and inverse correlation with TSS, indicating that interaction with particles directly controls Mn concentrations (e.g. from scavenging or Mn oxidation). Taken together, Fe correlated positively with Pt ($p = 0.0008$), while Mn had no significant correlation with Pt ($p > 0.05$) (Supplemental Fig. S3).

This tidal behaviour suggests that additional Mn sources, possibly stemming from sediment mobilization or contributions from urban and industrial runoff, become more pronounced during high tide conditions in all three estuaries. Tidal currents can disturb bottom sediments, remobilizing Mn that was previously bound and reintroducing it into the estuarine waters, which would be particularly relevant in Elbe estuary with robust tidal actions and the highest river inflow. The Mn variance observed here contrasts with findings by Speidel et al. (2024), who showed a tidal pattern for Mn with highest concentrations during low tide. However, the stations of tidal cycle sampling in their study were close to islands of Spiekeroog and Langeoog and the Otzumer tidal inlet, with distinct geographical and hydrological settings compared to the estuarine settings examined in our study.

Table 3
Global comparison of Pt concentration in different water samples.

Sample	Pt (pmol L ⁻¹)	Reference
Open seawater:		
Atlantic Ocean	0.16–0.30	(López-Sánchez et al., 2019)
North Pacific	0.19–0.25 0.25 ± 0.03	(Suzuki et al., 2014; Fischer et al., 2018)
Indian Ocean	0.20–1.60	(Jacinto and van den Berg, 1989)
Southern North Sea	0.41–2.2 (mean = 0.9)	This study
Coastal seawater and estuaries:		
Douro estuary, Portugal	0.40–1.03	(Abdou et al., 2023)
Ave estuary, Portugal	1.18–10.10	(Abdou et al., 2023)
Tagus estuary, Portugal	0.62–60.00	(Monteiro et al., 2021)
Gulf of St. Lawrence, Canada*	0.10–0.52	(Dang et al., 2022a, 2024)
Krka River estuary*	0.11–0.49	(Padan et al., 2020)
Gironde estuary, France	0.40–0.84	(Cobelo-García et al., 2014)
Lérez estuary, Spain	0.02–0.62	(Cobelo-García et al., 2013)
Coastal water of the North Yellow Sea	1.28–4.48	(Liu et al., 2018)
Sea of Okhotsk, Japan	0.20–0.24	(Suzuki et al., 2014)
Japan Sea, Japan	0.20–0.25	(Suzuki et al., 2014)
Ariake Sea, Japan	0.41–10.20	(Mashio et al., 2021)
Coastal water of Boso to Sanriku areas, Japan	0.20–1.50	(Mashio et al., 2017)
Tokyo and Otsuchi Bay, Japan	0.27–1.48 0.07–7.74	(Mashio et al., 2016) (Mashio et al., 2016)
Ara River estuary, Japan	5.00–13.60	(Obata et al., 2006)
Tama River estuary, Japan	4.80–35.20	(Obata et al., 2006)
River water:		
Marque River, France	1.03–3.08	(Abdulbur-Alfakhoury et al., 2021)
Zenne River, Belgium	15.40–66.60	(Abdulbur-Alfakhoury et al., 2021)
East Asia rivers	< 1.40 (mean = 0.38)	(Soyol-Erdene and Huh, 2012)
North German rivers	3.4–6.3	This study

