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Cycles of trace elements and isotopes in the ocean – GEOTRACES and beyond

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ABSTRACT

The water column profiles of dissolved Pt were determined in samples taken during the GEOTRACES GA02 section at three stations located in the North, Central and South West Atlantic Ocean. Average concentrations obtained in this study for dissolved Pt (0.22 ± 0.04 pM; $n = 59$) are in agreement with the only previous dataset for the Atlantic Ocean reported in the early nineties. However, results presented here do not show invariant concentrations with depth as previously indicated for the Atlantic and recently reported for the Pacific Ocean. Instead, these new data suggests that (i) atmospheric inputs can account for the observed Pt enrichment in surface waters of the North West Atlantic; (ii) conservative mixing control the Pt distribution in deep (> 1000 m) waters; and (iii) oxygen may play a major role on the Pt distribution in the oceans, since similar trends of Pt with dissolved oxygen were observed with Pt depletion at water depths of maximum oxygen utilization. There is still, however, important open questions on the (bio)geochemistry of Pt in natural waters including the redox behavior of the Pt(II)/Pt(IV) couple and its impact on particle (inorganic and/or biogenic) reactivity, which impedes a better characterization of the observed distribution in this study. Also, potential analytical artifacts that could be behind the differences in the Pt distributions observed for the different ocean basins must be further explored.

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1. Introduction

Platinum is a highly siderophile metal (Lorand et al., 2008) and, as such, is one of the least abundant elements at the Earth's surface with a typical crustal abundance of 0.5 ng g^{-1} (Rudnick and Gao, 2003). In natural waters, dissolved Pt typically displays picomolar and sub-picomolar concentrations (Obata et al., 2006; Soyol-Erdene and Huh, 2012; Cobelo-García et al., 2013; Cobelo-García et al., 2014a, 2014b). Current interest on the investigation of the environmental Pt geochemistry relies on the fact that its cycle at the Earth's surface is greatly impacted by anthropogenic activities, amounting up to, at least, 80% of its total mobilization (Sen and Peucker-Ehrenbrink, 2012). Among these activities, the use of Pt in automotive catalytic converters – accounting for 40% of the total World demand as for 2016 (www.platinum.matthey.com) – has been identified as the major source of anthropogenic Pt released into the environment; accordingly, elevated

Pt concentrations have been extensively reported in areas close to vehicular traffic (Cobelo-García et al., 2011) but also evidence for a global Pt environmental disturbance has been given (Soyol-Erdene et al., 2011).

The concern of a global Pt contamination and the still poorly understood geochemical behavior of this element has led in the recent years to increasing number of studies reporting Pt concentrations in natural waters (e.g. Soyol-Erdene and Huh, 2012) and its behavior in estuarine and coastal areas (Obata et al., 2006; Cobelo-García et al., 2013, 2014b; Mashio et al., 2016, 2017). In the oceans, data on dissolved Pt concentrations and distributions were reported in the early work of Goldberg et al. (1986) for the Pacific Ocean, Jacinto and van den Berg (1989) for the Indian Ocean, and Colodner (1991) and Colodner et al. (1993) for the Atlantic and Pacific Oceans, reporting concentrations ranging from 0.2 to 1.6 pM. In these studies, concentrations invariant with depth in the North Atlantic (Colodner et al.,

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1993) were reported; a scavenged-type profile in the Indian Ocean (Jacinto and van den Berg, 1989) was observed, whereas for the Pacific the available studies show discrepant behavior: recycled-type (Goldberg et al., 1986) and conservative (Colodner, 1991). As noted by other authors (e.g. Donat and Bruland, 1995), the behavior of platinum derived from these studies is not oceanographically consistent with respect to their basin-to-basin variation, suggesting the possibility of errors in some of available the data. Recently, a conservative vertical distribution was reported for the western (Suzuki et al., 2014) and eastern (Fischer et al., 2018) North Pacific Ocean, in agreement with the early observation of Colodner (1991).

