Distribution of dioxins in surface soils and river-mouth sediments and their relevance to watershed properties

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Abstract The dioxins toxic equivalent (TEQ) concentration in surface soils, river sediments and river-mouth sediments was measured by the CALUX assay in the Yasu and Ado River basins around Lake Biwa, Japan. In order to examine the distribution of dioxins in each watershed, we evaluated and compared the correlation between the dioxins TEQ concentration and the solid characteristics (i.e. organic carbon content and particle size distribution) of all samples. In both basins, the dioxins TEQ concentration in forest soil correspondingly showed a very good linear relationship to organic carbon content. On the other hand, the dioxins TEQ concentration in paddy field was significantly high, although organic carbon content was relatively low. Generally, the smaller particles have the higher dioxins TEQ concentrations in surface soils, and river sediments were composed of very coarse particles and had relatively low dioxins TEQ concentration. Therefore, we expected high dioxins TEQ concentration in river-mouth sediment, which was, however, not the case. Although the dioxins TEQ concentration in river-mouth sediments is low, the degree of dioxins pollution was different in each basin. The difference was considered to come from the difference of watershed properties including land use, river-slope, dam construction as well as the surface soil pollution.

Keywords Dioxins; CALUX assay; river sediment; river-mouth sediment; surface soil; watershed property

Introduction

In recent years, the contamination of the micro-organic pollutants (MOPs) has been of considerable concern and their risk not only to humans but also to the ecosystem is a worry. Because of persistency, bioconcentration potential, ubiquitous distribution and strong toxicity, dioxins are one of the most dangerous pollutants among the various MOPs. Dioxins are released into the atmospheric environment from incinerators of municipal/industrial wastes, and the deposition of them on the ground can occur via various pathways: dry gaseous, dry particulate and wet forms (Lohmann and Jones, 1998). Additionally, some chlorinated organic pesticides which contain dioxins as byproducts, such as pentachlorophenol (PCP) and chlorinitrofen (CNP), were applied in the paddy fields in Japan, especially during 1960–1980s (Masunaga *et al.*, 2001). Due to their high hydrophobicity, it is said that dioxins are mainly sorbed onto the organic component of surface soils. They are gradually washed away with the soil erosion caused by rain and/or snow, and flow into the water environment with particulate matter (i.e. SS and sediment). Then, highly-chlorinated dioxins exist and move with particulates in a higher ratio into the water environment. Therefore, the movement and fate of dioxins should be considered with particulate matter in watersheds.

In this research, the Yasu and River basins around Lake Biwa (the largest freshwater lake in Shiga prefecture, Japan, in Figure 1) were chosen, and a number of surface soils,

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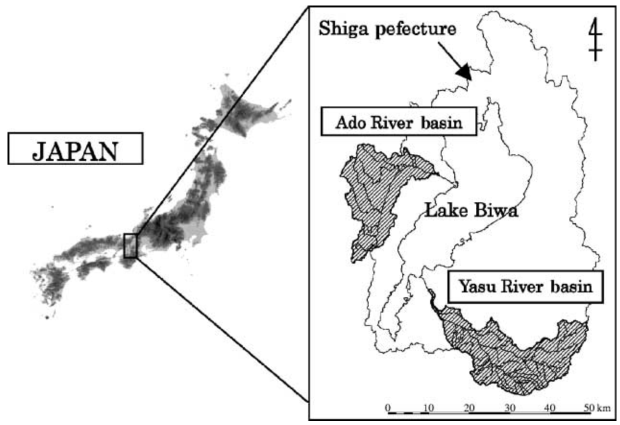

Figure 1 The location of the Lake Biwa, Yasu River basin and Ado River basin

river sediments and river-mouth sediments are collected in these basins. We measured the dioxins TEQ concentration in all of them by the chemically activated luciferase expression (CALUX) assay. We also measured the characteristics of the soil and sediment (i.e. organic carbon content and particle size distribution), and compared the relationship between the dioxins TEQ concentration and the characteristics of all samples to grasp the characteristics of dioxins distribution and movement in each watershed.

