Platinum input from German Rivers into the North Sea (cruise M169)

Adrienne Hollister[1], Saša Marcinek[2], Mai-Brit Schulte[1], Dario Omanovic[2] and Andrea Koschinsky[1]
[1]Constructor University, Bremen, Germany | [2]Ruđer Bošković Institute, Zagreb, Croatia

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 North Sea. Cruise M169 was conducted in December 2020 in the southern North Sea, from river endmembers (S = 0.4–0.5) to the more pristine Doggerbank region (S = 33–34). In addition, we followed a 12-h tidal cycle in each of the rivers. We found all three rivers to be a major source of Pt to the estuary, reaching a maximum of >6 pmol L^{-1} in the Weser endmember, compared to < pmol L^{-1} to the northwest near Doggerbank. In general, Pt concentrations followed a conservative distribution relative to salinity, although in the Elbe, an initial sharp drawdown at low salinity (S < 1.5) was observed, indicating particle adsorption and/or colloidal flocculation. All samples measured in the North Sea were elevated in Pt (minimum 0.4–0.5 pmol L^{-1}) relative to open-ocean values (~0.2 pmol L^{-1}). Further research is needed (e.g., size fractionation and particle analysis) to evaluate the sources of Pt (anthropogenic vs. naturally occurring) into north German rivers and North Sea.