3.1.3. Global comparisons

Platinum originates from a mix of natural and anthropogenic sources in estuaries with industrial catchment areas, including leaching of rocks and soils, waste inputs from hospitals and municipal sewage, or the dissolution from catalytic converter particulates. Research on Pt levels in natural waters reveals values ranging from tens of fmol L⁻¹ (Cobelo-García et al., 2013) to tens of pmol L⁻¹ (Abdulbur-Alfakhoury et al., 2021; Monteiro et al., 2021; Obata et al., 2006). In comparison to global estuarine and coastal data (Table 3), Pt levels in north German rivers and their mixing zones are notably higher than many reported values, for instance, for pristine rivers in East Asia with average concentration of 0.38 pmol L⁻¹ or European estuaries like the Gironde and Douro with 0.4–0.8 pmol L⁻¹ and 0.4–1.0 pmol L⁻¹, respectively. Even in these rivers and estuaries, Pt is elevated compared to levels measured at adjacent coastal seas or baseline natural levels such as ~0.2–0.3 pmol L⁻¹ typically measured in the Pacific and Atlantic Ocean surface water. The rare exceptions are pristine rivers such as the Lérez and Krka Rivers with a dilution effect on coastal seas. These two examples with a 0.02 pmol L⁻¹ of Pt measured in comparatively minor urban setting of the Lérez Estuary (Cobelo-García et al., 2013), and the pristine Krka River with 0.1–0.2 pmol L⁻¹ of Pt, underscore the presence of the natural subpicomolar Pt concentrations in rivers that are not extensively disturbed by urbanization. However, increasing evidence points to significant Pt pollution in rivers and estuaries passing through densely urbanized regions, especially from wastewater discharges, including those from medical facilities. Studies have found high Pt levels in areas such as the Ave estuary (Abdou et al., 2023) and inland seas of Japan (Mashio et al.,

2021), but exceptionally high concentrations were observed in rivers Ara and Tama running through densely populated areas of Tokyo, or in the Zenne River and Tagus estuary influenced by WWTP outflows (Abdulbur-Alfakhoury et al., 2021; Monteiro et al., 2021; Obata et al., 2006). Results by Monteiro et al. (2021) highlighted waste waters as a primary conduit for Pt into the Tagus estuary, gathering stormwater and sewage from large drainage urban basin in the most densely populated part of Lisbon region, with high Pt levels in the effluent of the WWTP most likely derived from Pt-based anticancer compounds.

3.2. Platinum in the North Sea

In the offshore North Sea stations ($S \geq 32.0$), Pt concentrations ranged between 0.4 and 2.2 pmol L⁻¹ showing a marked elevation compared to the ~0.2 pmol L⁻¹ levels observed in the Atlantic Ocean, as reported by López-Sánchez et al. (2019). Even in the offshore “pristine” Doggerbank area, Pt concentrations were found to be between 0.5 and 0.9 pmol L⁻¹. The slightly elevated Pt in Doggerbank compared to some of the other North Sea samples may be attributed to the slightly reduced salinity here and may indicate the influence from the Thames and possibly Rhine River plumes to the southwest. In all cases, Pt surpassed levels typically noted in open ocean waters (Colodner et al., 1993; Jacinto and van den Berg, 1989; López-Sánchez et al., 2019) (Table 3). Notably, Jacinto and van den Berg (1989) also documented Pt levels reaching up to 1.6 pmol L⁻¹ in the Indian Ocean, suggesting that higher Pt concentrations are not solely confined to the North Sea.

Pt in marine environments can exhibit diverse depth distribution patterns, identified as scavenged-type, recycled-type, hybrid-type or concentration-invariant profile (Berezhnaya and Dubinin, 2024; Colodner et al., 1993; Fischer et al., 2018; Goldberg et al., 1986; Jacinto and van den Berg, 1989; López-Sánchez et al., 2019; Suzuki et al., 2014). We observed no clear trend in Pt depth distribution patterns across the North Sea (Supplemental Fig. S4, Supplemental Table S2), which may stem from variable behaviour of Pt, or from the constrained sampling capabilities in relatively shallow stations. Moreover, the North Sea is well-mixed in winter without major stratification, and our sampling depth only reached 50–60 m in the study area. Interestingly, Pt concentration at station 165 near Heligoland was significantly elevated at 18 m depth (3.0 pmol L⁻¹), possibly reflecting sediment disturbance from dredging activities in the Elbe River (Irion et al., 1987; Schmidt and Schönfeld, 2022; Witt et al., 2004), a process that been shown to increase levels of some metals (e.g. Mn and Co; Silva et al., 2024). Mashio et al. (2017, 2021) reported vertical profiles of dissolved Pt in coastal seawater of Japan with increase in the Pt concentrations from the surface to the bottom (maximum sample depth range: < 20 m to 750 m), suggesting a possible benthic supply of Pt in seawater. They posit that sedimentary processes are the primary contributors of high Pt levels in the water column. Moreover, their model indicates a prolonged residence time of Pt in the marine environment compared to residence time of seawater, with the interaction between chloride ions and loosely bound sedimentary Pt potentially facilitating the desorption and subsequent release of Pt into overlying waters.

