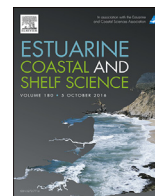




Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

Dissolved platinum in rainwater, river water and seawater around Tokyo Bay and Otsuchi Bay in Japan



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ARTICLE INFO

Article history:

Received 26 January 2016

Received in revised form

23 June 2016

Accepted 11 July 2016

Available online 14 July 2016

Keywords:

Platinum

Salinity

Estuary

ABSTRACT

Platinum, among the rarest elements in the earth's crust, is now widely used in various products such as catalytic converters in automobiles and anticancer drugs. Consequently, the concentration of Pt in urban aquatic environments might be increasing. However, little is known about the distributions and geochemical cycles of Pt in aquatic environments because its overall concentration remains low. In this study, we examined dissolved Pt in river water and seawater around Tokyo Bay and Otsuchi Bay (Iwate Prefecture, Japan) and rainwater in the Tokyo area. To determine sub-picomolar levels of dissolved Pt, we used isotope-dilution Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after column pre-concentration with an anion exchange resin. We observed seasonal variation in the dissolved Pt concentrations in Tokyo rainwater in 2002; higher concentrations were found from January to March, which might be related to the pH of rainwaters. At the source of the Arakawa River in the greater Tokyo area, the dissolved Pt concentration was found to be similar to that in rainwater. Further downstream, the dissolved Pt concentration increased sharply, which seemingly reflects the anthropogenic input of Pt into the river. In a rural area in Japan (Otsuchi Bay), the dissolved Pt concentrations were lower than in Tokyo Bay. In this area, a sharp increase in dissolved Pt concentrations was observed in a high salinity region. Contrasting Pt distribution patterns between urban and rural areas indicate that strong anthropogenic Pt sources exist in urban estuaries and that geochemical processes within estuaries affect the Pt distribution.

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1. Introduction

Platinum (Pt) belongs to the least abundant group of elements (the platinum group elements, or PGEs) in the Earth's crust (Wedepohl, 1995). Because of its physical and chemical properties, Pt has been applied to a variety of industrial and medical uses, which has resulted in anthropogenic Pt being emitted and dispersed throughout the environment (Schafer et al., 1999; Pyrzynska, 2000; Ravindra et al., 2004; Rauch and Morrison, 2008; Sobrova et al., 2012; Reith et al., 2014). For example, automobile catalysis was introduced into the exhaust systems of automobiles to reduce the emission of carbon monoxide, hydrocarbons, and nitrogen oxides in Japan in 1973, the USA in 1975, and Europe

in 1986. In this catalysis, small particles of Pt, Pd, and Rh are used, and thus automobile emissions include these metals in the form of not only metals but also oxides and carbonyl complexes (Moldovan et al., 2002). In the urban aquatic environment, direct release from storm sewers draining roadways and indirect release from sewage plants that treat road run-off are two possible sources of accumulated PGEs in sediment cores (Hodge et al., 1986; Ravizza, 2001). These sediment cores indicate recent changes in PGE contamination in coastal areas (Tuit et al., 2000; Abdou et al., in press). Sediment cores in an urban lake exhibited an exponential increase in PGE contamination following the introduction of automobile exhaust catalysts (Rauch et al., 2004). Observations of elevated concentrations in ice cores from central Greenland (Barbante et al., 2001) and snow pit samples from East Antarctica (Soyol-Erdene et al., 2011a) show that the emitted PGEs are dispersed on a global scale due to long-range transportation of these materials. Based on these results, global PGE deposition was estimated in the

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Northern Hemisphere (Rauch et al., 2005) and Antarctica (Soyol-Erdene et al., 2011a). On the other hand, Pt-based cytotoxic drugs, such as cisplatin, carboplatin, and oxaliplatin, which are widely used anticancer drugs, might also influence aquatic environments. Platinum emitted by hospitals is estimated to be 3–12% of the amount emitted by cars equipped with catalytic converters in European countries (Kümmerer and Helmers, 1997). Because of these anthropogenic emissions, Pt concentrations in aquatic environments might increase in urban areas (Moldovan et al., 2002; Kümmerer and Helmers, 1997; Ravindra et al., 2004; Vyas et al., 2014).