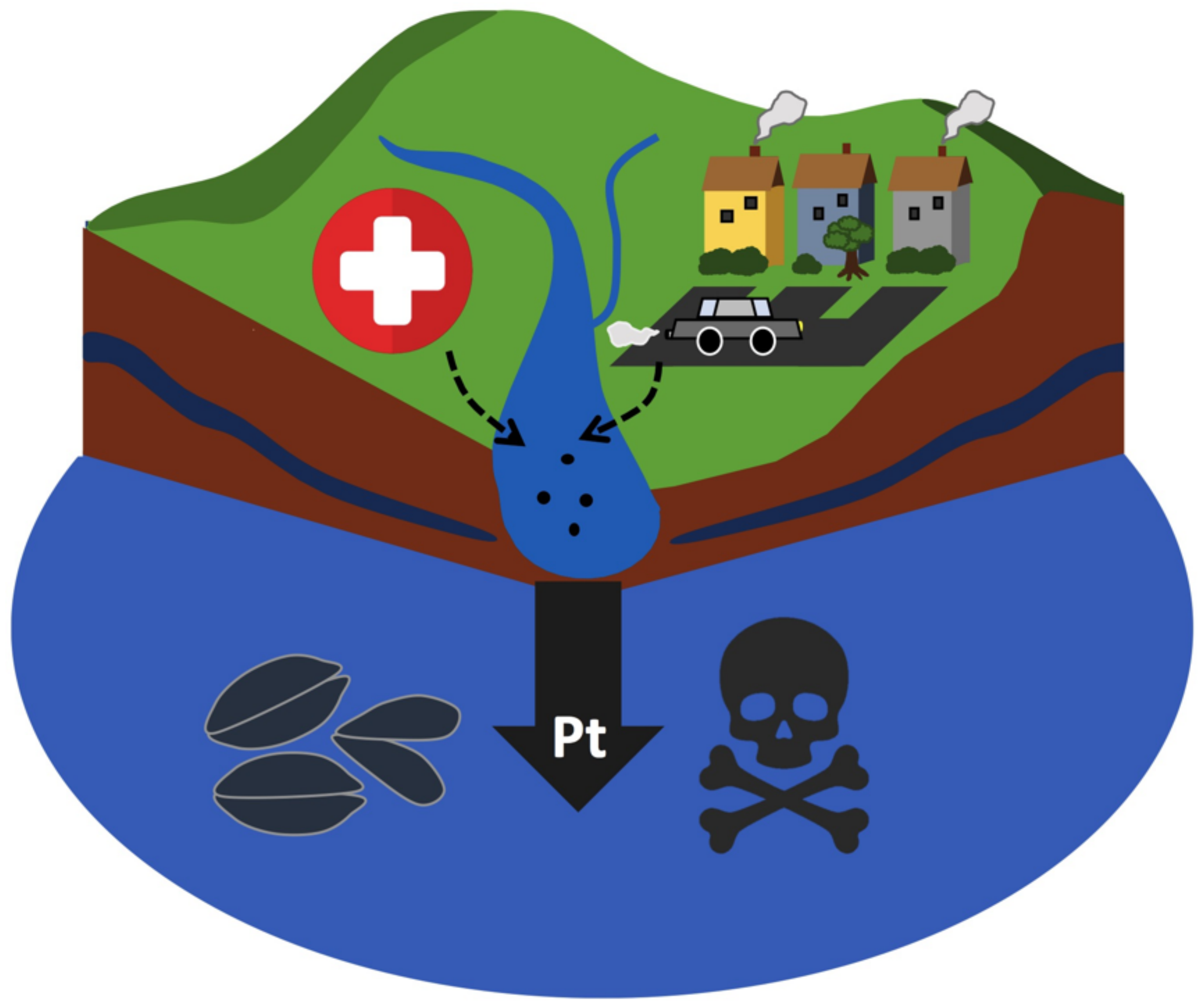


Figure 1. Diagram of Pt sources. Pt emerges from road runoff and sewage, enters rivers, and eventually enters estuaries/oceans, where it has the potential to be bioaccumulated.

Group photo from the M169 scientific team

Why Pt?

- 80% of Pt mass transfer anthropogenic in origin (Sen and Peucker-Ehrenbrink 2012)
- Main anthropogenic sources are sewage (cis-platin cancer treatment) and road runoff (catalytic converters) (Cobelo-García et al., 2011) (**figure 1**)
- Pt is known to bioaccumulate (e.g. in mussels) and is toxic in high concentrations (Neira et al. 2015), but the long-term biological effects remain unknown.

Cruise M169

- TRAM = Tracing geogenic and anthropogenic critical high-technology metals in the southern North Sea
- Conducted in the Southern North Sea and 3 major north German rivers (Ems, Weser, Elbe) (**figure 2**)

