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Spatiotemporal variations of platinum in seawater in Otsuchi Bay, Japan after the 2011 tsunami



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HIGHLIGHTS

- We revealed the Pt concentrations in Otsuchi Bay after the 2011 tsunami.
- The vertical profiles of Pt indicated that Pt supply from the sediments to seawater.
- Supplied Pt to the bottom water was derived from loosely adsorbed Pt onto the sediments.

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ABSTRACT

Huge tsunami waves devastated coastal areas on the Pacific Ocean side of northern Japan on March 11, 2011, and seriously damaged these coastal environments. Since the tsunami, we have not yet obtained data on the present state of and changes in trace metal concentrations in seawater in these areas. Platinum (Pt), one of the rarest elements in the Earth's crust, is now widely used in a range of products, such as catalytic converters in automobiles and anticancer drugs. Increasing use and dispersal of Pt has the potential to affect aquatic environments, although Pt concentrations in open ocean seawater have been found to be very low (approximately 0.2 pmol/L). In this study, we reveal the Pt concentrations in seawater and sediment in Otsuchi Bay after the tsunami, and evaluate the behavior of the Pt. The concentrations of dissolved Pt in seawater are 0.40-1.99 pmol/L and those in river water are below the detection limit of 0.015 pmol/L. Comparing the Pt concentrations in May, higher concentrations were obtained in 2013 than in 2012, especially in the deepest seawater. The total Pt concentrations in sediment samples were 0.46-14.4 ng/g in Otsuchi Bay. Using a sequential leaching technique on the sediments, Pt concentrations in the acetic-acid fractions were 0.19-1.13 ng/g, and those in the acetic acid + hydrochloric acid hydroxylamine fractions were less than 0.03-0.71 ng/g. Seasonal variations in dissolved Pt concentrations reflected changes in the water mass structure. During the stratification season, vertical profiles indicated that Pt concentrations tended to increase with depth due to supply from the sediments, whereas in winter, the water mass was vertically well mixed. The Pt was supplied to the bottom of the water from the sediments, probably due to loosely adsorbed Pt on sediment particles being remobilized during postdepositional processes. The increased internal input of Pt within Otsuchi Bay can be explained by the release of 1.3-5.6% of the leachable fraction from sediments, probably transported from the land by the tsunami, during the water residence time in the bay.

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1. Introduction

The 2011 Earthquake off the Pacific coast of Tohoku occurred on March 11, 2011 in the Pacific Ocean near northern Japan, and thereafter a huge tsunami devastated coastal areas. Otsuchi City, located in Iwate Prefecture on the Pacific Ocean side of northern

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Japan, received catastrophic damage. Many structures were devastated, and many artifacts on land were washed away by the tsunami. Coastal environments were drastically changed after the tsunami, as both natural substances, such as terrestrial sediments and plants, and anthropogenic substances were transported to coastal areas (Kazama and Noda 2012; Suppasri et al., 2012). In fact, many scientists have investigated the effects of the tsunami on the Pacific coast of Tohoku, focusing on deep sea floor environments (Kitahashi et al., 2014, 2016), sedimentary structures (Seike et al., 2016), subtidal soft bottoms (Seike et al., 2013; Goto et al.,

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2017), and nutrient status (Fukuda et al., 2016; Yamada et al., 2017). However, we have not yet obtained information on the distribution and biogeochemical cycles of trace metals in seawater in this area after the tsunami. In this study, we revealed the spatiotemporal variations in platinum (Pt), which is a useful tracer of anthropogenic substances on land (Cobelo-Garcia et al., 2015), in seawater in Otsuchi Bay.

Platinum has been applied to a variety of industrial and medical uses, such as automobile catalysis and anticancer drugs (Pyrzynska, 2000; Ravindra et al., 2004; Rauch and Morrison, 2008; Sobrova et al., 2012). Platinum belongs to the least abundant group of elements (platinum group elements, PGEs) in the Earth's crust (Wedepohl, 1995). Platinum concentrations are about 0.2 pmol/L in the open ocean, and its vertical profiles in the western North Pacific are conservative (Colodner et al., 1993; Suzuki et al., 2014). However, Pt concentrations in estuaries have been reported to be higher than those in the open ocean, ranging from 0.02 to 0.62 pmol/L in the Lérez Estuary in Spain (Cobelo-Garcia et al., 2013), ranging from 0.35 to 0.84 pmol/L in the Gironde Estuary in France (Cobelo-Garcia et al., 2014), and reaching very high concentrations (5-35 pmol/L) in Tokyo Bay in Japan (Obata et al., 2006). Anthropogenic Pt has been emitted and dispersed throughout urban aquatic environments. Direct release from storm sewers draining roadways and indirect release from sewage plants that treat road run-off have been suggested as two possible sources of accumulated PGEs in sediment cores from an urban lake near Boston, MA, USA (Rauch et al., 2004). Sediment cores have exhibited recent changes in PGE contamination in coastal areas (Tuit et al., 2000; Cobelo-Garcia et al., 2011; Abdou et al., 2019). The Pt concentrations in sediments in an urban lake have increased exponentially following the introduction of automobile exhaust catalysts (Rauch et al., 2004). Further, Pt-based cytotoxic drugs, such as cisplatin, carboplatin, and oxaliplatin, which are widely used as anticancer drugs, might also affect 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 are increasing in urban areas. Thus, Pt concentrations in the aquatic environment have been reported on in recent years, although few studies have been published on the Pt geochemical cycle in coastal areas. It is very important to increase our knowledge on the distribution of this emerging contaminant in coastal

In this study, we first reveal the spatiotemporal variation of the dissolved Pt concentrations in Otsuchi Bay after 2011. Then, by comparing the results with those reported previously (Mashio et al., 2016), we discuss the factors that affected the Pt concentrations in seawater in Otsuchi Bay after the tsunami.