Sampling

Surface soils and river sediments

In this research, sampling points of surface soils and river sediments were determined considering land use and tributaries in each watershed. Sampling points of surface soils and river sediments are shown in Figure 2. Both surface soils and river sediments were collected from approximately the top 5 cm by a stainless shovel after removal of crude materials such as fallen leaves and stones. After sampling, they were freeze-dried immediately by freeze-drier (FDU-830, EYELA), and then kept in refrigerator until further analysis.

River-mouth sediments

Sampling points of river-mouth sediments were determined considering the flow regime and water depth at the river-mouth. At the Yasu River-mouth (Figure 2c), we mainly collected them along three directions. On the other hand, at the Ado River-mouth (not shown), we collected them along the shore because water depth suddenly increased. By the way, the Yasu River had flowed into Lake Biwa from different points (north and south river mouths) until 1979. Therefore, we also sampled sediments near these old river-mouths. We expected that sediments collected near the present river-mouth and the old Yasu River-mouth had accumulated from mainly 1980 and until mainly 1979, respectively. River-mouth sediments were collected from about the top 10 cm by core sampler (diameter: 5 cm). After sampling, they were also freeze-dried and stored in the refrigerator.

Methods

Organic carbon content of all samples was analyzed by high temperature combustion (900 °C) using TOC analyzer (TOC-5000A, Shimadzu Co.) with a solid sample module (SSM-5000A, Shimadzu Co.). The measured value of the inorganic carbon content was

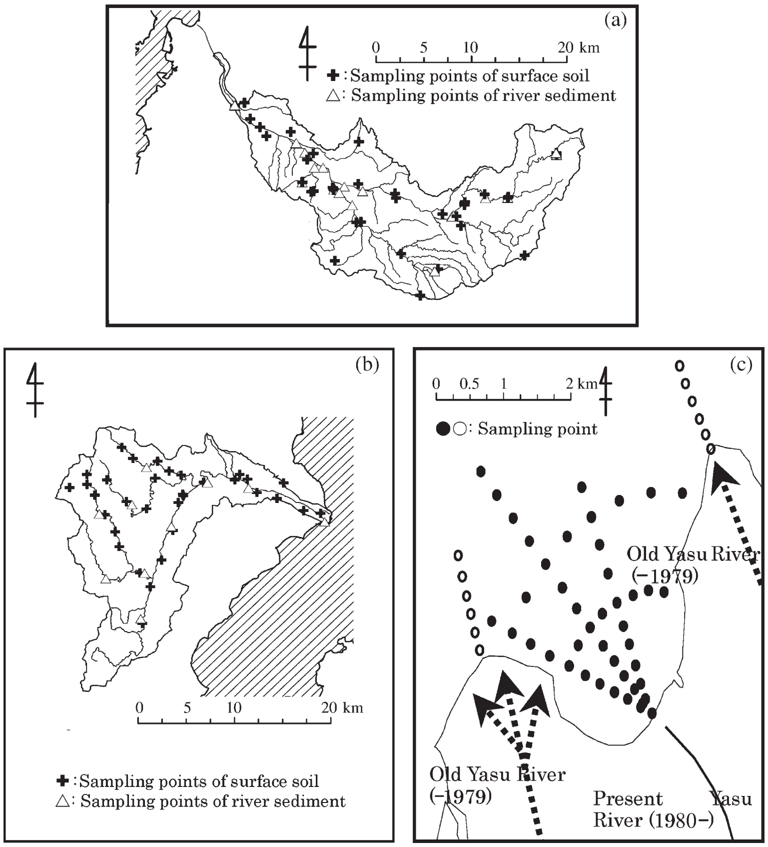

Figure 2 (a) Sampling Points in the Yasu River Basin (b) Sampling Points in the Ado River Basin (c) Sampling Points of Yasu River-mouth sediments (● and ○ collected near the present Yasu river-mouth and the old river-mouth, respectively)

relatively low and negligible. Therefore, we used the value of the total carbon as the value of organic carbon.