In order to shed further light on the oceanic behavior of dissolved Pt, we present here the distribution of this element in samples from three water column profiles from the North, Central and South Western Atlantic Ocean collected during the Dutch GEOTRACES Atlantic Ocean section GA02 (Rijkenberg et al., 2014).

2. Material and methods

2.1. Sampling

Samples were collected along the Atlantic Ocean GEOTRACES GA02 section (further details in Rijkenberg et al., 2014). Briefly, an all-titanium ultraclean CTD sampling systems for trace metals containing PVDF samplers was used for sample collection. Samples for dissolved Pt were filtered from the samplers using $< 0.2 \mu\text{m}$ cartridges (Sartobran 300, Sartorius) under filtered N_2 pressure applied via the top connector of the PVDF sampler and collected in acid-washed LDPE bottles (Rijkenberg et al., 2014). Samples were then acidified to a final concentration of 0.1 M ultraclean Seastar Base-line HCl (Seastar Chemicals).

The three water column profiles selected for this study were collected in the North (Cruise 64PE319, RV Pelagia, Station 11: 39.3993 W, 47.8007 N), Central (Cruise 64PE321, RV Pelagia, Station 36: 48.8835 W, 7.7664 N) and South Atlantic (Cruise 74JC057, RV James Cook, Station 8: 39.4425 W, 35.0083 S), respectively (Fig. 1).

2.2. Pt determination

Dissolved Pt determinations were carried out onshore inside an ISO-7 lab at the Instituto de Investigaciones Mariñas (Vigo, Spain; IIM-CSIC) where all sample processing and analysis for Pt determination was carried out in a laminar flow bench (ISO-5). Dissolved Pt was analyzed by means of catalytic adsorptive cathodic stripping voltammetry (Cat-AdCSV; van den Berg and Jacinto, 1988), using the procedure described in Cobelo-García et al. (2013). Briefly, samples were UV-digested in quartz tubes with PTFE caps using a 125-W high-pressure mercury lamp for 2 h. After digestion, sulphuric acid (final concentration 0.5 M; Trace Select, Fluka), formaldehyde (final concentration 3.5 mM; Riedel-de-Haen) and hydrazine sulfate (final concentration 0.45 mM; Fluka) were added. Samples were then transferred to a PTFE voltammetric cell and a deposition potential of -0.3 V (vs. Ag/AgCl) was applied for 10–30 min depending on platinum concentrations. After a quiescence of 10 s, the potential was scanned to -1.1 V in the differential pulse mode and the Pt peak at about -0.90 V quantified. A Metrohm 663 VA polarographic stand (Herisau, Switzerland), equipped with a HMDE (working electrode), a Ag/AgCl (reference electrode) and a glassy carbon rod (auxiliary electrode) was used. The detection limit of the technique, expressed as three times the standard deviation of the blanks ($0.026 \pm 0.008 \text{ pM}$; $n = 8$), determined in ultra-pure water (UPW; Milli-Q®, Millipore), was 0.02 pM using the longest deposition time (i.e. 30 min; Cobelo-García et al., 2013). Since the electrolyte composition of the sample solution (e.g. UPW vs. saline water) has an impact on the shape of the voltammetric scans and on the sensitivity, the method of standard additions was used in all determinations. Given that there is no water reference material for Pt at present, the accuracy of the

analytical procedure was checked by means of the analysis of spiked oceanic waters, obtaining typical recoveries of $102 \pm 10\%$. All samples were analyzed in triplicate and average results are presented, with typical RSDs below 15% (Table 1).

2.3. Water masses

The hydrological parameters along the GEOTRACES GA02 section have been reported and discussed previously in detailed (e.g. Dulaquais et al., 2014; Rijkenberg et al., 2014; Casacuberta et al., 2014; Middag et al., 2015), and here we provide a brief description. Station 11 (39.3993 W, 47.8007 N) is located at the rim of the subarctic gyre (SAG); here, the upper water column ($< 750 \text{ m}$) is composed of North Atlantic Central Waters (NACW), whereas the rest of the waters column is composed of NADW of different types. Accordingly, Labrador seawater (LSW) becomes dominant at depths between approx. 1000 and 3000 m, and Denmark Strait Overflow Water (DSOW) below 3500 m.