2. Materials and methods

2.1. Study area

We selected Otsuchi Bay, Iwate Prefecture, Japan, as our study area. Otsuchi Bay, located on the Pacific side of northern Japan, is a long, narrow bay, whose mouth is about 3.5 km wide and whose length is about 8 km. The main rivers flowing into Otsuchi Bay are the Otsuchi River (12.5 km in length), Kozuchi River (11.8 km in length), and Unozumai River (23.1 km in length). The study area, experienced catastrophic damage during the tsunami in 2011. Many structures were devastated and many artifacts on land were washed away by the tsunami.

The Otsuchi area is almost covered by forest, but Otsuchi City, whose population was approximately 15,000 in 2010, was built

near the coastal area of Otsuchi Bay. We think that there was little anthropogenic effect in this area.

3. Sampling

The sampling points are indicated in Fig. 1. Seventeen seawater samples were collected by the research boats Grand Maillet and Yayoi (International Coastal Research Center, AORI) in May and November 2012 and in March and May 2013. Three river water samples from the three main rivers flowing into Otsuchi Bay were also collected at the same time. Seawater samples were collected with a 12 L acid-precleaned Niskin-X bottle. River water samples were collected using a cleaned polypropylene bucket. The collected samples were filtered with a 0.2 µm capsule filter (Acropak; PALL Co.). The bottom depths were 45 m (Station 2), 37 m (Station 6), 20 m (Station 11), and 9 m (Station 16). At all stations, the samples for the deepest waters were collected at 1 m above the seafloor. All samples were acidified to a pH less than 1.5 using high-purity hydrochloric acid (HCl, Tamapure-AA-100, Tama Chemicals Co., Ltd., Japan) and stored in 500 mL low density polyethylene bottles precleaned with 3 M HCl and Milli-Q water (MQW, Millipore, USA). Moreover, we collected six surface sediment samples from Otsuchi Bay in May 2017. These sediments were collected using a Smith-Macintyre Bottom Sampler and were stored in polyethylene bags and kept in a freezer stocking.

4. Analytical method

We used a small anion exchange resin column in order to reduce procedural blank values (Suzuki et al., 2014). Briefly, seawater samples were acidified to 0.5 M HCl, a ¹⁹²Pt enriched spike solution was added in the amount expected to minimize the F value and the mixture was left to stand for 24 h to reach isotopic equilibrium. The solution was transferred to a Teflon column filled with anion exchange resin at a flow rate of 2 mL/min. Prior to introduction of the sample, the column was cleaned using a mixed eluent (5 M HNO₃ and 5 M HClO₄) and conditioned with 0.5 M HCl. Sample aliquots of 500 mL were passed through the column, which was rinsed with 0.05 M HCl and MQW to remove salts and loosely held metal ions. Adsorbed Pt on the anion exchange resin was eluted with 5 M HNO₃ and 5 M HClO₄ in the direction opposite to that of sample introduction. Eluents were collected in Teflon beakers and evaporated until the volumes was reduced to less than 0.1 mL. The concentrated samples were diluted with 1.5 mL of 5% HCl. Platinum concentrations were determined by analysis of ¹⁹²Pt and ¹⁹⁵Pt with a quadrupole inductively coupled plasma mass spectrometer (ICP-MS; Agilent 7700). This method can analyze pico-mole level Pt in seawater and isotopic equilibrium in sufficient after 24 h (Suzuki et al., 2014). We preconcentrated Pt from one aliquot of each sample and analyzed the eluents ten times by ICP-MS. Blank values for this procedure were less than 0.01 pmol/L and the detection limit (3σ of the procedural blank) was 0.015 pmol/L. Recovery of the spiked Pt was 51-100% during the preconcentration procedure.

To analyze total Pt in the sediments, we dissolved them using nitric acid, hydrochloric acid and hydrofluoric acid. Sample aliquots of 100 mg of sediment to which a Pt spike was added were dissolved with 68% HNO₃ for 24 h. After that, 70% HClO₄ and 38% HF were added to the sediment solutions and were heated by hotplate. The sediments were dissolved completely, slowly dried up and finally dissolved with 0.5 M HCl. The dissolved samples were analyzed by the same isotope dilution (ID)-ICP-MS method of anion exchange column preconcentration as that used for the seawater samples. Moreover, 6% acetic acid (fraction I) and 6% acetic acid + 1 M hydroxylamine hydrochloride (fraction II) were used

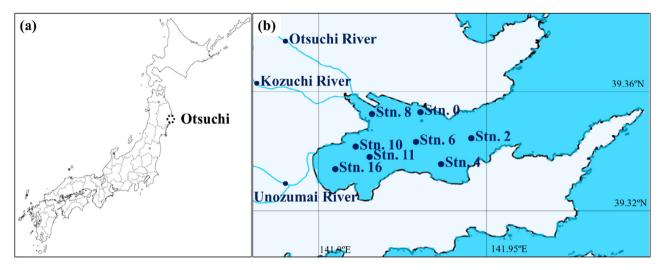


Fig. 1. Location of sampling stations in Otsuchi Bay, Japan. (a) Location of Otsuchi Bay in northern Japan; (b) Sampling stations at 8 points in Otsuchi Bay.

for sequential leaching of the sediments (Kato et al., 1995). Pt is expected to occur as a loosely adsorbed form in fraction I and as an adsorbed form onto oxides in fraction II. The sediment samples were extracted from each solution at 70 for 5 h and were filtered by a 0.45 μ m syringe filter. The filtered solution was spiked with a 192 Pt enriched solution, dried up on a hotplate, and dissolved by 5% HCl for analysis by ICP-MS. The blank value for this procedure was 1.6 pg/g for fraction I, and 2.1 pg/g for fraction II. Recovery of spiked Pt was 88.5–101%. We also analyzed a reference material, JSd-2, in the same manner as the samples. The Pt content in JSd-2 was 18.0 \pm 1.6 ng/g, which is within the range of the certified value (16.7 \pm 2.8 ng/g). We confirmed that the Hf concentrations in the preconcentrated sample, a possible interference of 195 Pt, were at the same level as that in the blank solution.

