Distribution of Dioxins in Surface soils and River-mouth Sediments and their Relevance to Watershed Properties

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Introduction

Dioxins are released into the atmospheric environment from incinerators of municipal/industrial wastes, and deposition of them on the ground can occur in various pathways: dry gaseous, dry particulate and wet forms[1)]. Additionally, some pesticides contained dioxins as byproducts, such as pentachlorophenol (PCP) and chloronitrofen (CNP), were applied in the paddy fields in Japan, especially during 1960s-1980s[2)]. Due to their strong hydrophobicity, dioxins are sorbed onto the organic component of surface soils. They are gradually washed away with the soil erosion caused by rain, and finally flowed into the water environment with particulate matters (i.e., SS and sediment). Therefore, the movement and fate of dioxins should be considered with that of particulate matters in watersheds.

In this research, the Yasu and Ado river basins around Lake Biwa (the largest freshwater lake in Japan) were chosen, and a number of surface soil, river sediment and river-mouth sediment were collected in these basins. We measured the dioxins TEQ concentration in all of them by CALUX (Chemically Activated Lusiferase Expression) assay. We also measured the characteristics of soil and sediment which may influence the movement of dioxins (i.e. the organic carbon content and particle size), and compared the relationship between the dioxins TEQ concentration and the characteristics of all samples to grasp the dioxins distribution and movement in each watershed.

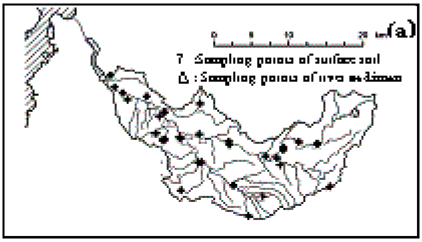
Sampling

1. Surface soil and river sediment

In this research, sampling points of surface soil and river sediment were determined considering land use and tributaries in each watershed. Sampling points of surface soil and river sediment were shown in Figure 1 (a), (b). Both surface soil and river sediment were collected approximately top 5 cm by a stainless shovel after removal of crude materials such as fallen leaves. After sampling, they were freeze-dried immediately by freeze-drier (FDU-830, EYELA), and then kept in refrigerator until further analysis.

2. River-mouth sediment

Sampling points of river-mouth sediment (Figure 1(c)) were determined considering the flow regime at the river-mouth. By the way, Yasu River had flowed into Lake Biwa from different points (north and south river mouths) until 1979. Therefore, we sampled sediment near these old river-mouths. We could collect only a few river-mouth sediments near the Ado river-mouth, since the water depth changes dramatically at the river-mouth. River-mouth sediment were collected about top 10 cm by core sampler (diameter: 5 cm). After sampling, they were also freeze-dried and stored. With the space limited, Figure of Sampling points in Yasu river-mouth is only shown.



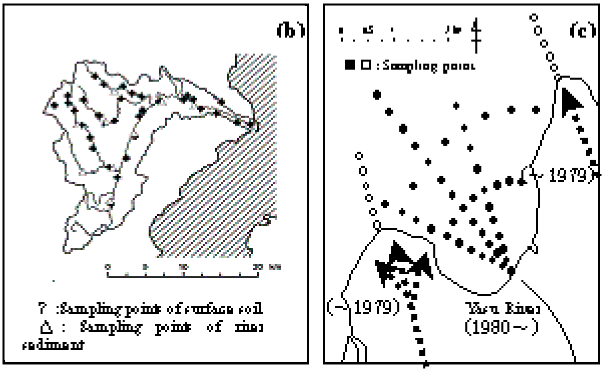


Figure 1: (a) Sampling Points in the Yasu River Basin
(b) Sampling Points in the Ado River Basin
(c) Sampling Points of Yasu River-mouth sediments (● and ○ collected near the present Yasu river-mouth and the old river-mouth, respectively)

Materials and Methods

Organic carbon content of all samples was analyzed by a high temperature combustion method (at 900) using TOC analyzer (TOC-5000A, Shimadzu Co.) with a solid sample module (SSM-5000A, Shimadzu Co.). In this research, as the measured value of inorganic carbon content was relatively low and negligible, so we regard the value of total carbon as the value of organic carbon.

Surface soil and river sediment were fractionated by using the stainless sieves (JIS-Z8801, diameter: 2,000, 500, 250, 106 m) to know the particle size. River-mouth sediment was very small particle size, so we analyze its particle size distribution by using a particle size analyzer (SALD-2100, Shimadzu Co.).