Upper water column at Station 36 (48.8835 W, 7.7664 N) is characterized by Equatorial Surface Water (ESW) at $< 75 \text{ m}$, from where South Atlantic Central Water (SACW) dominates down to 500 m depth. Below 1000 m, water is composed of NADW with influence of Antarctic Intermediate Water (AAIW) in its upper part ($\sim 1000 \text{ m}$) and Antarctic Bottom Water (AABW) at depths $> 4000 \text{ m}$.

At Station 8 (39.4425 W, 35.0083 S), SACW dominates in the upper water column ($< 500 \text{ m}$), then appearing Antarctic Intermediate Water (AAIW) which is centered at around 900 m depth. The NADW penetrates the Circumpolar Deep Water (CDW), dividing the CDW in Upper – flowing below the AAIW northwards – and Lower CDW. Below 3500 m AABW becomes the main water mass towards the bottom.

3. Results and discussion

3.1. Levels of platinum in the water column of the West Atlantic

Dissolved Pt concentrations (Table 1) observed in this study ranged from 0.11 to 0.32 pM, with an average value of $0.22 \pm 0.04 \text{ pM}$ (mean $\pm 1 \text{ SD}$; $n = 59$). Average concentrations for the three stations were almost identical, with values of $0.23 \pm 0.05 \text{ pM}$ (0.12–0.30 pM; $n = 18$) at Station 11, $0.22 \pm 0.05 \text{ pM}$ (0.11–0.32 pM; $n = 17$) at Station 36 and $0.21 \pm 0.02 \text{ pM}$ (0.16–0.25; $n = 24$) at Station 8. The only previous dataset of dissolved Pt in waters of the Atlantic Ocean were reported by Colodner (1991), who found concentrations of $0.26 \pm 0.08 \text{ pM}$ (0.14–0.39 pM; $n = 19$) in the water column near Bermuda ($32^\circ 10' \text{N}$, $64^\circ 30' \text{W}$) and $0.30 \pm 0.07 \text{ pM}$ (0.11–0.41 pM; $n = 17$) near Azores ($26^\circ 20' \text{N}$, $33^\circ 40' \text{W}$). It is remarkable that – despite of the temporal lapse between the Colodner and the present work (samples collected in 1989 vs. 2010/2011 in the present work) and the different analytical techniques used (isotope dilution – ICPMS after column preconcentration in Colodner (1991) vs. voltammetry in this study) – quite reasonable agreement is observed for both datasets, providing further reassurance on the typical dissolved Pt concentrations in the Atlantic Ocean.

3.2. Vertical Pt distribution in the West Atlantic Ocean

The surface distribution of dissolved Pt at Station 11 (39.3993 W, 47.8007 N) located in the northern subarctic gyre showed an apparent scavenged-like profile in the top 250 m, with a surface (25 m) maximum of 0.30 pM decreasing with depth to 0.12 pM at 250 m (Fig. 2). Dissolved Pt concentrations increased below the oxygen minimum with maximum concentrations at 1000–2000 m ($0.29 \pm 0.01 \text{ pM}$; $n = 3$), from where concentrations decreased towards the bottom waters ($0.23 \pm 0.02 \text{ pM}$, $n = 4$, below 4000 m).

Contrary to the observations at Station 11, no apparent surface maximum was observed at Station 36 (48.8835 W, 7.7664 N). Instead, dissolved Pt increased from surface waters ($< 50 \text{ m}$; $0.15 \pm 0.03 \text{ pM}$,

Fig. 1. Map showing the three stations studied in this work, collected during the Atlantic Ocean GEOTRACES GA02 section: Station 11 (Cruise 64PE319, RV Pelagia, 39.3993 W, 47.8007 N), Station 36 (Cruise 64PE321, RV Pelagia, 48.8835 W, 7.7664 N) and Station 8 (Cruise 74JC057, RV James Cook, 39.4425 W, 35.0083 S). Also included the location of the Bermuda station reported in Colodner (1991).