5. Results

5.1. Hydrography

The temperature–salinity (T–S) diagram for Station 2 is shown in Fig. 2. From the diagram, waters in this area was assigned to

one of six bodies of water (Hanawa and Mitsudera, 1987). Based on this assignation, the samples collected in March 2013 were derived from the Oyashio water system, and the others were almost all from the surface-layer water system. In March 2013, open ocean seawater entered Otsuchi Bay, which was different from the other samples. In May 2012 and 2013, we observed thermocline formation at a depth of approximately 5 m at the sampling stations, above which the water temperature was high and salinity was low. In contrast, in November 2012 and March 2013, thermoclines were not observed at all the stations, and temperature and salinity were uniform down through the depths (Fig. S1-S4). From summer to autumn, surface water near the halocline showed a counterclockwise lateral circulation pattern related to the Tsugaru Warm Current (Ishizu et al., 2017). From winter to early spring, this pattern weakened and the influence of the Oyashio Current occasionally increased (Ishizu et al., 2017).

At the first observation in May 2012, the water column in the bay was stratified and waters from the Tsugaru Warm Current system occurred in the bottom layers. Other waters were influenced by river waters. In November 2012, open ocean water intruded slightly into Otsuchi Bay, but only the surface water was warmed, whereas part of the Tsugaru Warm Current system occurred in the

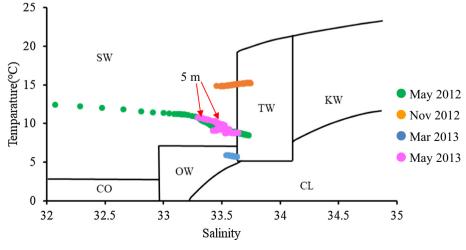


Fig. 2. Temperature vs. salinity diagram at Station 2 for each sampling time. Water masses are classified into 6 bodies: the Tsugaru Warm Current water system (TW), the Oyashio water system (OW), the Kuroshio water system (KW), the cold lower-layer water system (CL), the surface-layer water system (SW), and the Coastal Oyashio water system (CO) (Hanawa and Mitsudera, 1987).

Table 1Dissolved Pt concentrations in Otsuchi Bay. The unit is pmol/L. The error is the value calculated by error propagation of the standard deviation of the ICP-MS measurement value.

	May 2012	Nov 2012	Mar 2013	May 2013
Depth (m)				
Stn. 2				
1	0.61 ± 0.03	0.56 ± 0.02	0.49 ± 0.11	1.19 ± 0.04
5	0.64 ± 0.02	0.65 ± 0.03	0.42 ± 0.13	1.31 ± 0.02
10	0.63 ± 0.02	0.70 ± 0.02	0.49 ± 0.07	1.29 ± 0.03
20	0.83 ± 0.03	0.79 ± 0.03	0.43 ± 0.06	1.32 ± 0.02
44	0.87 ± 0.04	0.93 ± 0.03	0.59 ± 0.07	1.99 ± 0.03
Stn. 6				
1	0.74 ± 0.02	0.68 ± 0.03	0.40 ± 0.06	0.94 ± 0.03
5	0.64 ± 0.03	0.63 ± 0.05	0.45 ± 0.03	1.02 ± 0.03
10	0.67 ± 0.01	0.65 ± 0.03	0.53 ± 0.05	0.93 ± 0.03
20	0.62 ± 0.02	0.67 ± 0.04	0.41 ± 0.05	1.11 ± 0.02
37	0.87 ± 0.02	0.66 ± 0.03	0.46 ± 0.04	1.65 ± 0.04
Stn. 11				
1	0.96 ± 0.02	1.11 ± 0.04	1.20 ± 0.08	0.85 ± 0.02
5	0.97 ± 0.02	1.38 ± 0.05	1.22 ± 0.03	0.94 ± 0.02
10	0.98 ± 0.02	1.11 ± 0.05	0.84 ± 0.07	1.13 ± 0.02
18	1.02 ± 0.02	0.70 ± 0.04	0.55 ± 0.04	1.95 ± 0.02
Stn. 16				
1	0.98 ± 0.01	1.11 ± 0.05	1.00 ± 0.10	0.54 ± 0.02
5	1.14 ± 0.02	1.15 ± 0.05	1.16 ± 0.08	0.62 ± 0.03
8	1.16 ± 0.01	1.05 ± 0.04	1.01 ± 0.07	0.79 ± 0.03

bottom waters at all stations. In winter (March 2013) there was an influx of Oyashio Water, and the waters in the bay became entirely mixed. Again, by May 2013, the water column was stratified similarly to that in May 2012.

6. Platinum concentrations

The concentrations of dissolved platinum in seawater were 0.40–1.99 pmol/L (Table 1). The concentrations in river water samples were below the detection limit (0.015 pmol/L), which was similar to previous results in the Otsuchi and Kozuchi Rivers in 2007 (Mashio et al., 2016). The highest concentration (1.99 pmol/L) was observed in the deepest seawater at Station 2 in May 2013. The distribution was almost vertically uniform from May

2012 to March 2013, except at Station 11, where a high concentration was observed in the surface seawater in November 2012 and March 2013 (Fig. 3). At Station 2, the temporal variation in Pt concentrations indicated lower concentrations in March (an average concentration of 0.46 pmol/L). Compared with the Pt concentrations in May, higher concentrations were observed in 2013 than those in 2012 at Station 2 and Station 6, especially in the deepest seawater.