Surface soil and river sediment were fractionated by using the stainless sieves (JIS-Z8801, open diameter: 2,000, 500, 250 and 106 μm) to know the particle size distribution. Since river-mouth sediment consisted of very small particles, we analyzed its particle size distribution by using the particle size analyzer (SALD-2100, Shimadzu Co.). High Resolution Gas Chromatography with High Resolution Mass Spectrometry (HRGC/HRMS) is officially used for the measurement of the dioxins concentration in Japan. The HRGC/HRMS method has many strong points, but it takes labor and costs to measure the dioxins concentration. Therefore, this method was not fit to use in this research, because there were a number of samples which must be measured. The CALUX assay is relatively rapid (only five days) and requires only approx. 2–10 g of the solid samples (Denison *et al.* (1998)).

Additionally, a good correlation has already been confirmed between the results from the CALUX assay and TEQ values from HRGC/HRMS. Therefore, in this research, the CALUX assay was used to measure the dioxins TEQ concentration. The CALUX assay method is based on the cellular response mechanism to dioxin toxicity for estimating TEQ concentration. The dioxins bind to a cytosolic protein, the aryl-hydrocarbon (Ah) receptor; then the receptor-chemical complex migrates to the cell's nucleus and binds with the AH-receptor nuclear translocator protein (Arnt). This Ah receptor–Arnt complex interacts with specific DNA sequences and swiches the gene expression of regulated genes on. The CALUX assay uses a genetically modified mammalian cell line (mouse hepatoma H1L6.1) that contains the firefly luciferase under transactivational control of the Ah-receptor.

Results and discussion

Distribution of dioxins in surface soils and river sediments

The relationship between organic carbon content and the dioxins TEQ concentration in surface soils (forest and paddy soils) and river sediments of the Yasu and Ado River basins are shown in Figure 3. In both basins, the dioxins TEQ concentration in forest soil showed a very good linear relationship to organic carbon content. However, the regression lines of forest soil in both basins were different from each other. The location of incinerators around Shiga prefecture is shown in Figure 4. It is found that the number of incinerators around the Yasu River basin is more than that of the Ado River basin. Therefore, we can estimate that, generally, the dioxins concentration in the atmosphere around the Yasu River basin is higher than that around the Ado River basin. The difference of the inclination of the regression lines could come from the difference of dioxins concentration in the atmosphere.

In paddy fields, although organic carbon content is relatively low, the dioxins TEQ concentration is quite high. It was indicated that the dioxins in pesticides (e.g., PCP and CNP) as impurities still remain even now (Masunaga *et al.*, 2001). Moreover, as a result of the fractionation of surface soils of both river basins by sieves, it is found that smaller particles have higher dioxins TEQ concentration per unit mass (data not shown). This result comes from the fact that smaller particles have larger surface area per unit mass. On the other hand, river sediments consist of relatively coarser particles than surface soils, and have substantially lower organic carbon content and dioxins TEQ concentration value. Therefore, we considered that the smaller particles, likely to have the higher dioxins TEQ concentration, flow more easily downstream and/or to the river mouth. Then, is the river-mouth the "haunt" of hydrophobic organic pollutants?

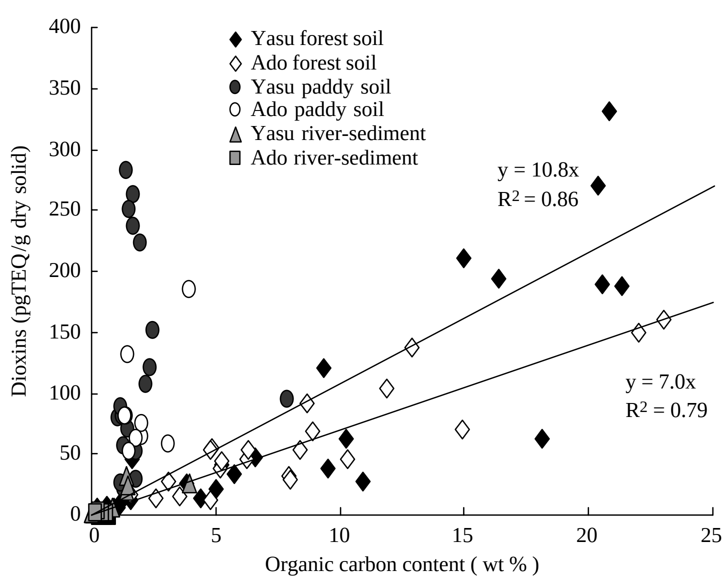

Figure 3 Correlations of dioxins TEQ concentration and organic carbon content in surface soil and river sediment