The CALUX assay was used to measure the dioxins TEQ concentration. The CALUX assay is relatively rapid, cheap measurement technique of dioxins and requires a small quantity of the solid sample (approximately, 2-10 g). Moreover, there is a good linear relationship between the TEQ value from CALUX assay and one from HR/GCMS[3]. In this research, CALUX assay was chosen in order to examine the TEQ value in many samples.

Results and Discussions

1. Surface soil and river sediment

The relationships between the dioxins TEQ concentration values and the organic carbon content in surface soil (forest soil, paddy field) and river sediment of the Yasu and Ado river basins are shown in Figure 2. In both basins, the dioxins TEQ concentration in forest soil showed a very good linear relationship to the organic carbon content. However, the regression lines of forest soil in both basins are different each other. Generally, the source of dioxins in forest soil is mainly incinerators of municipal/industrial wastes. Therefore, it considered that the difference of regression slope comes from the difference of atmospheric concentration of dioxins in both basins. On the other hands, in paddy field, although the organic carbon content is relatively low, the dioxins TEQ concentration is quite high. The dioxins in pesticides (e.g., PCP, CNP) as impurities still remain even now.

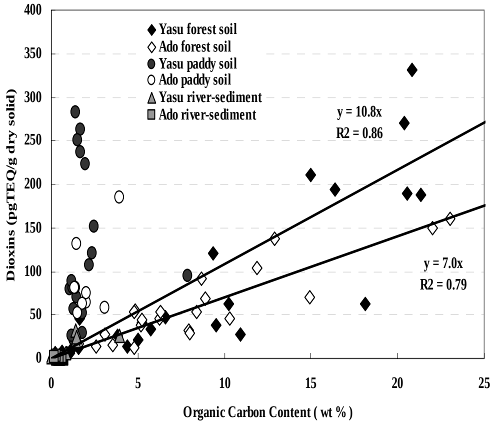


Figure 2:Correlation of dioxins TEQ concentration and organic carbon content in surface soil and river sediment.

Moreover, it is found that, in surface soil of various land uses, the smaller particle size has the higher organic carbon content (date not shown). River sediment consists of relatively coarser particles than surface soil, and has the quite low organic carbon content and the dioxins TEQ concentration value. Therefore, we considered that the smaller particle that is likely to have the higher dioxins TEQ concentration, flows more easily to downstream and/or river mouth. Then, river mouth a "haunt" of hydrophobic organic pollutants?

2. River-mouth sediment Relationship between the dioxins TEQ concentration value and the organic carbon content in both river-mouth sediments is shown in Figure 3, the correlation of the

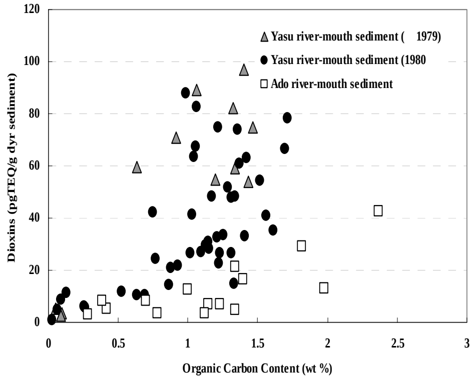


Figure 3:Correlation of Dioxins TEQ concentration and organic carbon content in river-mouth sediment

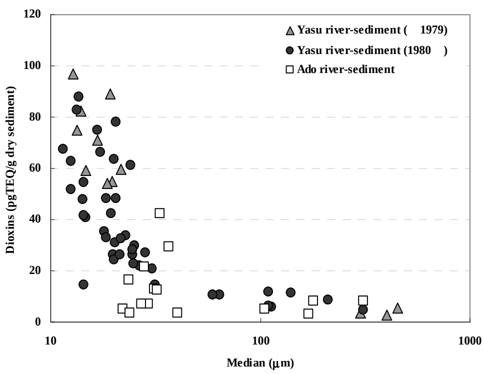


Figure 4:Correlation of dioxins TEQ concentration and particle size in river-mouth sediment

dioxins TEQ concentration and the median particle size is also shown in Figure 4. Unexpectedly, the dioxins TEQ concentration in river-mouth sediment is not so high in both river mouths, although particle size is quite small. If you focus your attention on river-mouth sediments collected from the present (1980) and past (1979) river-mouth of Yasu river, the past is relatively high dioxins TEQ concentration than the present. It seems to be caused by the usage of pesticides mainly during 1960 1980. While, the dioxins TEQ concentration in Yasu river-sediment is higher than Ado river-sediment. It is thought that there are possibilities of reflecting the watershed properties as well as the surface soil pollution.