The Pt concentrations in sediment samples in Otsuchi Bay were 0.46–14.4 ng/g (Table 2). The highest Pt concentration was observed at Station 0 near the dock of a ship building company. Excluding Station 0, the average Pt concentration in the sediments was 1.14 ng/g. Using the sequential leaching technique, we obtained Pt contents in the following fractions: 0.19–1.13 ng/g in

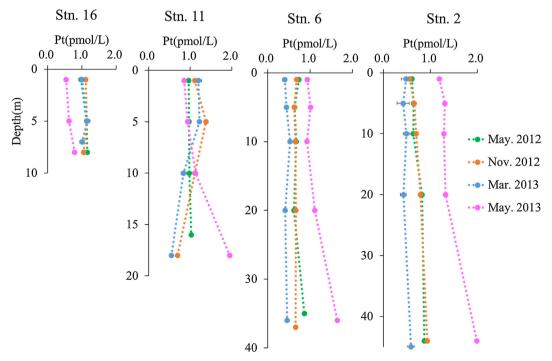


Fig. 3. Vertical distribution of Pt concentrations at each station.

Table 2 Pt concentrations in sediment samples. Fraction \underline{I} is acetic acid leachable fraction and Fraction \underline{I} is acetic acid + hydrochloric acid hydroxylamine leachable fraction. The unit is ng/g. The error is the standard deviation when measured three times.

Sampling points	Total	Fraction I	Fraction II
Stn. 0 Stn. 2 Stn. 4 Stn. 6 Stn. 8 Stn. 10 ISd-2	14 ± 6 0.46 ± 0.29 0.73 ± 0.65 1.4 ± 0.4 2.0 ± 0.2 1.1 ± 1.0 18.0 ± 1.6	0.25 ± 0.23 0.35 ± 0.27 0.19 ± 0.11 0.55 ± 0.21 1.1 ± 1.0 0.45 ± 0.43	0.25 ± 0.17 0.072 ± 0.058 0.11 ± 0.08 0.71 ± 0.20 0.036 ± 0.029 less than 0.03

fraction I and less than 0.03–0.71 ng/g in fraction II. The leachable fraction indicated 1.8% (Station 0) to 75.7% (Station 2) for fraction I and below 51.8% for fraction II.

7. Discussion

7.1. Concentrations of Pt in surface waters before and after the tsunami

The Pt concentrations in surface waters in 2007 (1 m depth at Stations 2, 6, 11, 16) and those in this study were plotted versus salinity for all sampling times and are shown in Fig. 4. The results in 2007 are referenced from Mashio et al. (2016). Platinum concentrations in open ocean seawater are approximately 0.22 pmol/L (Suzuki et al., 2014). The Pt concentrations in the water at salinity ranges from 27 to 34 were higher than those of a simple mixing line between river water, in which the Pt concentration was less than detection limit at a salinity of almost 0, and seawater, in which the Pt concentration was 0.2 pmol/L at salinity 35. In the 0-15 salinity range, the Pt concentrations in the waters in 2007 were lower than the mixing line (Mashio et al., 2016). Platinum occurs as Pt(OH)₂ in low salinity waters, which is easily removed (Turner et al., 2006). In areas where the salinity has increased, Pt would be transformed to PtCl₅(OH)²⁻, which is relatively stable in water (Cobelo-Garcia et al., 2013; Mashio et al., 2016). Platinum might be released as PtCl₅(OH)²⁻ from suspended particles with increasing salinities (Turner, 2007). However, dissolved Pt concentrations were elevated in high salinity areas ranging from 30 to 35 for each sampling time. Pt speciation should differ in lower salinity areas ranging from 0 to 14 considering the Pt-salinity relationship in Fig. 4. Therefore, it had been thought that dissolved Pt was supplied from inside of Otsuchi Bay (Mashio et al., 2016). In Fig. 4, we observed the same tendency during the current sampling campaign, but the concentrations levels were higher than those in 2007 (Mashio et al., 2016). Dissolved Pt was not supplied from river waters, because all river water samples were below the detection limit (less than 0.015 pmol/L) in 2007 and during the current sampling campaign. Moreover, in such rural study areas as Otsuchi Bay, there seemed to be little influence from direct anthropogenic input. From the vertical profiles of dissolved Pt in Japanese coastal areas, Mashio et al. (2017) estimated that the Pt was supplied from coastal sediments, which might be applicable to the current observations. Although the Pt concentrations in Otsuchi Bay seawater from 2007 to 2013 increased because of sediment including many terrestrial materials transported by the tsunami (Arij et al., 2014), the same mechanism controlling Pt distributions existed before and after the tsunami.

Since we only have surface water data from 2007, we could not compare Pt vertical profiles in Otsuchi Bay before and after the tsunami. However, the increase of Pt in surface waters after the tsunami might be derived from the sediments within the bay.

8. Vertical profiles of Pt in Otsuchi Bay after the tsunami

The dissolved Pt concentrations in Otsuchi Bay (Table 1) were higher than those in open ocean seawater (0.2–0.4 pmol/L; Colodner et al., 1993; Suzuki et al., 2014; Fischer et al., 2018), but similar to those in coastal area seawater (0.2–1.5 pmol/L; Mashio et al., 2017). In the latter study, dissolved Pt in coastal area seawater was found to be affected by anthropogenic substances. Moreover, it was thought that Pt was supplied to the seawater via coastal sediments (Mashio et al., 2017). In our results, Pt concentrations increased with depth, as reported in a previous study (Mashio et al., 2017). It is assumed that Pt concentrations were affected by anthropogenic or terrestrial substances at the sea floor.