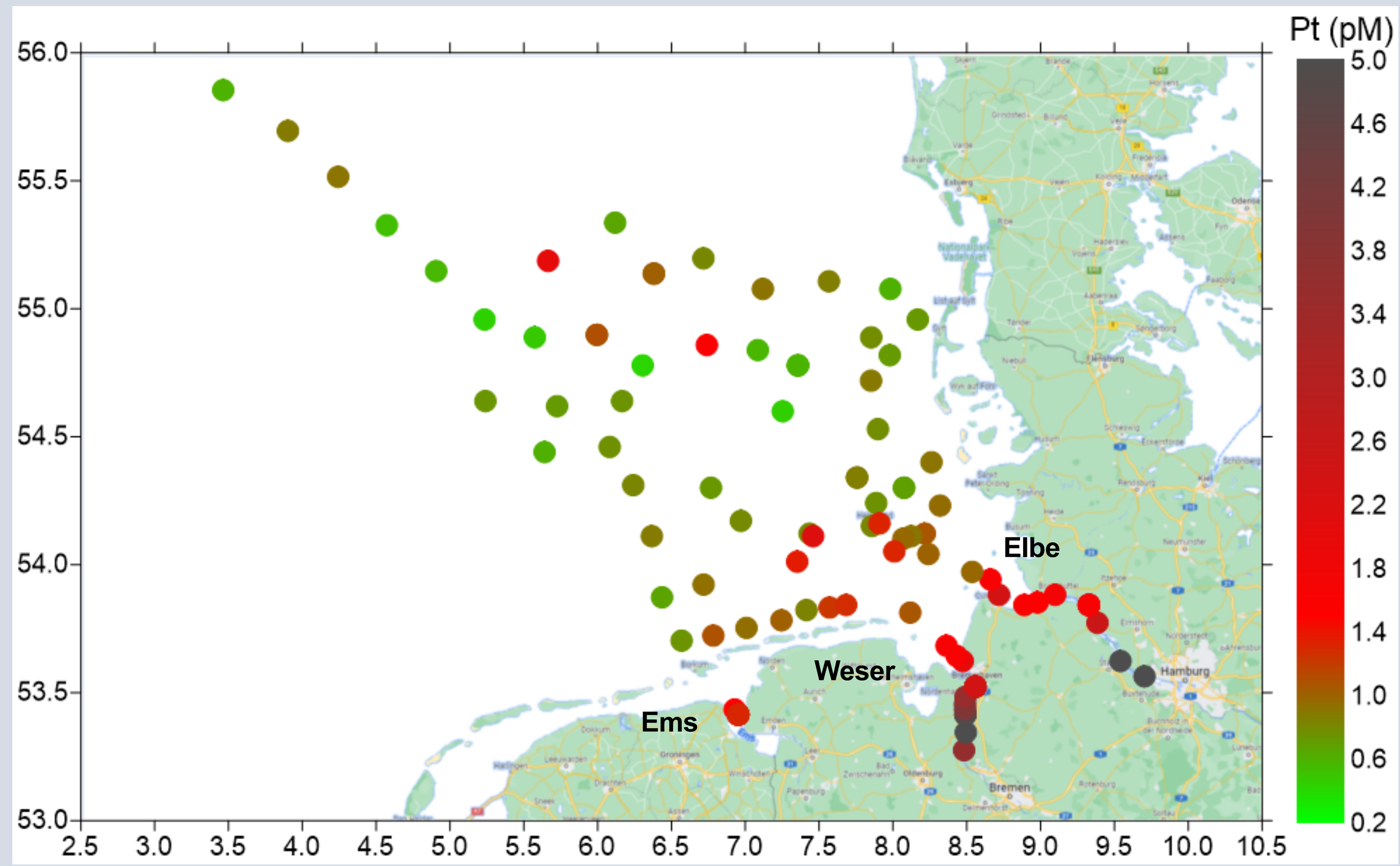


Figure 2. Dissolved (<0.2 µm) Pt distribution in the southern North Sea and three German rivers (Ems, Weser and Elbe). Longitude and latitude are shown on the x and y axes.

Flow-chart of sampling and analysis

GoFlo sampling → 0.2 µm filtration → Acidification to pH 1.8 → UV irradiation → Voltammetric analysis (Pađan et al. 2020)

References. 1. Sen, I. S., Peucker-Ehrenbrink, Environ. Sci. Technol. 2012, 46(16), 8601–8609. 2. Cobelo-García, A., López-Sánchez, D. E., Schäfer, J., Petit, J. C. J., Blanc, G., Turner, A. Mar. Chem. 2014, 167, 93–101. 3. Neira, P., Cobelo-García, A., Besada, V., Santos-Echeandía, J., Bellas, J. Sci. Total Environ. 2015, 514, 366-370. 4. Pađan, J., Marcinek, S., Cindrić, A.-M., Layglon, N., Garnier, C., Salaün, P., Cobelo-García, A., Omanović, D. Environ. Chem. 2020, 17, 77-84. 5. López-Sánchez, D. E., Cobelo-García, A., Rijkenberg, M. J. A., Gerringa, L. J. A., de Baar, H. J. W. Chem. Geol. 2019, 511, 204–211. 6. Soyol-Erdene, T.-O., Huh, Y. Geochem. Geophys. Geosys. 2012, 13(6), Q06009. 7. Dang, D. H., Omanović, D., Mucci, A., Wang, W., Sikma, A., & Chatzis, A. Mar. Chem. 2022, 242.

Results

- Surface Pt vs salinity follows a mostly conservative mixing trend (**figure 3**); highest concentrations in Weser
- In all stations, Pt was elevated relative to Atlantic (0.2 pM) (López-Sánchez et al. 2019) and other estuaries (e.g. Soyol-Erdene and Huh 2012; Pađan et al. 2020; Dang et al. 2022)
- Only the Weser tidal cycle (**figure 4**) showed significant correlation ($p<0.05$) between salinity and Pt → non-conservative behavior in the Elbe and Ems?
- Pt depth profiles showed near clear trend, but a Pt signal at Helgoland was observed, possibly from sediment deposition (**figure 5**)