In estuarine areas, Pt concentrations were reported to be higher than in open ocean seawater. For example, dissolved platinum concentrations range from ~0.02 to 0.62 pM in Lérez Estuary in Spain (Cobelo-García et al., 2013) and from 0.35 to 0.84 pM in Gironde Estuary in France (Cobelo-García et al., 2014), while very high concentrations (5–35 pM) were reported in Tokyo Bay in Japan (Obata et al., 2006).

In this study, we examined the dissolved Pt concentrations in the waters (river water, rainwater, and estuarine water) around Tokyo Bay and Otsuchi Bay, and compared the patterns observed in these Pt concentrations with those in other estuarine areas, in order to understand the geochemical process of Pt in aquatic environments.

2. Experiments

2.1. Sampling

In 2002, rainwater samples were collected with a cleaned polyethylene box (38 cm × 54 cm) placed on the roof of the Ocean Research Institute (ORI), University of Tokyo, located in Tokyo (35° 41.15' N, 139° 40.47' E). All samples were filtered using 0.45 μm membrane filters (HA, Millipore, USA) immediately after collection following the previous study (Zhang, 2003). The date of collection, amount of precipitation, pH, and dissolved Pt concentration are presented in Table 1.

In 2003 and 2011, river water and estuarine water samples were collected along two urban rivers, at five sites along the Arakawa River, and eight sites along the Tama River (Tables 2 and 3). The Arakawa River originates in Mt. Okuchichibu in Saitama Prefecture, and the Tama River originates in Okutama Lake in Tokyo as shown in Fig. 1. Both rivers flow through densely populated areas of Tokyo and into Tokyo Bay. The sampling locations are shown in Fig. 1. The samples were collected on April 11, 2003 and March 19, 2004 in the Arakawa River, and on September 29, 2010 and February 1, 2011 in the Tama River, using a cleaned polyethylene bucket. After collection, the water samples were immediately filtered with a 0.2 μm pore-size membrane filter (Steradisk, Kurabo Industries).

In Tokyo Bay, seawater samples were collected in May 2004 from the R/V Taisei-maru during the research cruise KT-04-08. The sampling locations are shown in Fig. 1 and hydrographic data are given in Table 3. Seawater samples were collected with 12 L acid-cleaned X-Niskin bottles, and were filtered immediately on board. In Otsuchi Bay, seawater samples were collected by the Research Boat Yayoi (International Coastal Research Center, ORI) in May 2006, and river water samples from the Otsuchi River and the Kotsuchi River, flowing into Otsuchi Bay (Fig. 1), were collected in May 2007. Surface seawater samples were collected using a cleaned polyethylene bucket. The collected samples were filtered with a 0.2 μm pore-size membrane filter (Steradisk, Kurabo Industries). All the samples were acidified to a pH < 1.5 by using high-purity hydrochloric acid (HCl, Tamapure-AA-100, Tama Chemicals Co., Ltd., Japan) and stored in polyethylene cubic containers, cleaned with 3 M HCl and Milli-Q water (MQW; Millipore, USA), until analyses.

Table 1

Dissolved Pt in rain waters with sampling data.