Fig. 3 shows vertical profiles of dissolved Pt at each station. Pt concentrations in March 2013 were lower than those for the other sampling times, except for surface water at Stations 11 and 16, which showed the effect of river water. From the T–S diagram in Fig. 2, it is apparent that the water mass in March 2013 was very different from that for the other sampling times, which implies

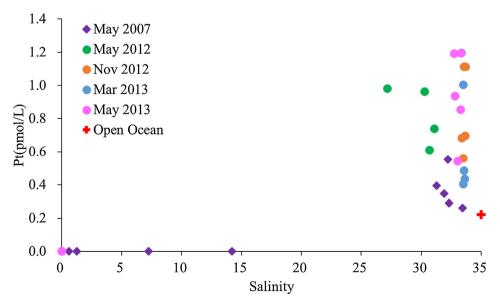


Fig. 4. The relationship between dissolved Pt concentrations and salinity classified by sampling time. Open ocean data referenced from Suzuki et al. (2014).

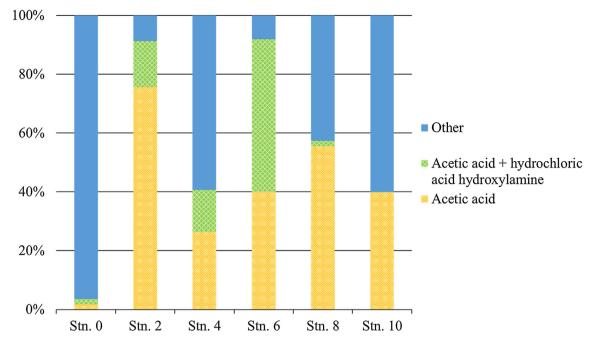


Fig. 5. The ratio of Pt concentrations in sediment samples dissolved by acetic acid and acetic acid + hydrochloric acid hydroxylamine. The "other" fraction was calculated by taking the difference from 100%.

that Oyashio water, the Pt concentrations of which were very low, had entered Otsuchi Bay. At the mouth and center of the bay (Stations 2 and 6), abrupt increases were observed from March to May 2013. In March 2013, Pt concentrations were almost uniform (0.4–0.5 pmol/L), and the concentration levels were similar to those in the open ocean, because Oyashio water was dominant in the bay. In May 2013, Pt concentrations were elevated throughout all depths and increased with depth. In May 2013, the water mass structure had changed to a surface seawater body (Fig. 2) in Otsuchi Bay. We also observed that the thermocline in the bay had formed at 8 m in May 2013. Below the thermocline, Pt concentrations increased toward the bottom, which implies that Pt had been supplied from seafloor sediments within the two month intervals.

9. Platinum supply to seawater

Previously, the Pt concentration levels in Otsuchi Bay had been higher than those in the Pacific Ocean (Colodner et al., 1993; Suzuki et al., 2014). Generally, Pt concentrations in estuaries ranging from 0.02 to 0.84 pmol/L were reported to be higher than those in the open ocean (Cobelo-Garcia et al., 2013; Cobelo-Garcia et al., 2014; Mashio et al., 2016). In highly populated areas, such as Tokyo Bay, Pt concentrations were reported to be 5-35 pmol/L (Obata et al., 2006) because of the direct supply of anthropogenic substances. After the tsunami, coastal cities in the Tohoku area were catastrophically damaged. In Otsuchi Bay, the tsunami reached a maximum height of 15.1 m and approximately 6.68 km² of the town was inundated and about 5600 buildings collapsed (Yanagawa and Sakai, 2014). Moreover, many pieces of infrastructure, such as sewage treatment systems, were disrupted (Qi et al., 2014). The town was destroyed, such that few people live there. At the time of this study, there was little direct input of dissolved Pt from the land into the bay.

The Pt concentration in the crust was reported to be 0.4 ng/g (Wedepohl, 1995), whereas that in sediments in the North Pacific Ocean were 1.5-5.0 ng/g (Colodner et al., 1993). In comparison, the average Pt concentration in sediments of the Leréz Estuary was $1.2 \pm 0.5 \text{ ng/g}$, which is higher than that in the continental

crust (Cobelo-Garcia et al., 2013). The highest concentration in the Leréz Estuary was 2.2 ng/g, which was within the range of concentrations in suspended particulate matter (0.7–1.6 ng/g). Moreover, Pt concentrations in sediments were reported to be 0.022–2.8 ng/g at low traffic stations and 0.45–40 ng/g at high traffic stations, whereas dissolved Pt concentrations in interstitial waters were 0.7–3.6 pmol/L in the Tagus Estuary, Portugal (Almécija et al., 2016). In these previous studies, the high Pt concentrations in sediments resulted from the supply of anthropogenic substances. In our study area, except for Station 0 near the dock, the Pt concentrations in sediments were 0.46–2.0 ng/g and were comparable to those in other estuarine areas, although the study area was less populated.

We carried out the fractional dissolution of Pt in sediments in the study area. Fraction I was a higher percentage than other fractions at Stations 2 and 6, implying that Pt was loosely associated with the sediment particles (Fig. 5). Platinum emitted from automobile catalysis is estimated to occur as Pt metal or Pt oxide (Moldovan et al., 2002), which seemingly, is not leached in the acetic acid fraction. In fact, solubility experiments of PGEs from automobile catalysis indicate that the maximum solubility of Pt is 0.03% in NaCl solutions (Zereini et al., 1997). The fraction of soluble Pt found in airborne dust samples varied between 30 and 43% of the total amount of Pt, but only 2.5 to 6.9% in tunnel dust (Alt et al., 1993). At this moment, we have not examined the ability of acetic acid to leach Pt from automobile catalysis, but it is unlikely that leached Pt originated directly from automobile catalysis. Platinum adsorbed loosely onto sediment particles is more likely to be leached in fraction I. In contrast, fraction II is leachable fraction under reductive conditions, but not likely to be mobile in the oxic environment of the study area. High concentrations of Pt were also reported in South Pacific pelagic sediments (~30 ng/g, Lee et al., 2003) and in marine manganese nodules (up to 900 ng/g, Koide et al., 1991), which suggests that relatively high Pt concentrations in coastal sediments may, at least partly, be attributed to the presence of marine particles. However, Pt in these sediments and nodules should be included in fraction II, which would not be the main possible source for Pt in bottom waters under oxic conditions.