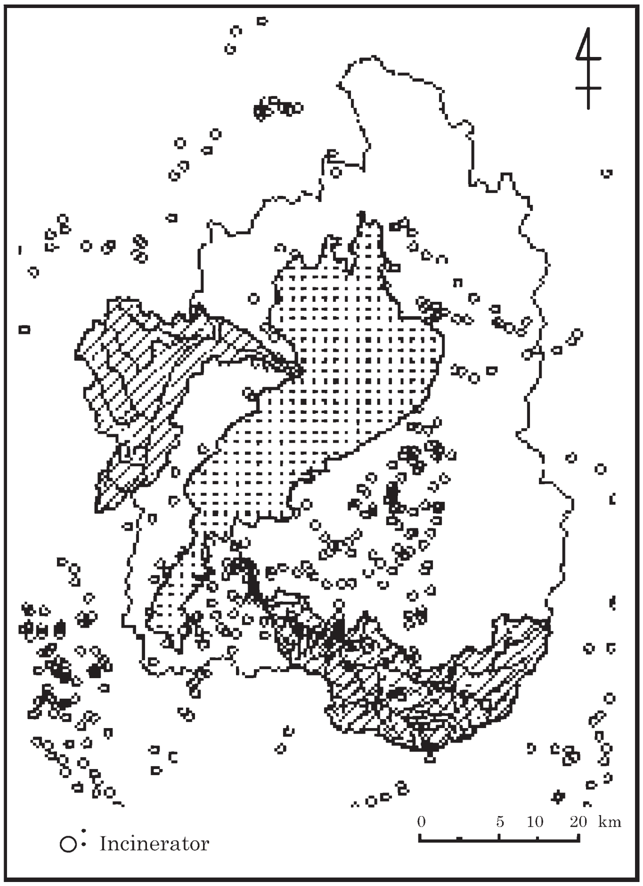

Figure 4 Location of incinerators discharging dioxins around Shiga prefecture

Distribution of dioxins in river-mouth sediment

Particle size distribution and organic carbon content in river-mouth sediment. The relationship between the median particle size (chosen as a representative particle size) and organic carbon content are shown in Figure 5. It indicates that the values of organic carbon content in river-mouth sediments are relatively lower than those of surface soils. Furthermore, we can find that the particle size of river-mouth sediments is very fine, that is, they are almost all composed of silt and clay. Therefore, it could be estimated that river-mouth sediments are mainly derived from smaller surface soil particles and that the organic matter of surface soils is torn off and/or decomposed by various physical, chemical and biological reactions through various hydrological processes. From Figure 5, there is almost no difference in the relationship between the median particle size and organic carbon content between the Yasu and Ado River-mouth sediments.

Dioxins TEQ concentration in river-mouth sediment. The relationship between the dioxins TEQ concentration value and organic carbon content in both river-mouth sediments is shown in Figure 6, and the relationship between the dioxins TEQ concentration and the median particle size is shown in Figure 7. Generally, in both river-mouth sediments, the dioxins TEQ concentration increases with increase in organic carbon content and with a reduction in the median particle size. However, the dioxins TEQ concentration in river-mouth sediments is unexpectedly not so high in either river mouth, although the median particle size is quite a bit smaller than that of surface soils.

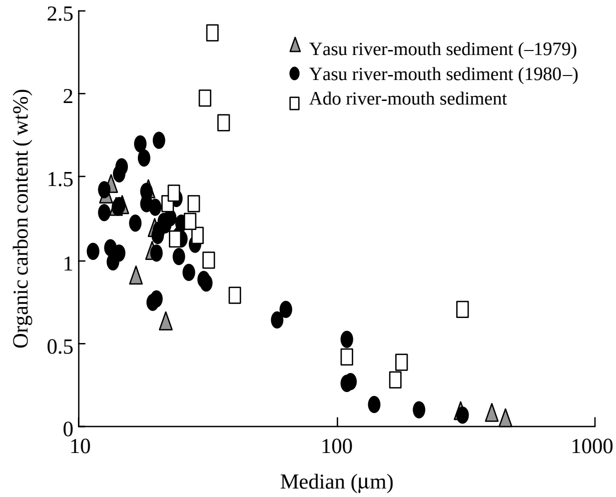

Figure 5 Relationship between the median particle size and organic carbon content in river-mouth sediment