$n = 3$) showing a sub-surface maximum (0.22 pM) centered around 300 m from where concentrations decreased again with a minimum at 750 m (0.17 pM). As for Station 11, concentrations increased below the oxygen minimum zone reaching the highest Pt concentrations in the profile at 1500 m (0.32 pM) and then decreasing towards the bottom waters (0.22 ± 0.01 , $n = 2$, for depths below 4000 m).

For Station 8 (39.4425 W, 35.0083 S), the Pt distribution does not appear to present similarities with respect to the other two stations but does follow a mimetic pattern to that of dissolved oxygen (Fig. 2). Here, rather invariant concentrations are observed in the shallow layers (< 500 m, 0.21 ± 0.01 pM, $n = 11$). A maximum is found at 750 m (0.25 pM) from where the concentrations decrease down to 1200–1500 m (0.16 pM). Platinum concentrations then increase towards the bottom waters below 4500 m (0.23 ± 0.01 pM, $n = 3$).

3.3. Factors influencing the water column distribution of Pt in the Atlantic

3.3.1. Pt enrichment in surface waters at station 11 (39.3993 W, 47.8007 N)

The distribution of Pt in at Station 11 suggests an enrichment in the

upper water column (< 500 m; Fig. 2), following a trend similar to that of Mn (Fig. 3; $r^2 = 0.69$, $p < 0.05$, $n = 7$). Such correlation of Pt and Mn suggesting an atmospheric input to the upper water column has been also observed in two profiles of the Indian Ocean (Jacinto and van den Berg, 1989). However, no surface Pt maximum was found for the other two stations located at lower latitudes.

Main atmospheric Pt sources include meteoric smoke fallout, volcanic dust and anthropogenic inputs (Gabielli et al., 2004; Soyol-Erdene et al., 2011). Previous studies have shown that the anthropogenically-derived Pt – especially arising from automobile exhaust catalysts – is subject to a long range transport (Barbante et al., 2001) and that deposition rates in the Northern Hemisphere, estimated from Greenland snow, are about 2 orders of magnitude than those derived from Antarctic snow (Soyol-Erdene et al., 2011), which could be behind the absence of any evident Pt enrichment at stations 36 and 8.

In order to check whether atmospheric deposition may account for the observed surface enrichment at station 11, we used a Pt deposition rate of $80 \pm 40 \text{ ng m}^{-2} \text{ yr}^{-1}$ obtained from an ice-core in Central Greenland (Rauch et al., 2005). This deposition rate was calculated in unfiltered melted, acidified ice samples and, as such, represents soluble

Table 1

Concentrations with standard deviations of dissolved Pt at Station 11 (39.3993 W, 47.8007 N), Station 36 (48.8835 W, 7.7664 N) and Station 8: 39.4425 W, 35.0083 S) (Fig. 1).

	Depth (m)	Pt [pM]	SD
Station 11	25	0.30	0.03
	49	0.26	0.03
	100	0.21	0.01
	150	0.25	0.04
	198	0.15	0.01
	252	0.12	0.02
	401	0.22	0.03
	751	0.15	0.02
	1001	0.29	0.04
	1248	0.27	0.04
	1749	0.30	0.04
	2500	0.22	0.02
	2999	0.26	0.01
	3500	0.23	0.03
	4000	0.23	0.02
	4251	0.20	0.02
	4496	0.23	0.02
	4546	0.25	0.02
Station 36	10	0.17	0.02
	25	0.11	0.02
	50	0.17	0.02
	101	0.19	0.02
	151	0.21	0.03
	201	0.19	0.02
	300	0.22	0.02
	501	0.19	0.03
	753	0.17	0.01
	1002	0.23	0.03
	1500	0.32	0.03
	2501	0.29	0.03
	3000	0.27	0.02
	3499	0.24	0.03
	3749	0.24	0.02
	4250	0.21	0.02
Station 8	4315	0.23	0.03
	9	0.22	0.02
	25	0.23	0.03
	51	0.20	0.01
	76	0.22	0.03
	101	0.19	0.01
	151	0.21	0.01
	201	0.20	0.02
	253	0.21	0.03
	304	0.20	0.02
	404	0.21	0.02
	505	0.19	0.02
	758	0.25	0.03
	1011	0.21	0.03
	1264	0.17	0.01
	1517	0.16	0.02
	1769	0.18	0.02
	2025	0.20	0.02
	2533	0.20	0.01
	3044	0.23	0.03
	3556	0.23	0.02
	4068	0.20	0.01
	4581	0.22	0.02
	4877	0.24	0.02
	4930	0.22	0.01