3.3. Outlook and environmental implications

This study showed that northern German rivers represent a major source of Pt to the southern North Sea, resulting in elevated concentrations relative to the open ocean. However, the origin of the Pt (prior to reaching the river endmember) remains unknown. Further investigation of both river and sediment samples is needed to determine the specific sources of Pt and to gain a comprehensive understanding of its estuarine behaviour, particularly in light of the diverse pathways through which Pt enters these aquatic environments. Given that the majority of Pt mass transfer in the environment is anthropogenic in origin (Sen and Peucker-Ehrenbrink, 2012), it is probable that input from industrial centres (e.g. through road runoff or sewage) is

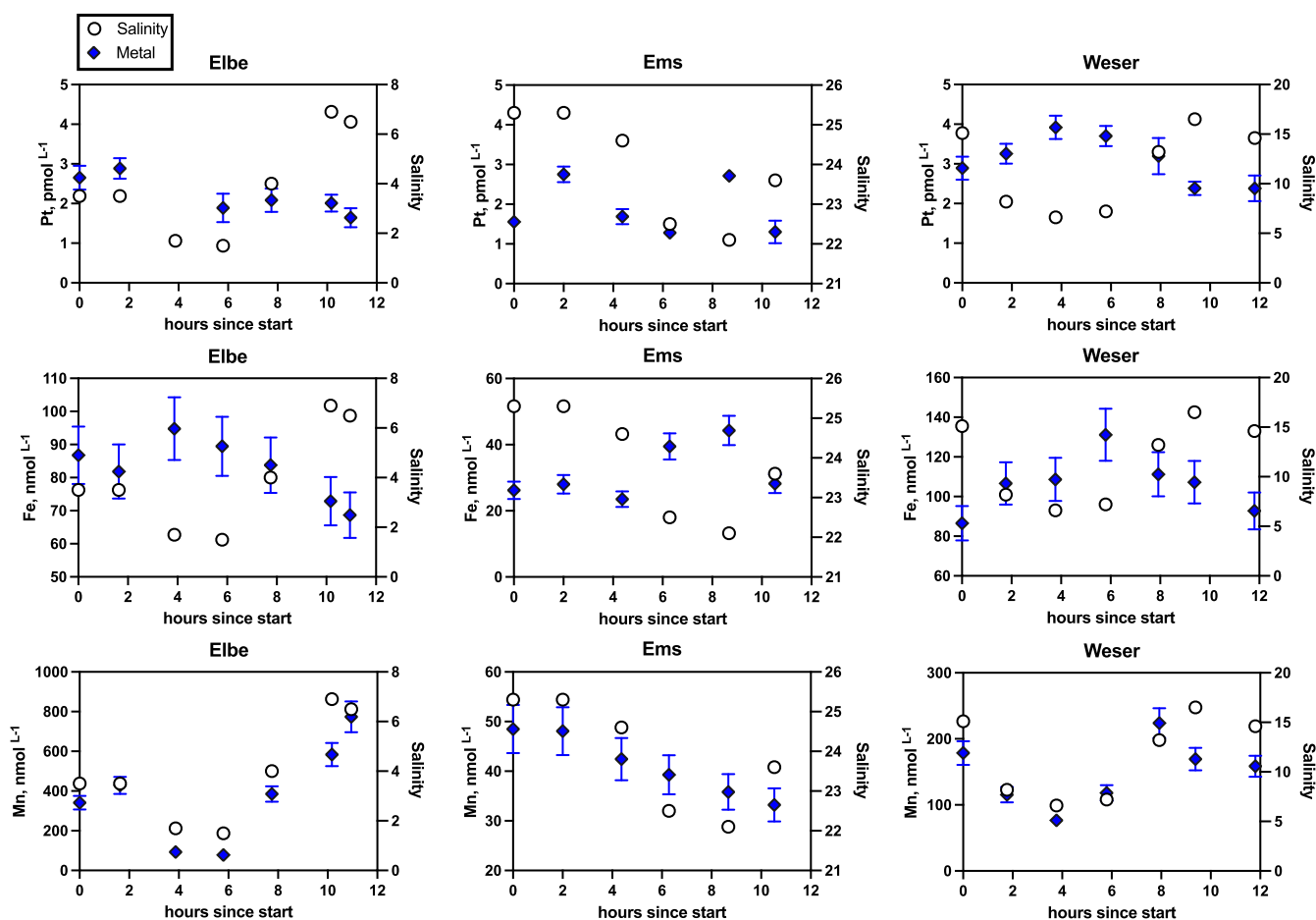


Fig. 4. Tidal cycles in the Elbe, Ems and Weser River transects. Dissolved ($< 0.2 \mu\text{m}$) Pt, Fe and Mn concentrations (blue diamonds) and salinity (white circles) are plotted against time. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

contributing to Pt input into the North Sea. Looking at Pt ratios with elements known to be either geogenic or anthropogenic in origin would help differentiate between these sources. For example, Gd is commonly found in wastewater, and Pt/Rh ratios have been used to determine to trace Pt to traffic emissions (Abdou et al., 2023).

Moreover, the potential environmental impacts of Pt at these concentrations (e.g., several pmol L^{-1}) are poorly understood. Biological uptake and accumulation of Pt by aquatic animals such as algae, mussels, oysters, snails or different fish species has been demonstrated in both laboratory experiments and field