In the sediments, Pt loosely adsorbed on sediments and not derived directly from automobile catalysis might be desorbed from the solid phase under post-depositional conditions. In a previous study, the particulate-aqueous distribution coefficient K_D (ml/g) for Pt on suspended particles was reported to be a few hundred in a mixture of filtered river water and seawater, but the K_D in seawater was lower than that in river water (Turner, 2007). In freshwater, Pt exists as Pt(OH)₂, but PtCl₅(OH)²⁻ would be dominant as salinity increases (Cobelo-Garcia et al., 2013; Mashio et al., 2016), which affects the distribution coefficient. After the tsunami, the Pt (Pt(OH)₂) adsorbed onto particles in freshwater may have been transported to the bay, deposited to the seafloor, and then desorbed from the particles as PtCl₅(OH)²⁻ under the highsalinity conditions. Although Pt was rapidly and almost completely adsorbed onto cohesive and non-cohesive sediments within 2 days. less than 3% of the Pt was desorbed from the sediments even in 171 mmol/L chloride solution at pH 7 (Couceiro et al., 2007). An experimental study on the post-depositional mobility of Pd, Rh, and Pt in semi-arid soil and sediment samples indicates that the interaction of Pt(IV) with organic rich matrices may lead to a high removal rate of Pt(IV) from solution compared to its interaction with a relatively organic poor soil (Sako et al., 2009). After organic matter degradation in the sediments, Pt might be remobilized and transported to overlying waters (Tuit et al., 2000). Within the bay, the total inorganic nitrogen (ammonium + nitrate + nitrite) to phosphate ratio (TIN/P) in seawater was low during November 2011 to January 2012, but then increased and finally became higher than before the earthquake (Fukuda et al., 2016). One reason why a low TIN/P water was formed near the bottom was the release of PO₄³- from anoxic sediments, which implies vigorous post-depositional degradation of organic matter in the sediments during this period. The post-depositional change in the seafloor environment after the tsunami might have affected the mobility of Pt in the sediments.

10. Estimated Pt fluxes

To estimate the Pt flux in Otsuchi Bay, we adopted the standard estuarine mixing model (Boyle et al., 1974; Andreae et al., 1983):

$$IE = RC * - RC_0 = R(C * - C_0)$$

where IE is the internal input, R is the river water discharge, C_0 is the river endmember concentration, and C^* is the model's effective river concentration for Pt by extrapolating the linear gradient. By using linear regression of the Pt data at salinities of 27–35 in 2012 and 2013, C^* was estimated to be 9.4 pmol/L after the tsunami. The river flow rates into Otsuchi Bay were estimated to be 31.9 m³/s, and the Pt input was less than 0.015 pmol/L.

The IE was calculated as

$$IE = R(C* - C_0) = 31.9 \text{ m}^3/\text{s} \times 9.4 \text{ pmol/L} = 0.30 \text{ } \mu\text{mol/s}$$

In a previous study, the Pt flux in 2007 was estimated to be IE = 0.07 μ mol/s (Mashio et al., 2016). From these results, IE clearly increased after the tsunami.

Additionally, we roughly estimated that the potential acetic-acid leachable fraction of Pt in the sediments was released to seawater. Calculated from the sediment volume of Otsuchi Bay (i.e., the area is $20.2~{\rm km}^2$ with a depth of $10~{\rm cm}$ and density of $2.7~{\rm g/cm}^3$) and the average concentration of fraction I (0.49 ng/g), we can estimate the acetic-acid leachable Pt fraction in the sediments to be

$$Q \ = \ 20.2 \ km^2 \times \ 10 \ cm \ \times \ 2.7 \ g/cm^3 \times \ 0.49 \ ng/g \ = \ 2672 \ g$$

$$= \ 13.7 \ mol$$

The residence time of water in Otsuchi Bay was estimated to be on the order of a week, or less than a month (Fukuda et al., 2016). If we assume the residence time to be one week to one month, the potential benthic flux (BF) of Pt from the sediments is calculated to be

$$BF = 13.7 \text{ mol} / 1 \text{ week to 1 month} = 5.29 - -22.7 \mu \text{mol/s}$$

This is the potential Pt flux if all the acetic-acid leachable fraction in sediments were released into seawater during the residence time. The IE in Otsuchi Bay in 2013 was calculated to be 0.30 µmol/s. Therefore, as a rough estimate, 1.3–5.6% of the leachable fraction of Pt in the sediments appears to have been released into seawater during the water residence time in the bay. We could not measure the leachable fraction of Pt in the sediments before the tsunami. However, the IE increased after the tsunami and corresponded to the acetic-acid leachable fraction in the surface sediments. This finding suggests the release of the Pt from the seafloor sediments that had been transported into the bay from the land by the tsunami.

11. Conclusions

We studied the Pt concentrations in Otsuchi Bay seawater and sediments after the 2011 earthquake. Dissolved Pt concentrations were 0.40-1.99 pmol/L in seawater and below the detection limit of 0.015 pmol/L in river water. Platinum concentrations in sediment samples were 0.46-14.4 ng/g in Otsuchi Bay. In addition, Pt concentrations in the acetic-acid fractions were 0.19-1.13 ng/g, whereas those in the acetic acid + hydrochloric acid hydroxylamine fractions were less than 0.03-0.71 ng/g. There was seasonal variation in the dissolved Pt concentrations that followed the changes in water mass structure. During the stratification season, the vertical profiles indicated increasing Pt concentrations with depth. Judging from the sequential fraction analysis of sediments, Pt was loosely adsorbed on sediment particles. Increased internal input of dissolved Pt into Otsuchi Bay can be explained by 1.3-5.6% of the leachable fraction in sediments, probably transported from the land by the tsunami, and was released during the water's residence in the bay. The huge tsunami that occurred in the study area has influenced the cycles of anthropogenic substances in the bay. After the catastrophic disaster of the tsunami, we need to continually investigate the anthropogenic substances within the water column as well as in the seafloor sediments.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.134659.