and loosely-bound particulate Pt; given that the solubility of emitted particulate Pt from catalytic converters is greatly enhanced to values around 20–40% in the presence of complexing ligands (e.g. chlorides, organic ligands; Nachtigall et al., 1996; Bruder et al., 2015), the value given by Rauch et al. (2005) was assumed as soluble Pt. Also, it has to be kept in mind that this deposition rates were calculated using ice layers dated between 1990 and 1995 (Rauch et al., 2005); given that the number of vehicles equipped with Pt containing catalytic converters has significantly increased since the early nineties (the World Pt demand for autocatalysts raised from 43 tons in 1990 to 94 tons in 2016;

www.platinum.matthey.com), it is not adventurous to hypothesize that currently higher deposition rates may be expected.

Thus, using the deposition rate of $80 \pm 40 \text{ ng m}^{-2} \text{ yr}^{-1}$ as a conservative estimate, and integrating it over the upper 50 m, results in an input of $0.008 \pm 0.004 \text{ pM}$ of Pt per year via atmospheric deposition. In order to account for the Pt concentrations in surface waters at Station 11, a residence time of Pt of several decades in surface waters would be necessary. This appears to be realistic as a significantly longer residence time to that of Mn (which is in the order of 5–20 years; Jickells et al., 1994) is expected based on the 300 times higher Pt/Mn ratio in sea-water compared to crustal rock (Jacinto and van den Berg, 1989).

The absence of such surface maximum at Stations 36 and 8 probably indicates lower Pt deposition rates at those locations (Soyol-Erdene et al., 2011). This is especially relevant for Station 36, which is located in an area of high aeolian input from the Saharan dust – as depicted from the surface Al concentrations (e.g. Rijkenberg et al., 2014; Middag et al., 2015; Fig. 3). However, there is no data at present of the Pt solubility in such aerosol sources to the surface ocean, but the likely crustal background Pt concentrations in the Saharan mineral particles and a low soluble fraction may explain the lack of a surface dissolved input.

On the other hand, the presence of other processes such as biological uptake and its role on the behavior of dissolved Pt in surface water – which could mask the atmospheric inputs – has not been evaluated yet, despite that it has been suggested as one of the possible causes of the low dissolved Pt concentrations in surface waters of coastal areas of Japan (Mashio et al., 2017). So far, the only work reporting Pt concentrations in phytoplankton is the recent study by Abdou et al. (2018) in the Gironde Estuary and Arcachon Bay (France) and Genoa harbor (Italy) which obtained concentrations in the range of $1.3\text{--}8.0 \text{ ng g}^{-1}$ (Pt in phytoplankton) and $0.08\text{--}0.11 \text{ ng L}^{-1}$ ($0.4\text{--}0.6 \text{ pM}$; dissolved Pt). This results in a phytoplankton/dissolved partition coefficient ($K_{\text{Ph/D}}$) of $2\text{--}7 \cdot 10^4 \text{ L kg}^{-1}$. When these $K_{\text{Ph/D}}$ values are compared with those for other elements with a known biological role and which are generally depleted in surface waters due to phytoplankton uptake, they are slightly lower than for Cu and Ni ($\sim 10^5$), but at least two orders of magnitude lower than for Cd, Fe or Co ($> 10^6$) – calculated $K_{\text{Ph/D}}$ using the phytoplankton concentrations in Kuss and Kremling (1999) and typical North Atlantic surface dissolved concentrations given in Donat and Bruland (1995). This agrees with the results presented in this study, where no clear surface depletion was observed (Fig. 2); however, the $K_{\text{Ph/D}}$ (Pt) derived from Abdou et al. (2018) indicates that its biological uptake is not expected to be negligible – if compared to the $K_{\text{Ph/D}}$ data for Cu or Ni – and the extent of this process on the cycling of Pt in the upper water column should be further assessed.