studies (e.g., Abdou et al., 2019, 2020a, 2020b, 2023; Neira et al., 2015; and references reviewed in Ruchter et al. (2015) and Zimmermann et al. (2015)). Time series studies of 20 years (Neira et al., 2015) and 25 years (Abdou et al., 2019) have shown an increase in Pt content in mussels (up to 8-fold in Abdou et al., 2019), corresponding to increased use of catalytic converters. However, the full extent of its long-term biological impact on marine ecosystems and the potential for biomagnification remains unknown. Pt has been shown to be toxic and genotoxic to plants and animals (Gagnon et al., 2006), but the studied concentrations (0.1–10 ppm) far exceeded concentrations typically observed in rivers and estuaries worldwide. Given its propensity to bioaccumulate, further studies are needed to determine the threshold of Pt toxicity to aquatic life.

4. Conclusion

This study examined, for the first time, Pt dynamics across the southern North Sea and Elbe, Weser and Ems estuaries. Platinum

concentrations were highest in river endmembers (3.4–6.3 pmol L^{-1}) and decreased towards the North Sea (0.4–2.2 pmol L^{-1} ; mean = 0.9 pmol L^{-1}), with an inverse correlation to salinity, underscoring rivers as key Pt sources to marine environments. The higher Pt values in the North Sea region may indicate additional influence from the Thames and Rhine rivers. Analysis of Pt concentrations during estuary tidal cycles also indicated an inverse trend with salinity in the Weser River, although this correlation was not significant in the Elbe and Ems. Thus, in addition to these dilution effects, Pt concentration was also influenced by non-conservative processes including potential adsorption and de-adsorption mechanisms.