3. Surface soil, river sediment and river-mouth sediment

In order to examine a little further the difference between the Yasu and Ado river-mouth sediment, the correlation of the dioxins TEQ concentration and the organic carbon content in surface soils, river sediments and river-mouth sediments in the Yasu and Ado river basins were shown in Figures 5 and 6, respectively. As compared with Figures 5 and 6, it is apparently found that there is different tendency between the plots of Yasu river-mouth sediment and Ado river-mouth sediment. That is to say, although the plots of Yasu river-mouth sediment are mainly located near these of paddy fields, the plots of Ado river-mouth sediment are located between these of forest soil and river sediment. It is supposed that Yasu river-mouth sediment is more strongly influenced by soil of

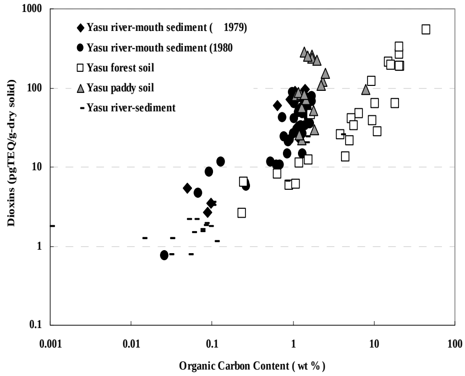


Figure 5:Comparative correlation of Dioxins TEQ concentration and organic carbon content in all samples in Yasu river basin

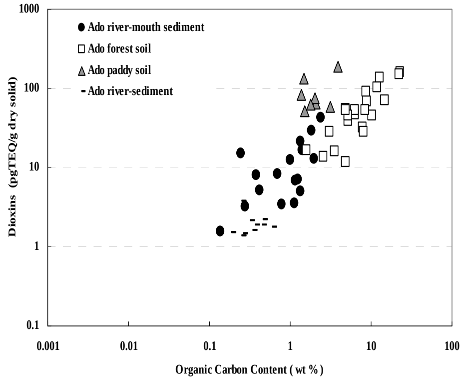


Figure 6:Comparative correlation of Dioxins TEQ concentration and organic carbon content in all samples in Ado river basin

paddy fields than Ado river-mouth sediment. This difference is considered to come from the difference of various watershed properties. With the limited space, we focus on the following watershed properties here: land use, river slope and dam construction.

4. Watershed properties

Land use

The land use ratio of the Yasu and Ado river basins are shown in Table 1. These two basins have different land usage ratios. Especially, what is important is the different ratio of paddy field. One of the most notable factors of different degree of the dioxins TEQ concentration in river-mouth sediment is different ratio of paddy field, polluted by dioxins contained in pesticides as byproducts.

River slope and dam construction

The slope of mainstream and the locations of dam and sluice gate are schematized in Figure 7. As shown in Figure 7, the slope of mainstream in Ado River is steeper than that in Yasu River. Furthermore, although there are two dams and two sluice gates in the Yasu mainstream, the Ado mainstream has no dam and/or sluice gates at all. Consequently, the arrival ratio of soil derived from forest to river-mouth is probably influenced by these situations (i.e., the movement if SS is disturbed by the dam).

Table 1: Land usage ratio of Yasu and Ado basins

Land Usage Ratio	Yasu Basin	Ado Basin
Area (km2)	395.08	309.3
Forest	61.1% (26)	91.5% (24)
Paddy field	19.3% (30)	3.9% (10)
Others	19.6% (8)	4.7% (0)

*; the values in parenthesis indicate the number of samples

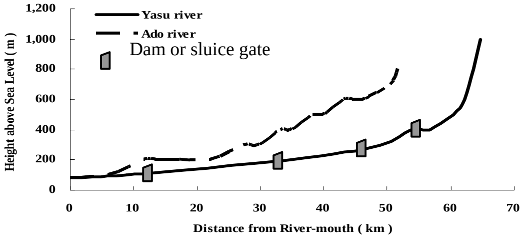


Figure 7:The slope of mainstream and location of dam and sluice gate

5. Mass balance of dioxins in watersheds

As mentioned above, the dioxins TEQ concentration in rive-mouth sediment are relatively low. Therefore, considering the mass balance of dioxins in a watershed, it is thought that bottom of the lake near river-mouth is not the “sink” of dioxins or the dioxins in surface soil may not move significantly. In order to know further the movement and fate of dioxins in a watershed, a continuous research including the analyses on lake sediment and river and lake waters must be carried out.

Acknowledgements

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