3.3.2. Pt minimum above the upper NADW at stations 11 and 36

As discussed above, Pt concentrations display minimum concentrations at depths shallower than 1000 m for Stations 11 and 36 (Fig. 2). Accordingly, between 200 and 750 m Pt has an average concentration of $0.16 \pm 0.04 \text{ pM}$ ($n = 4$) at Station 11 (shallower depths were not considered to avoid including depths likely to be enriched by atmospheric deposition; see above), which is considerably lower than the concentration obtained for the NADW (0.30 pM at 1000 m). A similar situation is observed for Station 36, with an average concentration at depths shallower than 750 m ($0.18 \pm 0.03 \text{ pM}$; $n = 9$) clearly lower than the maximum at 1500 m (0.32 pM).

These minimum concentrations at depths above 1000 m have been also observed for Ga in the Central Atlantic, and was explained by the intrusion of Ga-depleted AAIW waters (Shiller and Bairamadi, 2006). At Station 36, the intrusion of AAIW, flowing northward between the Atlantic Central Water in the main thermocline and the southward flowing NADW, is detected with the maximum influence of AAIW around 1000 m. This water mass is depleted in Pt (AAIW: $0.21 \pm 0.04 \text{ pM}$ Pt, $n = 3$) – as determined from Station 8 – compared to the NADW, so this mechanism may account for the Pt minimum above the NADW at

Fig. 2. Distribution of dissolved Pt (red) and oxygen (grey) at Station 11 (a), Station 36 (b), and Station 8 (c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Dissolved Pt (red dots), Mn (blue triangles) and Al (black squares) at the North West Atlantic (< 1000 m); (a) Station 11 (39.3993 W, 47.8007 N), (b) Station 36 (48.8835W, 7.7664N), (c) Station 8 (39.4425W, 35.0083S). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Station 36. However, this cannot explain the low concentrations at Station 11 since no upper AAIW is detected at this high latitude. Therefore, other processes are expected to have a significant impact on the distribution of Pt in this part of the water column.

The fact that dissolved Pt distribution in the three profiles is similar to that of dissolved oxygen, and that minimum dissolved Pt at stations 11 and 36 coincides with an oxygen minimum (Fig. 2), may suggest a higher particle-reactivity/lower solubility at decreasing oxygen levels.

This can be especially critical for an element like Pt, which can be present at two oxidation states (II and IV). Platinum is known to be enriched in sediments as redox potential decreases through reduction to its metallic state (Terashima et al. 1993), but the oxidizing conditions in this study (even at the oxygen minimum) makes this processes unlikely here.

The Pt speciation and reactivity of the different Pt species in natural waters is far from being well understood in order to provide a

Fig. 4. Dissolved Pt vs S plot for the NADW water masses at Stations 11 and 36, and for NADW, UCDW and AABW for Station 8.

reasonable explanation of these minimum concentrations. In a previous study (Cobelo-García et al., 2013) we concluded that, using the thermodynamic data available in the literature, Pt(IV) – as $\text{PtCl}_5(\text{OH})^{2-}$ – greatly predominates over Pt(II) – as PtCl_4^{2-} – at typical seawater oxygen and pH conditions. However, it has to be noted that the available thermodynamic data for Pt(IV) – which displays even slower reaction kinetics than Pt(II) (Cosden and Byrne, 2003) – present a significant uncertainty and, importantly, the behavior and reactivity of the different possible Pt species in seawater at varying conditions (pH, oxygen, organic ligands, etc.) has not been sufficiently approached yet. To this aim, further studies are currently being carried out to get a better characterization of the factors controlling the speciation and reactivity of Pt in natural waters.