Sample no.	Collected date	Precipitation (mm)	pH	Pt (pmol/kg)
1	Jan. 21, 2002	31.3	4.9	0.40 ± 0.13
2	Mar. 5, 2002	3.1	4.3	0.62 ± 0.31
3	Mar. 31, 2002	6.5	5.2	0.13 ± 0.03
4	Apr. 29, 2002	2.9	5.5	0.39 ± 0.22
5	May 17–18, 2002	16.2	5.8	0.23 ± 0.06
6	May 26, 2002	19.8	5.8	0.26 ± 0.11
7	Jun. 18–19, 2002	53.1	5.8	0.12 ± 0.02
8	Jun. 20–21, 2002	14.5	5.8	0.14 ± 0.07
9	Jul. 8–11, 2002	60.3	5.8	0.18 ± 0.11
10	Aug. 2, 2002	51.6	5.5	0.26 ± 0.13
11	Oct. 18, 2002	53.0	6.1	0.15 ± 0.07
12	Nov. 2–5, 2002	27.0	5.8	0.30 ± 0.05

2.2. Analytical method

Polyethylene labware was washed with 5% Extran MA01 (Merck and Co. Inc.), 3 M HCl, and MQW, successively. Teflon funnels, tubes, and vessels were used in the preconcentration system to prevent contamination. Teflon vessels were cleaned by heating in aqua regia (a 3:1 mixture of 12 M HCl and 16 M HNO₃) and in MQW. Teflon columns and funnels were soaked in 3 M HCl for one day, and cleaned by heating in a mixture of HNO₃, H₂SO₄, and HClO₄ acids (1:1:1, v/v/v), 6 M HCl, and MQW, successively. The stored samples at pH < 1.5 were further acidified to pH 1 by using HCl (Tamapure AA-100). Tokyo Bay seawater samples, Arakawa River samples and rainwater samples were spiked with a ¹⁹²Pt tracer (Oak Ridge National Laboratories, USA; measured ¹⁹²Pt/¹⁹⁵Pt = 5.21 ± 0.07) at least 24 h before passing them through the anion exchange resin (100–200 mesh, Cl-form, AG1-X8; Bio-Rad Laboratories Inc., USA) packed in a polypropylene column (12 mm inner diameter, 5 cm length). The resin was cleaned with hot 12 M HNO₃ initially, then successively with 8 M HNO₃, MQW and 0.5 M HCl (Obata et al., 2006). Dissolved Pt preconcentration through the column was carried out for 500 or 1000 mL of samples at 1–2 mL/min. After the samples were passed through the anion exchange resin column, the columns were rinsed with 50 mL of 0.1 M HCl and 50 mL of Milli-Q water. Adsorbed Pt on the anion-exchange resin was eluted with 120 mL of a mixture of 5 M HNO₃ and 5 M HClO₄ at room temperature. The eluted samples were collected in Teflon beakers and evaporated with a hotplate, until their volumes were reduced to less than 0.1 mL. Concentrated samples were diluted with 2–5 mL of 1% HCl. Each sample and standard solution was measured at least three times using a Quadrupole Inductively Coupled Plasma Mass Spectrometer (ICP-MS; HP 4500 Series, Hewlett Packard Co., USA) with a micro-flow nebulizer (G3139A, Agilent Technologies Inc., USA). Blank values for this procedure were <0.04 pmol/kg, and the detection limit (3σ of the procedural blank) was 0.18 pmol/kg.

Later, we improved our method to reduce the procedural blank values by using a small anion exchange resin column detailed in Suzuki et al. (2014). We applied the improved methods to the Otsuchi Bay seawater and Tama River water samples. Briefly, the samples were acidified to 0.5 M HCl so that all Pt-formed PtCl₄²⁻ or PtCl₆²⁻, and the ¹⁹²Pt enriched spike solution was added to each seawater sample. The mixture was left to stand for 24 h to reach isotopic equilibrium, then transferred to a 6 cm-long Teflon column (inner diameter 8 mm) filled with an anion exchange resin (100–200 mesh, Cl-form, AG1-X8; Bio-Rad Laboratories Inc., USA) at a flow rate of 2 mL/min. We examined the isotopic equilibration time for river water (Tama-5) experimentally by changing the equilibration time to be 1 h, 12 h, 24 h and 5 days (Fig. 2). The Pt concentrations after being equilibrated for 24 h and 5 days were consistent, therefore, we set the equilibration time to 28–35 h.

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