These results are attributed to the exfoliation and decomposition of the organic matter in surface soils through various hydrological processes. On the other hand, if we focus our attention on the river-mouth sediments collected from the present and past (−1979) river-mouths of the Yasu river, we can find that the past Yasu River-mouth sediment has relatively higher dioxins TEQ concentration than the present. It seems to be caused by the usage of pesticides such as PCP and CNP mainly in 1960–1980. Figure 8 shows the organic carbon normalized dioxins TEQ concentration in the Yasu River-mouth. In Figures 6 and 7, we can also find that the dioxins TEQ concentration in the Yasu River mouth is higher than that in the Ado River mouth in general. The difference of the dioxins TEQ concentration per unit organic carbon content is not only due to the

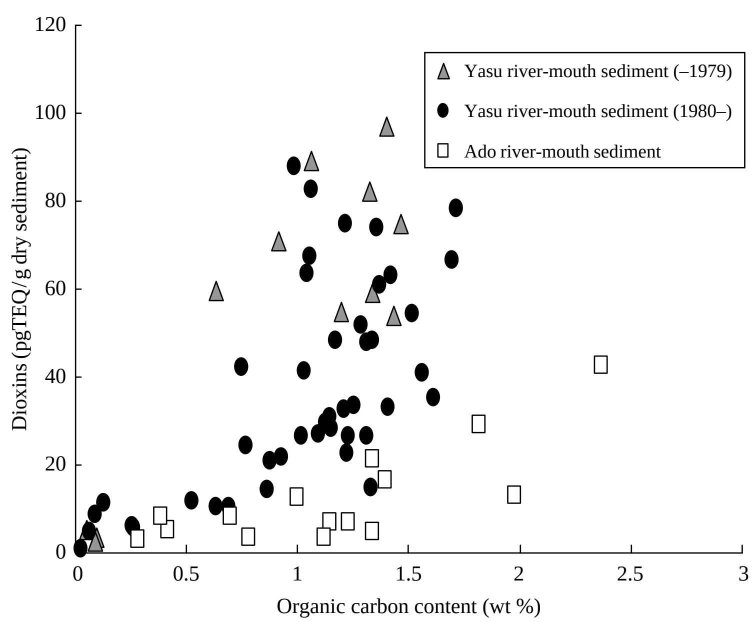

Figure 6 Relationship between the dioxins TEQ concentration and organic carbon content in river-mouth sediment

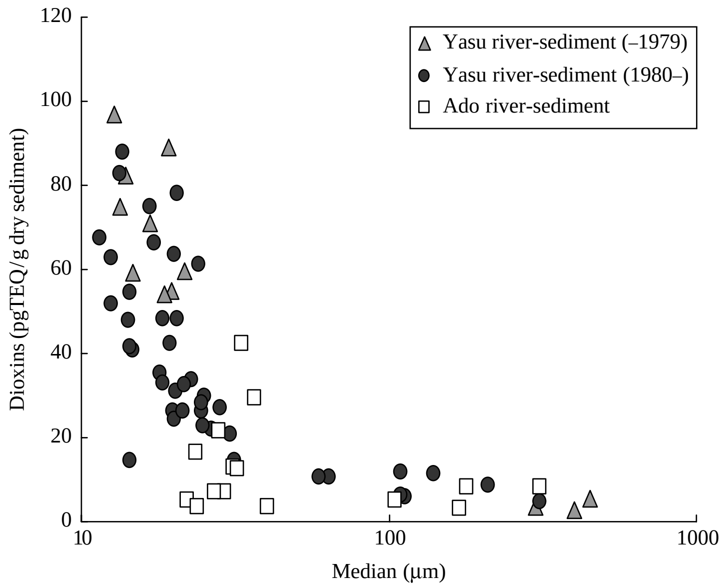

Figure 7 Relationship between the dioxins TEQ concentration and particle size in river-mouth sediment

different degree of pollution by dioxins in both basins (see Figure 4) but also due to some watershed properties.