3.3.3. Pt Mixing in the NADW region

For the north and central profiles, there is a consistent Pt maximum at the upper NADW (LSW) region coincident with the end of the oxygen minimum (at 1000 m in Station 11 and 1500 m in Station 36; Fig. 1); concentrations then decrease conservatively, suggesting the mixing of two end members. When plotting the Pt concentrations in the NADW versus salinity (Fig. 4), a conservative mixing is observed. At the southernmost station (Station 8), the mixing of NADW with the Pt-depleted CDW results in a different mixing line. AABW displays concentrations that do not follow the trends observed for the NADW, with higher concentrations that the mixing line obtained for the NADW which may be due to a sediment resuspension source detected in this area (e.g. Middag et al., 2015).

3.4. Discrepancies with previous reported Oceanic Pt profiles

Results presented in this study do not lead to the conclusion of a dissolved Pt conservative water column profile given by Colodner (1991) in the North Atlantic, which was also recently reported for the western (Suzuki et al., 2014) and eastern (Fischer et al., 2018) North Pacific Ocean. Our results are also different from the scavenged-type behavior observed for the Indian Ocean (Jacinto and van den Berg, 1989) or the recycled-type for the East North Pacific (Goldberg et al., 1986). Even though most of the studies report consistent similar concentrations, it is highly unlikely that the widely varying behaviors reported are due to a natural variability and discrepancies probably arise from analytical considerations. Here we will focus on the two major analytical methods used, cathodic stripping voltammetry (CSV) and isotope-dilution ICPMS (ID-ICPMS).

It is interesting noting that all the reported conservative Pt behaviors were obtained using ID-ICPMS by different groups (e.g. Colodner, 1991; Suzuki et al., 2014; Fischer et al., 2018). The use of CSV led to a scavenged-type profile (Jacinto and van den Berg, 1989) and the results presented in this study. When our results are compared to those

Fig. 5. Comparison of the Pt profiles (with standard deviations) at Stations 11 and 36 (this study) with the reported by Colodner (1991) for the Bermuda Station (Fig. 1).

reported by Colodner (1991) at the Bermuda station (Figs. 1, 5), two significant considerations are obtained; first, the range of variation of Pt throughout the water column is not different in both studies. Accordingly, concentrations reported by Colodner (1991) ranged from 0.14 to 0.39 pM which is similar to the 0.12–0.30 and 0.11–0.32 pM we obtained for Station 11 and 36, respectively (Table 1; Fig. 5). Apart from the similar concentrations, both studies lead to a 3-fold variation in the Pt concentrations throughout the water column. Second, the standard deviation of the measurements is generally higher for Colodner (1991), who indicated errors ranging from 9 to 38% with a mean of 16%. In our study, samples were analyzed in triplicate and average results present typical RSDs below 15% (Table 1). Given that Pt concentrations display a small degree of variation in the water column in both studies (factor of 3), the lack of a Pt trend in the water column given by Colodner (1991) may respond to the higher measurement uncertainty in that study.

Apart from the uncertainties in the determination, discrepancies between CSV and ID-ICPMS may arise if one (or both) techniques are not detecting all dissolved Pt. In ID-ICPMS, which is based on the spike of an isotope tracer to the sample (and then preconcentrated on an anion-exchange resin), this could be possible in the presence of an inert fraction (e.g. organic complexes) that does not reach equilibrium with the tracer and displays different recovery efficiency. Suzuki et al. (2014) did not observe any change in the isotope ratio for samples allowed to equilibrate with the spike from one to six days. Also, no changes were found for samples heated to 80 °C for 24 h with those maintained at room temperature. However, it has to be noted that Pt displays extremely slow kinetics, especially in the IV oxidation state (e.g. Cosden and Byrne, 2003), which is the form of the isotope spike. Further studies should be conducted to evaluate any changes in the isotope ratios for samples allowed to equilibrate for several weeks or even months.

