OCCURRENCE OF PERSITENT ORGANIC POLLUTANTS IN TSUNAMI SEDIMENT LEFT FROM THE GREAT EAST JAPAN EARTHQUAKE

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Introduction

The Great East Japan Earthquake disaster and its resultant tsunami occurring in March, 2011 left huge amounts of sand and muddy matter (tsunami sediment) on the Pacific coast of the Tohoku district. The amount of sediments generated in six prefectures devastated by tsunami (*i.e.*, Aomori, Iwate, Miyagi, Fukushima, Ibaraki, Chiba) was estimated to be approximately 13 million to 28 million tons[1]. Although its main component is seawater flotsam from coastal seas, its properties and composition are diverse, including debris of homes and other structures destroyed by tsunami, petroleum products, and other chemical materials and products. Hazardous compounds such as persistent organic pollutants (POPs) (*e.g.*, dioxins, PCBs, and POPs pesticides) from establishments located in stricken areas might be incorporated into sediments, which is of our concerns. From early times since March after the earthquake, we collected surface sediment samples in Iwate and Miyagi prefectures and conducted chemical characterization in terms of general properties and POPs by analytical approach.

Materials and methods

We gathered tsunami sediment in tsunami-stricken areas from late March to June. We gathered 62 surface sediment samples in Iwate and Miyagi prefectures. The samples were then analyzed to ascertain their multiple chemical properties (detailed analyses covering general properties, oil content, and persistent organic pollutants (POPs)) to provide a comprehensive assessment of sediment for reference to domestic regulation standards and reference guidelines. Information related to sites where samples were gathered, items of analyses and results of analyses are compared to provide an overall view of properties of sediment for later processing of sediment.

Analysis items are lined up below.
- General properties (density, pH, drying loss (moisture content), ignition loss (IL), electric conductivity (EC), ion concentration (chloride ion, cation, and anion), particle size)
- Oil contents (*n*-hexane extract)
- Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/DFs)
- Polychlorinated biphenyl (PCB)
- Perfluoro octane-1-sulfonic acid) (PFOS) and perfluorooctanoic acid (PFOA)
- POPs pesticides (DDTs, chlordane, dieldrin, aldrin, endrin, heptachlor, hexachlorobenzene (HCB), pentachlorobenzene (PeCBz), mirex, hexachlorocyclohexane (HCH))

PCDD/DFs, PCB and POPs pesticides were extracted from the samples firstly with acetone by shaking extraction, which was followed by soxhlet extraction with toluene. The combined extracts were dewatered and cleaned up by individual adsorption chromatography. For analysis of those compounds an HRGC/HRMS system was used. PFOS and PFOA were extracted by methanol, cleaned up by an SPE cartridge and determined by an LC/MS/MS.

Results and discussion

Abstracts of the analytical results were summarized below. The results of analyses obtained were compared with related regulation standards and reference guidelines, in addition to previously reported data of analyses for Sendai city and neighboring jurisdictions[2-7].

General property.

Density was not very different from that of general soil. It was around 2.7 g/cm^3. In addition, coarse grains with diameter greater than 75 μm occupied nearly 90% of sediment. pH was mostly 7.0–9.0 roughly, but some

samples showed strong acidity or alkalinity. EC, an index of salinity, covered a wide range (a few mS/m to greater than 5,000 mS/m), perhaps because of various influences such as desalination by rainfall after deposition or by immersion in seawater before displacement by tsunami. Chloride ion concentration, a related index of salinity, showed widely various values of 0–2.1 dry weight % (median 4.7 mg/g-dry, geometric mean 6.5 mg/g-dry). These results indicate that EC has a close correlation with the chloride ion concentration, and that the former might be useful as a salt index. Ignition loss (the mass lost after heating to 600°C for 3 hr) is mainly used as the index of organic matter contents. In our samples, values were 1.2–16.3%, varying by an order of magnitude. The great difference is likely attributable to organic matter in sea mud, but some samples contained oil.

Oil content (n-hexane extract).
N-hexane extract is an index of oil content. The Japan Fisheries Conservation Association has suggested a reference standard as the standard value of bottom mud for fisheries water (less than 0.1% of *n*-hexane extract for dry sediment from sea areas: 0.1% = 1,000 ppm)[2]. This value provides a standard in conjunction with environmental quality to protect aquatic organisms. High content of 1% order was detected in a sample gathered under a transformer pole and in one other sample from Sendai city gathered near an industrial waste processing petrochemical factory.

PCDD/DFs.
The regulation standard of dioxin includes the standard value of soil (1,000 pg-TEQ/g), the examination standard of soil (250 pg-TEQ/g to request necessary monitoring examination), and the environmental standard of sediment (150 pg-TEQ/g).
In our sediment samples, one sample from Minamisanriku town, showed particularly high dioxin content of 520 pg-TEQ/g. That sample was taken from open burning residue. Its homolog and isomer composition were those of combustion-related samples (*i.e.*, incineration gas and ash). For other samples, TEQ on a soil basis was 0.11–78 pg-TEQ/g. These were less than both the environmental standard values of soil and sediment.
For reference, the 0.00011–53 pg-TEQ/g of soil in Sendai city in environmental research measured in 2005–2009 and 0.76–15 pg-TEQ/g of sediment in Miyagi seawater area in the same five years are approximately equal to those found in present samples[3].