References

- Abdou, M., Schäfer, J., Hu, R., Gil-Díaz, T., Garnier, C., Brach-Papa, C., Chiffoleau, J.F., Charmasson, S., Giner, F., Dutruch, L., Blanc, G., 2019. Platinum in sediments and mussels from the northwestern Mediterranean coast: Temporal and spatial aspects. Chemosphere 215, 783-792.
- Alt, F., Bambauer, A., Hoppstock, K., Mergler, B., Tölg, G., 1993. Platinum traces in airborne particulate matter. Determination of whole content, particle size distribution and soluble platinum Fresenius' Journal of Analytical Chemistry 346, 693-696.
- Andreae, M.O., Byrd, J.T., Froellch, P.N., 1983. Arsenic, antimony, germanium, and tin in the Tejo Estuary, Portugal: Modeling a polluted estuary. Environmental and Science Technology 17, 731–737.
- Arii, M., Koiwa, M., Aoki, Y., 2014. Applicability of SAR to marine debris surveillance after the Great East Japan Earthquake. IEEE J. Sel. Top. Appl. Earth Obs. Remote Sens. 7, 1729-1744.
- Boyle, E., Collier, R., Dengler, A.T., Edmond, J.M., Ng, A.C., Stallard, R.F., 1974. On the chemical mass-balance in estuaries. Geochim. Cosmochim. Acta 38, 1719–1728.
- Cobelo-Garcia, A., Neira, P., Mil-Homens, M., Caetano, M., 2011. Evaluation of the contamination of platinum in estuarine and coastal sediments (Tagus Estuary and Prodelta, Portugal). Mar. Pollut. Bull. 62, 646-650.
- Cobelo-Garcia, A., López-Sánchez, D.E., Almecija, C., Santos-Echeandia, J., 2013. Behavior of platinum during estuarine mixing (Pontevedra Ria, NW Iberian Peninsula). Mar. Chem. 150, 11-18.
- Cobelo-Garcia, A., López-Sánchez, D.E., Schäfer, J., Petit, J.C.J., Blanc, G., Turner, A., 2014. Behavior and fluxes of Pt in the macrotidal Gironde Estuary (SW France). Mar. Chem. 167, 93-101.
- Cobelo-Garcia, A., Filella, M., Croot, P., Frazzoli, C., Du Laing, G., Ospina-Alvarez, N., Rauch, S., Salaun, P., Schäfer, J., Zimmermann, S., 2015. COST action TD1407: Network on technology-critical elements (NOTICE)-from environmental processes to human health threats. Environmental Science Pollution Research 22. 15188-15194.
- Colodner, D.C., Boyle, E.A., Edmond, J.E., 1993. Determination of rhenium and platinum in natural waters and sediments, and iridium in sediments by flow injection isotope dilution inductively coupled plasma mass spectrometry. Anal. Chem 65 1419-1425
- Couceiro, F., Turner, A., Millward, G.E., 2007. Adsorption and desorption kinetics of rhodium (III) and platinum (IV) in turbid suspension: Potential tracers for sediment transport in estuarine flumes. Mar. Chem. 107, 308-318.
- Fischer, L., Smith, G., Hann, S., Bruland, K.W., 2018. Ultra-trace analysis of silver and platinum in seawater by ICP-SFMS after off-line matrix separation and preconcentration. Mar. Chem. 199, 44-52.
- Fukuda, H., Katayama, R., Yang, Y., Takasu, H., Nishibe, Y., Tsuda, A., Nagata, T., 2016. Nutrient status of Otsuchi Bay (northeastern Japan) following the 2011 off the Pacific coast of Tohoku Earthquake. J. Oceanogr. 72, 39-52.
- Goto, R., Sakamoto, S., Hayakawa, J., Seike, K., 2017. Underwater observations of the giant spoon worm Ikeda taenioides (Annelida: Echiura: Ikedidae) in a subtidal soft-bottom environment in northeastern Japan, which survived tsunamis of the 2011 off the Pacific Coast of Tohoku Earthquake. J. Oceanogr. 73, 103-113.
- Hanawa, K., Mitsudera, H., 1987. Variation of water system distribution in the Sanriku Coastal area. Journal of Oceanographic Society Japan 42, 435–466.
- Ishizu, M., Itoh, S., Tanaka, K., Komatsu, K., 2017. Influence of the Oyashio Current and Tsugaru Warm Current on the circulation and water properties of Otsuchi Bay, Japan. J. Oceanogr. 73, 115-131.
- Kato, Y., Tanase, M., Minami, H. and Okabe, S., 1995. Remobilization of transition elements in pore water of continental slope sediments. In Biogeochemical Processes and Ocean Flux in the Western Pacific, Eds. Sakai, H. and Nozaki, Y., pp. 383-405.
- Kazama, M., Noda, T., 2012. Damage statistics (Summary of the 2011 off the Pacific Coast of Tohoku Earthquake damage). Soils Found. 52 (5), 780-792.
- Kitahashi, T., Jenkins, R.G., Nomaki, H., Shimanaga, M., Fujikura, K., Kojima, S., 2014. Effect of the 2011 Tohoku Earthquake on deep-sea meiofaunal assemblages inhabiting the landward slope of the Japan Trench. Mar. Geol. 358, 128-137.
- Koide, M., Goldberg, E.D., Niemeyer, S., Gerlach, D., Hodge, V., Bertine, K.K., Padova, A., 1991. Osmium in marine sediments. Geochim. Cosmochim. Acta 55 (6), 1641-1648.
- Kümmerer, K., Helmers, E., 1997. Hospital effluents as a source for platinum in the environment. Sci. Total Environ. 193, 179-184.
- Lee, C.A., Wasserburg, G.J., Kyte, F.T., 2003. Platinum-group elements (PGE) and rhenium in marine sediments across the Cretaceous-Tertiary boundary:

- Constraints on Re-PGE transport in the marine environment. Geochim. Cosmochim. Acta 67 (4), 655-670.
- Mashio, A.S., Obata, H., Tazoe, H., Tsutsumi, M., Santos, Ferrer I, A. and Gamo, T, 2016. Dissolved platinum in rainwater, river water and seawater around Tokyo Bay and Otsuchi Bay in Japan. Estuar. Coast. Shelf Sci. 180, 160-167.
- Mashio, A.S., Obata, H., Gamo, T., 2017, Dissolved platinum concentrations in coastal seawater: Boso to Sanriku areas, Japan. Arch. Environ. Contam. Toxicol. 72 (2), 240-246.
- Moldovan, M., Palacios, M.A., Gómez, M.M., Morrison, G., Rauch, S., McLeod, C., Ma, R., Caroli, S., Alimonti, A., Petrucci, F., Bocca, B., Schramel, P., Zischka, M., Pettersson, C., Wass, U., Luna, M., Saenz, J.C., Santamaría, J., 2002. Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic. Sci. Total Environ. 296, 199-208.
- Obata, H., Yoshida, T., Ogawa, H., 2006. Determination of picomolar levels of platinum in estuarine waters: A comparison of cathodic stripping voltammetry and isotope dilution-inductively coupled plasma mass spectrometry. Analytical Chimica Acta 580, 32-38.
- Pyrzynska, K., 2000. Monitoring of platinum in the environment. J. Environ. Monit. 2, 99N-103N.
- Qi, W.-K., Sunaba, T., Norton, M., Li, Y.-Y., 2014. Effect of the great east Japan earthquake and tsunami on sewage facilities and subsequent recovery measures. J. Water Sustainability 4, 27-40.
- Rauch, S., Hemond, H.F., Peucker-Ehrenbrink, B., 2004. Recent changes in platinum group element concentrations and osmium isotopic composition in sediments from an urban lake. Environ. Sci. Technol. 38, 396-402.
- Rauch, S., Morrison, G.M., 2008. Environmental relevance of the platinum-group elements. Elements 4, 259-263.
- Ravindra, K., Bencs, L., Van Grieken, R., 2004. Platinum group elements in the environment and their health risk. Sci. Total Environ. 318, 1-43.
- Sako, A., Lopes, L., Roychoudhury, A.N., 2009. Adsorption and surface complexation modeling of palladium, rhodium and platinum in surficial semi-arid soils and sediments. Appl. Geochem. 24, 86-95.
- Seike, K., Shirai, K., Kogure, Y., 2013. Disturbance of shallow marine soft-bottom environments and megabenthos assemblages by a huge tsunami induced by the 2011 M9.0 Tohoku-oki Earthquake. PLoS ONE, 8 6, 1-10.
- Seike, K., Kitahashi, T., Noguchi, T., 2016. Sedimentary features of Onagawa Bay, northeastern Japan after the 2011 off the Pacific coast of Tohoku Earthquake: sediment mixing by recolonized benthic animals decreases the preservation potential of tsunami deposits. J. Oceanogr. 72, 141-149.
- Sobrova, P., Zehnalek, J., Adam, V., Beklova, M., Kizek, R., 2012. The effects on soil/ water/plant/animal systems by platinum group elements. Cent. Eur. J. Chem. 10, 1369-1382.
- Suppasri, A., Koshimura, S., Imai, K., Mas, E., Gokon, H., Muhari, A., Imamura, F., 2012. Damage characteristic and field survey of the 2011 great east Japan tsunami in Miyagi Prefecture. Coastal Engineering Journal 54 (1). 1250005-1-1250005-30.
- Suzuki, A., Obata, H., Okubo, A., Gamo, T., 2014. Precise determination of dissolved platinum in seawater of the Japan Sea, Sea of Okhotsk and western North Pacific Ocean. Mar. Chem. 166, 114–121.
- Tuit, C.B., Ravizza, G.E., Bothner, M.H., 2000. Anthropogenic platinum and palladium in the sediments of Boston Harbor. Environ. Sci. Technol. 34, 927-932.
- Turner, A., Crussell, M., Millward, G.E., Cobelo-García, A., Fisher, A.S., 2006. Adsorption kinetics of platinum group elements in river water. Environmental Science Technology 40 (5), 1524–1531.
- Turner, A., 2007. Particle-water interactions of platinum group elements under estuarine conditions. Mar. Chem. 103, 103–111.
 Wedepohl, K.H., 1995. The composition of the continental crust. Geochim.
- Cosmochim. Acta 59 (7), 1217–1232.
- Yamada, Y., Kaga, S., Kaga, Y., Naiki, K., Watanabe, S., 2017. Changes of seawater quality in Ofunto Bay, Iwate, after the 2011 off the Pacific coast of Tohoku Earthquake, I. Oceanogr, 73, 11-24.
- Yanagawa, R., Sakai, S., 2014. Topographical, propagating tsunami and suffering building features by the Great East Japan Earthquake Tsunami in the Iwate coastal region. Jornal of Japan Society for Natural Disaster Science 33 (2), 145-159 (in Japanese).
- Zereini, F., Skerstupp, B., Alt, F., Helmers, E., Urban, H., 1997. Geochemical behavior of platinum-group elements (PGE) in particulate emissions by automobile exhaust catalysts: experimental results and environmental investigations. Sci. Total Environ. 206 (2–3), 137–146.