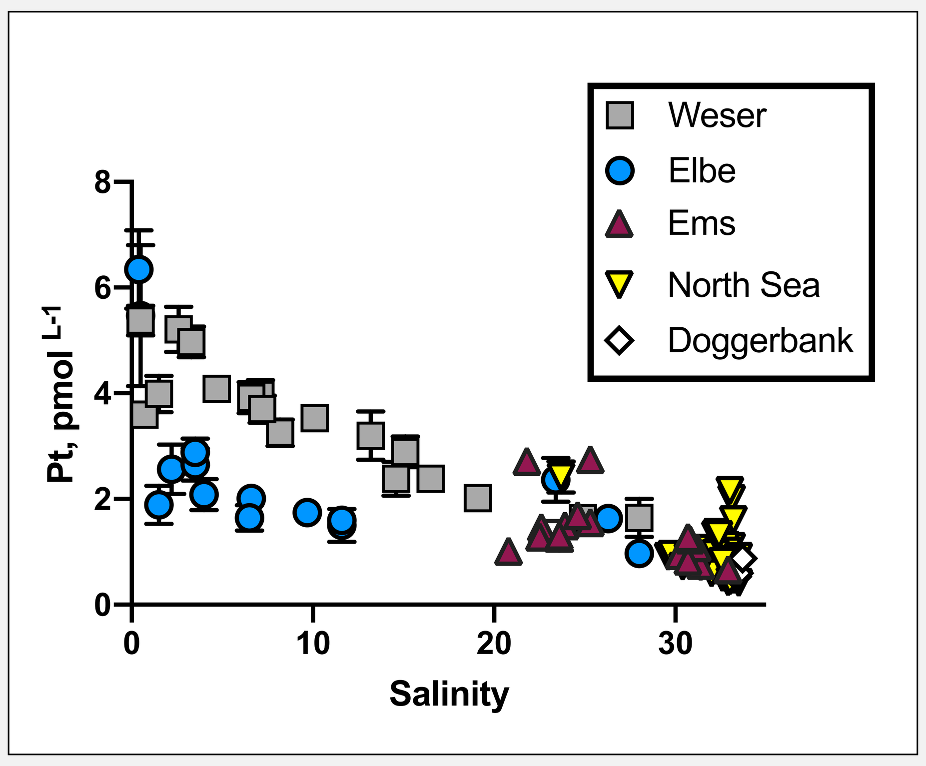
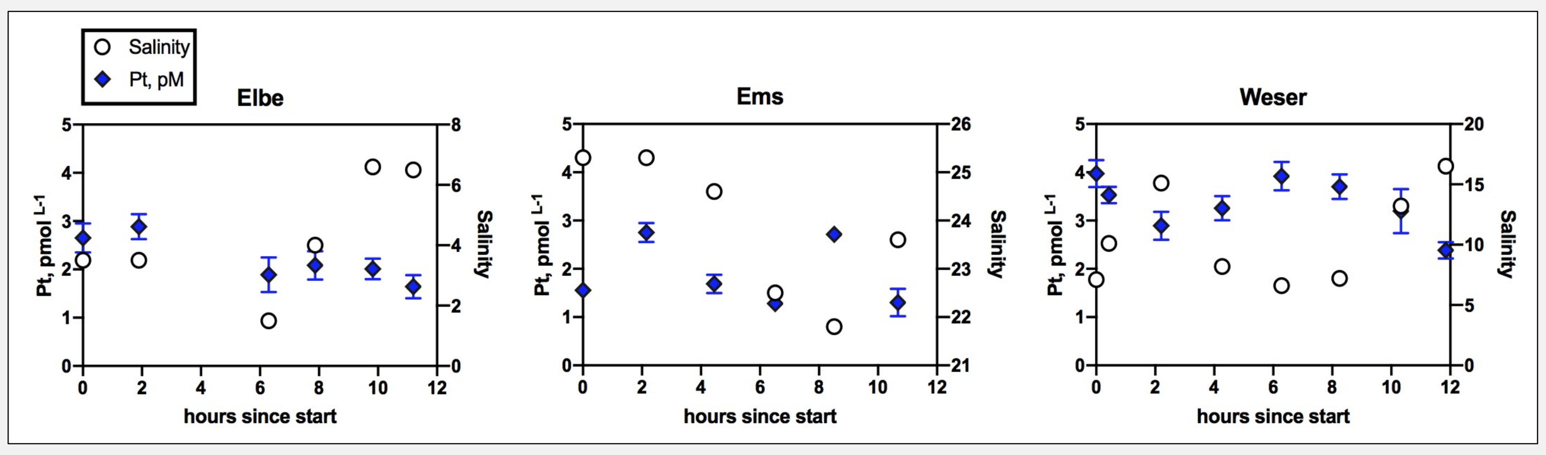
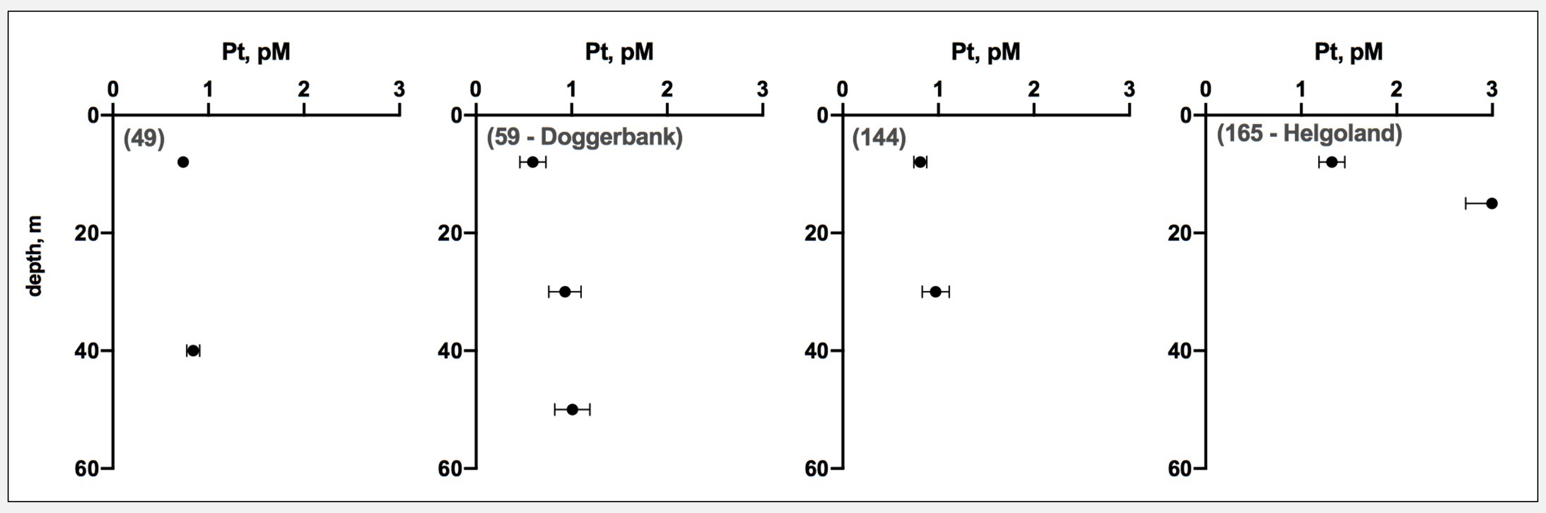


Figure 3 (top): Dissolved (<0.2 µm) Pt (pM) vs salinity in the Weser, Elbe, and Ems rivers and estuary mixing zones, as well as the North Sea (S ≥32) and Doggerbank.

Figure 4 (middle): Dissolved Pt and salinity plotted against time (h) for 12-h tidal cycles in the Elbe, Ems and Weser. The vessel stayed in a stationary location while water was collected.

Figure 5 (bottom): Example depth profiles from the North Sea, including Doggerbank and Helgoland.





Conclusion and outlook

- Rivers were shown to be important sources of Pt to the southern North Sea, most likely from anthropogenic inputs.
- Future studies of Pt closer to potential sources (e.g., sewage treatment plants and roadsides), size fractionation analysis and comparison to other elements will help track Pt input pathways.