Comparison of the dioxins TEQ concentration in surface soils, river sediments and river-mouth sediments

In order to examine the distribution of dioxins in both basins in detail, the dioxins TEQ concentrations in surface soils, river sediments and river-mouth sediments are plotted together against organic carbon content in Figure 9 (the Yasu River basin) and Figure 10 (the Ado River basin), respectively. In Figure 9 (the Yasu River basins), the plots of river-mouth sediments are close to paddy soils. On the other hand, in Figure 10

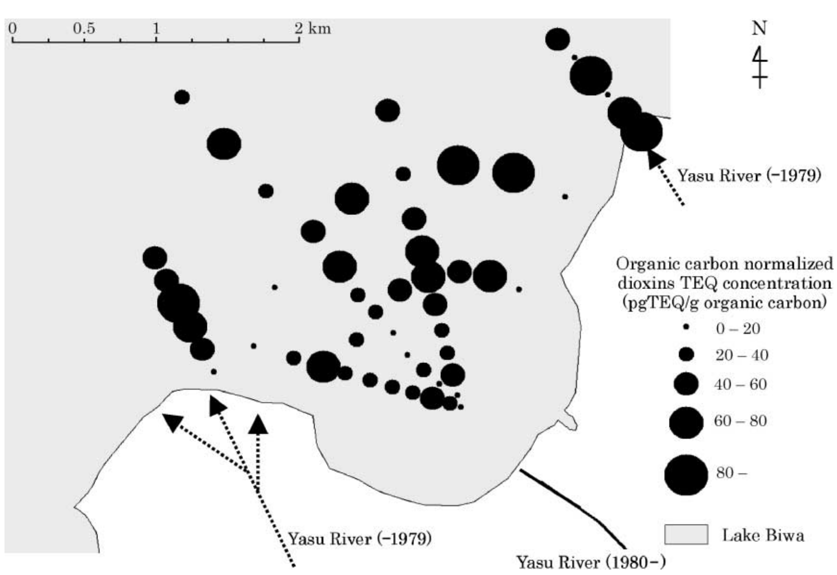

Figure 8 Organic carbon normalized dioxins TEQ concentration in the Yasu River-mouth

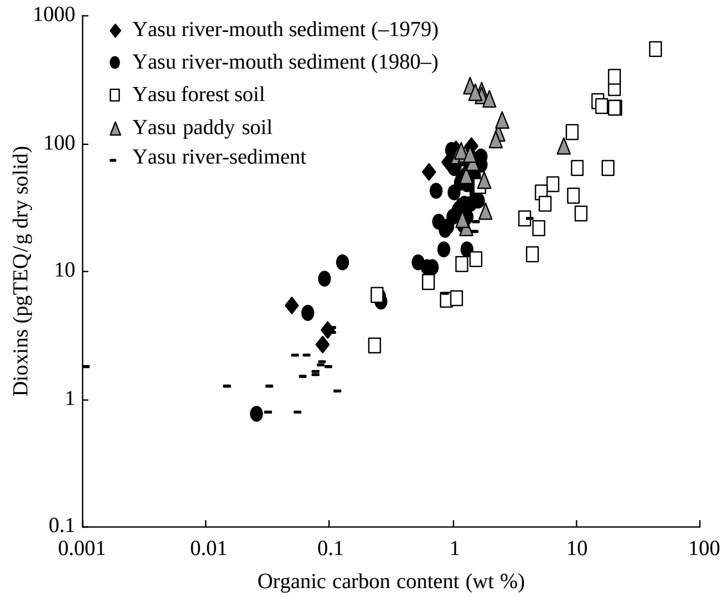

Figure 9 Comparative correlation of dioxins TEQ concentration and organic carbon content in all samples in Yasu river basin

(the Ado River basins), those of river-mouth sediments are widely extended between forest soil and river sediment. It may be concluded that the Yasu River-mouth sediments are more influenced by paddy soils than forest soil, and that Ado River-mouth sediments are more influenced by forest soils than paddy soils. These results may be explained by the difference of watershed properties, therefore we focus on the watershed properties in the next section (i.e. land use, river slope, dam construction, and rain intensity).