PCBs.
One standard value of PCB is the provisional removal standard (greater than10 mg/kg: a standard whereby one is encouraged to remove polluted bottom sediment that would cause pollution of public water and fishery products). In addition, the Treatment Standard of PCB for waste oil is 0.5 mg/kg, and waste with PCB below this standard is not a specially controlled waste.
All PCB contents of the present investigation were more than one order below the level of the Treatment Standard of 0.5 mg/kg described above and were between 0.0003–0.18 mg/kg. However, the concentration level was distributed over a wide range, showing three orders of difference between samples gathered at different locations. Samples with relatively high PCB concentrations were found in Ishinomaki city (one spot) and Sendai city (two spots). Their respective concentrations were 0.18, 0.16, and 0.13 mg/kg. Homolog patterns of these samples suggest that the high level samples described above are of PCB formulation origin, as industrial products.
For reference, PCB analysis results for three specimens from the bottom of Sendai Bay and Matsushima Bay, in a 2009 monitoring investigation by Ministry of Environment of Japan[3] were 0.0051, 0.0050, and 0.0051 mg/kg. In addition, results of a five-year investigation by the same agent during 2005–2009, were 0.002–0.011 mg/kg at those locations. These values are of the level of concentrations of the present investigation described above, except for three samples described in the second paragraph of this section.

PFOS and PFOA.
PFOS, an organic fluorochemical used as a surface treatment agent and surfactant, was designated as POPs in the Stockholm Convention in 2010. To date, no environmental standard for soil and sediment has been set in Japan. A discharge target of treated residues (sludge, incineration ash, fly ash, and others) after proper treatment of waste containing PFOS has been discussed to propose 3,000 ng/g (3 mg/kg)[4].

All of our sediment samples yielded PFOS concentrations of less than the discharge target described above by more than three orders, 3.5 ng/g at a maximum. For reference, PFOS analyses of three specimens from the bottom sediment of Sendai Bay and Matsushima Bay in 2009 monitoring investigation by Ministry of Environment of Japan[3] were 0.29, 0.31, and 0.26 mg/kg. In addition, the result of measurement by the same agent of bottom sediment of the whole country was less than 0.0037–1.9 ng/g.
We examined PFOA as well. In our sediment samples, PFOA of 0.005–0.54 ng/g was detected. The PFOA analysis of three bottom mud specimens from Sendai Bay and Matsushima Bay in a 2009 monitoring investigation that the Ministry of the Environment of Japan conducted gave 0.034, 0.047, and 0.042 ng/g[3]. In addition, the measurement of bottom sediment of whole country in that same investigation gave concentrations of < 0.0033–0.5 ng/g. Accordingly, PFOS and PFOA concentrations of our sediment samples are approximately of the same level as those of general bottom sediment.

POPs pesticides.
The analysis of POPs pesticides was mainly compared with the results of an annual environmental survey conducted by the Ministry of Environment of Japan[3]. In addition, as reference guidelines, we compared our results with (i) Japanese soil guidance level for POPs pesticides (content)[5], (ii) the low POPs content standard value of general technical guidelines for POPs waste in the Basel Convention (50,000 ng/g)[6]. (iii) the discharge target value of residues after treatment of abolished POPs pesticides[7].
As a general tendency, the level of these substances in sediment was within the acceptable levels. Among pesticides, concentration of DDT was the highest, followed by HCH. Because DDT and HCH have been used as pesticides, they remain in rice fields, field soil, and river bottoms. Furthermore, chlordane has been used for termite extermination under residential floors. The tsunami must have mixed several pesticides used for different purposes and deposited them with sediment.
DDTs: *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD and *p,p'*-DDD concentrations were slightly higher than the level of the bottom sediment monitoring, and were of the same level as that of rice field soil[3]. However, they are much less than 50,000 ng/g of soil density guidance level ((i) above). DDT concentration was high at locations where oil or PCBs were low, suggesting the influence of the land area suffering mixing with rice paddy or field soil. A sample from Shichigahama town showed specifically high *o,p'*-DDT, which is usually a minor isomer in environmental samples of river water, bottom sediment, and living organisms. A reference reports that dicofol, a tick repellent, includes *o,p'*-DDT as a high-density impurity. Therefore, it is necessary to examine the finding above regarding this.
HCHs: *alpha*-HCH, *beta*-HCH, *gamma*-HCH, and *delta*-HCH were prevalent in samples from Ishinomaki city and Kesennuma city, and might have come from rice field pesticides. Compared to bottom sediment monitoring, they show slightly higher concentrations. Nevertheless, they are much less than the 50,000 ng/g of soil guidance level ((i) above).
Chlordanes (CHLs): *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, and oxychlordane were found in concentrations that were slightly higher than the level of the bottom sediment monitoring, but they were much less than 20,000 ng/g of the soil guidance level ((i) above).
Aldrin, dieldrin, and endrin: The highest concentration of dieldrin, 15 ng/g, was found in Sendai city. However, it is still much less than the 4,100 ng/g (sum of aldrin and dieldrin) of the soil guidance level ((i) above). The highest concentration of endrin, 8.4 ng/g, was found in sample from Ishinomaki city. However, it was much less than 8,300 ng/g of the soil guidance level ((i) above).

The number of samples was limited to 62 and considerations have been done through these restricted examinations. However, no severe POPs pollution has been apparently found from the results as mentioned above.

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