In the case of CSV, where a full Pt recovery requires the complete breakdown of organic matter, underestimation could result in the presence of organic complexes not effectively attacked by the UV-oxidation step. Also, formation of Pt(0) due to photo reduction of the Pt chloride complexes has been suggested during UV treatment (Fischer et al., 2018); underestimation would be expected if this Pt(0) is not reoxidized before the CSV determination. This, however, appears unlikely since the medium used for the CSV determination – 0.5 M H_2SO_4 and a strong complexing agent such as formazone – should bring all Pt(0) to Pt(II).

Accordingly, full recovery of spiked river, estuarine and oceanic waters – allowed to equilibrate for a week – was obtained in our previous work (Cobelo-García et al. 2013) using this procedure.

The only study to date comparing the performance of CSV and ID-ICPMS was reported by Obata et al. (2006) in estuarine waters of the Tokyo Bay with elevated Pt concentrations, where they obtained consistently similar results using both methods. In oceanic waters, values for the GEOTRACES SAFe intercalibration samples collected in the North East Pacific Ocean (SAFe S: surface; SAFe D: 1000 m; 30°N 140°W) have been reported by ID-ICPMS and CSV; accordingly, using the ID-ICPMS method, Fischer et al. (2018) reported concentrations of 0.25 ± 0.03 pM (SAFe S, bottle 578), 0.32 ± 0.03 pM (SAFe D2, bottle 41), and 0.30 ± 0.05 pM (SAFe D2, bottle 155). With CSV, Cobelo-García et al. (2014) reported values of 0.083 ± 0.005 pM (SAFe S, bottle 70), 0.196 ± 0.004 pM (SAFe D1, bottle 181) and 0.227 ± 0.051 pM (SAFe D2, bottle 327). Although the results by CSV (Cobelo-García et al. 2014) are in agreement with the recycled-type profile given by Goldberg et al. (1986) in this same area, they are significantly lower than those given by ID-ICPMS (Fischer et al., 2018), keeping the possibility of an incomplete recovery (e.g. presence of Pt-organic complexes not effectively attacked during the UV-digestion step) by the CSV method. In order to provide an unambiguous identification of the analytical issues explaining these discrepancies, an intercalibration between different labs and analytical techniques should be performed.

4. Conclusions

The dissolved Pt concentrations obtained for this study for the West Atlantic (0.22 ± 0.04 pM; $n = 59$) agree well with the only previous dataset reported in the early nineties for this basin (Colodner, 1991). However, we do not conclude with an invariant conservative water column profile given by Colodner (1991) in the North Atlantic, and recently observed for the West (Suzuki et al., 2014) and East (Fischer et al., 2018) North Pacific Ocean. Our results are also different from the scavenged-type behavior reported for the Indian Ocean (Jacinto and van den Berg, 1989) or the recycled-type for the East North Pacific (Goldberg et al., 1986). Instead, we have observed (i) surface enrichment at high latitudes of the West Atlantic; (ii) a conservative mixing for deep waters (> 1000 m), especially for the NADW; and (iii) a close overall Pt trend similar to that of dissolved oxygen, with Pt depletion at water depths of maximum oxygen utilization.

The oceanic residence of Pt has been estimated to be around $2.4 \pm 1.0 \cdot 10^4$ years (Soyol-Erdene and Huh, 2012), i.e. lower than the long residence times ($> 10^5$ years) of conservative elements and higher than for scavenged elements ($< 10^3$ years), but within the typical range of recycled elements (10^3 – 10^5 years; Donat and Bruland, 1995). The results presented in this study support the idea that Pt does not behave as a ‘pure’ conservative element in the West Atlantic Ocean. However, there is still a number of significant gaps in our knowledge on the major biogeochemical processes that may be behind the observed behavior, starting from the uncertainty on Pt speciation and redox behavior of the Pt(II)-Pt(IV) couple and the implications on phytoplankton uptake or particle-reactivity. These questions will need to be addressed in order to better characterize the observed oceanic behavior. Also, an intercalibration on the determination of Pt in oceanic waters by different groups and methods is needed in order to detect possible analytical artifacts that could be behind the disparate oceanic Pt profiles reported in the literature.

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