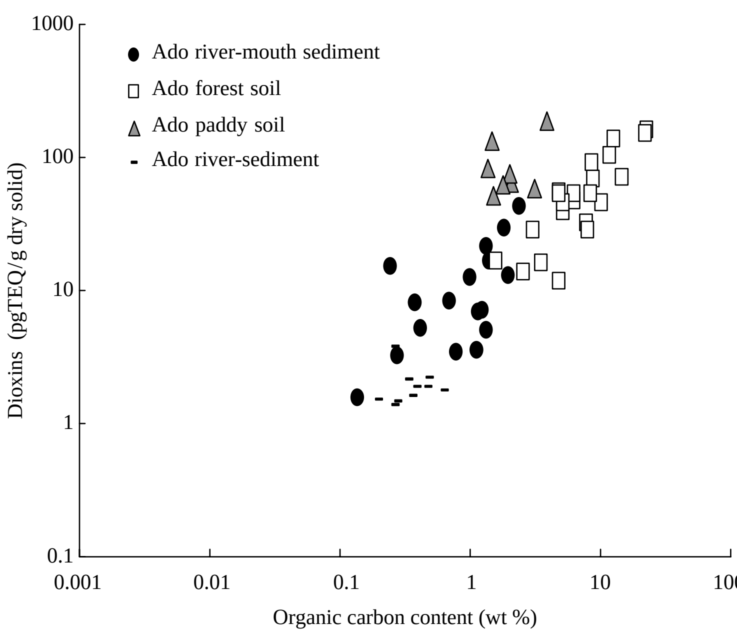

Figure 10 Comparative correlation of dioxins TEQ concentration and organic carbon content in all samples in Ado river basin

Watershed properties

Land use. The land use of the Yasu and Ado River basins is shown in Figure 11. Moreover, the ratio of each land use for the Yasu and Ado River basins is shown in Table 1. These two basins have different land use ratios. Especially important is the different ratio of paddy fields. One of the most notable factors of the different degree of the dioxins TEQ concentration in river-mouth sediment may be the difference in ratio of paddy field, polluted by dioxins contained in pesticides as byproducts.

River slope and dam construction. The slope of the Yasu and Ado River mainstream and the locations of dam and sluice gate are schematized in Figure 12. As shown in Figure 12, the slope of the Ado River mainstream is steeper than that that of the Yasu River mainstream. Furthermore, although there are two dams and two sluice gates in the Yasu River mainstream, the Ado River 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 downward movement of SS is disturbed by the dam).

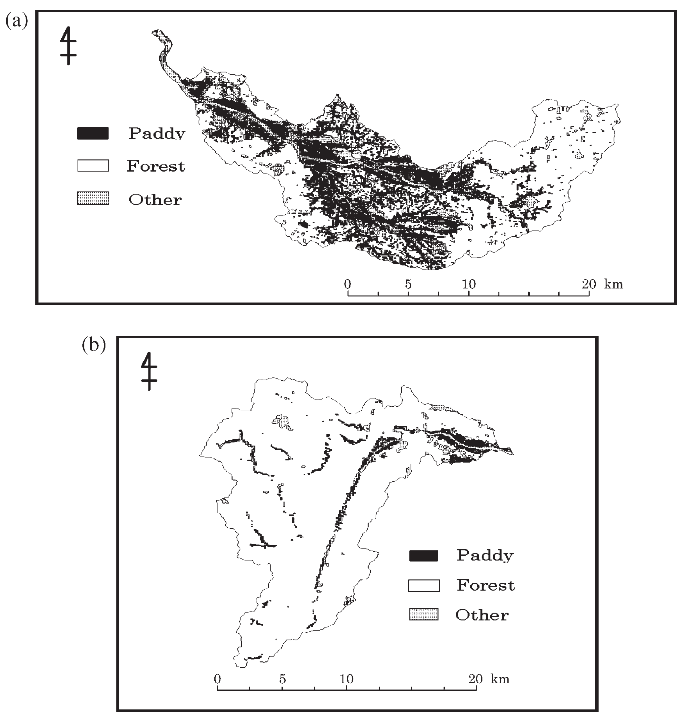

Figure 11 Land use of (a) the Yasu River basin and (b) the Ado River basin

Table 1 Land use ratio of the Yasu and Ado River basins

Land usage ratio	Yasu River basin	Ado River basin
Area (km^2)	395.1	309.3
Forest	61.1% (26)	91.5% (24)
Paddy	19.3% (30)	3.9% (10)
Others	19.6% (8)	4.7% (0)