Platinum concentrations are controlled by a variety of factors in estuary and marine environments. Previous studies have shown that Pt in ocean water columns shows a combination of scavenged-, recycled-, hybrid- and conservative-type profiles (see e.g. Berezhnaya and Dubinin, 2024 and references therein). In estuaries, large variability in Pt behaviour has also been observed, with it sometimes being highly reactive and non-conservative (e.g. due to particle adsorption/desorption, colloidal flocculation and/or Cl-ion complexation; Cobelo-García et al., 2013, 2014), and sometimes near-conservative and controlled primarily by mixing and dilution (Dang et al., 2022a; Pađan et al., 2020). Here we observed primarily conservative behaviour, with the exception of non-conservative drawdown at low salinity. We also compared Pt behaviour to Mn and Fe, whose concentrations are largely controlled by particle scavenging. Pt correlated the most strongly with Mn and Fe at lower salinities, indicating particle adsorption contributed to removal of Pt at low salinity, while at higher salinity, Pt concentration was

governed primarily by dilution. In contrast to the clear salinity trends in surface samples, North Sea water column profiles showed no consistent trends with respect to depth.

Compared to rivers and estuaries worldwide, Pt in the Elbe, Weser and Ems surpassed most (though not all) reported values, suggesting important regional inputs and behaviours. The detected range of Pt concentrations in the southern North Sea also exceeded the established natural background concentration typically found in the waters of both the Pacific and Atlantic Oceans ($\sim 0.2\text{--}0.3\text{ pmol L}^{-1}$), indicating a possible anthropogenic influence on the North Sea Pt levels from the three northern German rivers studied, as well as possibly the Rhine and the Thames.

Pt is an emerging critical metal with increasing anthropogenic input into the marine environment. Although we cannot determine specific sources of Pt into the rivers (e.g. natural vs. anthropogenic) with this study, our findings merit further investigation into Pt sources, sinks, and determine how much of this Pt input is anthropogenic in origin. In addition, toxicity studies are needed to determine whether the elevated Pt concentrations observed in these rivers and estuaries pose a potential threat to marine life.

CRediT authorship contribution statement

A. Hollister: Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **S. Marcinek:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **K. Schmidt:** Writing – review & editing, Investigation, Formal analysis. **D. Omanović:** Writing – review & editing, Supervision, Methodology, Funding acquisition. **Mai-Brit Schulte:** Writing – review & editing, Formal analysis. **A. Koschinsky:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Data availability

All trace metal (Pt, Fe and Mn) data are shown in Supplemental Tables S1–S2. Further information about cruise M169 can be found in the cruise report (doi: [10.48433/cr_m169](https://doi.org/10.48433/cr_m169)).

River flow data was obtained from the Federal Waterways and Shipping Administration (Wasserstraßen- und Schifffahrtsverwaltung des Bundes: WSV), provided by the Federal Institute for Hydrology (Bundesanstalt für Gewässerkunde; BfG) (<https://pegelonline.wsv.de>).

Acknowledgements

Research cruise M169 (project no. GPF-20-3_091) and the first evaluation phase were funded by the German Science Foundation (DFG). We thank the captain and crew of the R/V Meteor and the entire ship-based scientific team on cruise M169 (refer to cruise report (doi: [10.48433/cr_m169](https://doi.org/10.48433/cr_m169))). We also thank the land-based team (Michael Bau, Keran Zhang and Anna-Lena Zocher; Constructor University Bremen) for taking the Elbe, Ems and Weser river water campaign samples. Dennis Kraemer, Mirja Bardenhagen, Rene Himstedt, Mathias Hilsberg (BGR), and Franziska Klimpel (Constructor University Bremen) are thanked for their help during sample preparation and SeaFAST Fe and Mn analyses at BGR. We also thank Dr. Ana-Marija Cindrić (Ruder Bosković Institute) for her assistance in platinum analysis methods. We further acknowledge the help of Dennis Kraemer and Robert Sommerfeldt (BGR) for their support with processing the OPUS turbidity sensor data.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marchem.2024.104439>.

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