*The values in parenthesis indicate the number of samples collected in this research

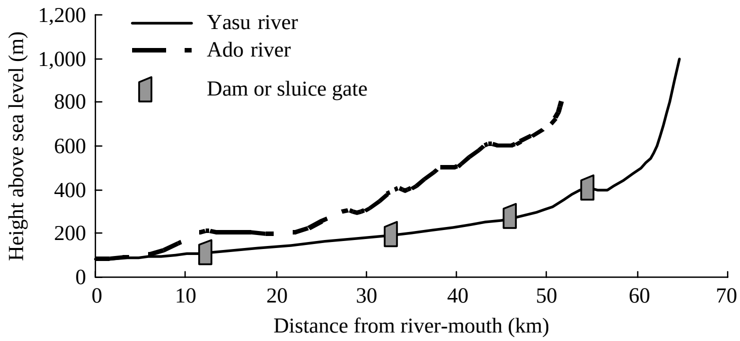

Figure 12 Slope of mainstream and location of dam and sluice gate

Rain intensity. The amount of rainfall is considerably different between the Yasu River basin and the Ado River basin; the amounts of rainfall in Yasu River basin and in the Ado River basin are about 1,600–1,800 mm and about 2,000–2,600, respectively (http://www.longlife.pref.shiga.jp/). This difference comes from the different climate in winter of both basins. That is to say, in winter, the rain and/or snow falls more in the Ado River basin than in Yasu River basin. Therefore, the amount of forest soil erosion by rain and/or snow in the Ado River basin may be more than that in Yasu River basin. This may be one of the reasons why the Ado River-mouth sediments are more influenced by forest soils than Yasu River-mouth sediments.

Mass balance of dioxins in watersheds

As mentioned above, the dioxins TEQ concentration in river-mouth sediments is relatively low. Therefore, considering the mass balance of dioxins in a watershed, we thought that the bottom of the lake near river-mouth is not the “sink” of dioxins and/or dioxins in surface soils may not move significantly. In order to know more about the movement and fate of dioxins in a watershed, future research including the analyses of lake sediment and river and lake waters must be carried out.

Conclusions

In this research, the dioxins TEQ concentration in surface soils, river sediments and river-mouth sediments was measured by the CALUX assay in the Yasu and Ado river basins around Lake Biwa, Japan. We evaluated and compared the correlation between the dioxins TEQ concentration and the solid characteristics (i.e. organic carbon content and particle size distribution) of all samples. The following conclusions were derived from the results and discussion:

1. In both the Yasu and Ado River basins, the dioxins TEQ concentration in forest soils showed a good linear relationship to organic carbon content. However, the regression lines of forest soils in both basins were different from each other. This result may be attributed to the different dioxins concentration in atmosphere in each basin.
2. It was found that river-mouth sediments were mainly composed of very fine particles such as silt and clay derived from surface soils. However, the dioxins TEQ concentration and organic carbon content were relatively low. This result is due to the exfoliation and decomposition of the organic matter in surface soils through various hydrological processes.
3. As a whole, the value of the dioxins TEQ concentration in river-mouth sediments collected from the old Yasu River-mouth (–1979) were relatively higher than that collected from the present Yasu River-mouth (1980–). This finding leads to a

conclusion that the influence of the dioxins contained in pesticides ever used in the past remains even now.

4. As a noticeable characteristic common to all, the dioxins TEQ concentration increases with increase in organic carbon content and with reduction in the particle size in river-mouth sediments. However, it was revealed that the degree of dioxins pollution varied between the Yasu and Ado River-mouth sediments. This may be attributed to watershed properties such as land use, river slope, dam/sluice gate construction and precipitation as well as the different degree of dioxins pollution in surface soils.

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