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Behavior of Dioxins and the Relevance to Soil Characteristics in a River Basin of Lake Biwa, Japan

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Introduction

The dioxins, a class of chlorinated organic compounds, are toxic chemicals generated unintentionally. The sources of dioxins into the environment are not only the incineration of municipal solid wastes but also the application of certain agricultural chemicals. The recent investigation[1] clearly indicated that some Chlorinated Organic Pesticides (COP) sprinkled in the past on agricultural fields contained dioxins as their byproducts. It is important for our safe to reduce their release into the aquatic systems and the risk of our being exposed by them. To evaluate the concentrations and the behavior and/or movement of dioxins in the environment is, therefore, definitely necessary. The dioxins concentrations and behavior is, however, poorly documented because the intricacy of dioxins and environmental samples.

Based on these backgrounds and considerations, the specific objectives of this research are set as follows:

1. To investigate the concentrations of dioxins in various land uses. The relationship between the relevant characteristics of surface soils (*i.e.*, particle size and organic carbon content) and the dioxins concentrations are further analyzed.
2. To qualitatively estimate the behavior of dioxins in a watershed through the dioxins concentrations in surface soils and river sediments.

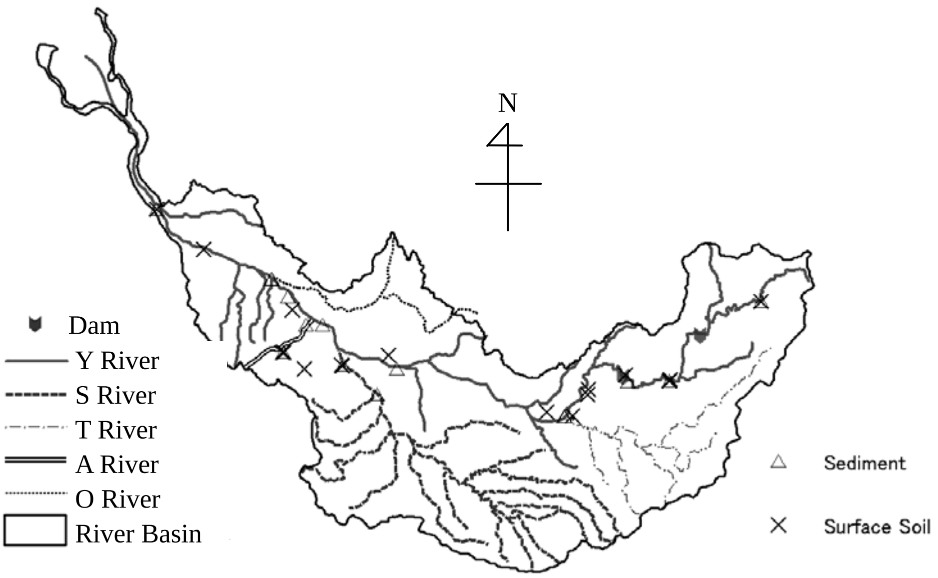

Figure 1. Sampling points of surface soils and river sediments.

Materials and Methods

In this research, a river basin in the Lake Biwa watershed in Japan was chosen for surface soil and sediment sampling. The selected river basin has one of the largest watersheds among those in Lake Biwa. Lake Biwa is the biggest lake in Japan and the important water resource for 14 million people downstream. Figure 1 shows the sampling points for surface soils and sediments. These sampling points were determined with consideration of land use (i.e., forest, farm land, urban area, and golf course, etc.) and four tributaries of the main stream. A sample was collected at each point. The maximum depth of both surface soil and sediment was approx. 5 cm.

The sampled surface soils and sediments were fractionated using stainless sieves (JIS-Z8801) of 2,000, 500, 250, 106, and 53 μ m calibers after lyophilized using freeze dryer (FDU-830, EYELA). Then, organic carbon content of each fraction was analyzed using TOC analyzer (TOC-5000A, Shimadzu Co.) with a solid sample module (SSM-5000A, Shimadzu Co.). In this research, the measured values of total carbon were regarded as the total organic content as the inorganic carbon content were low enough to be negligible.

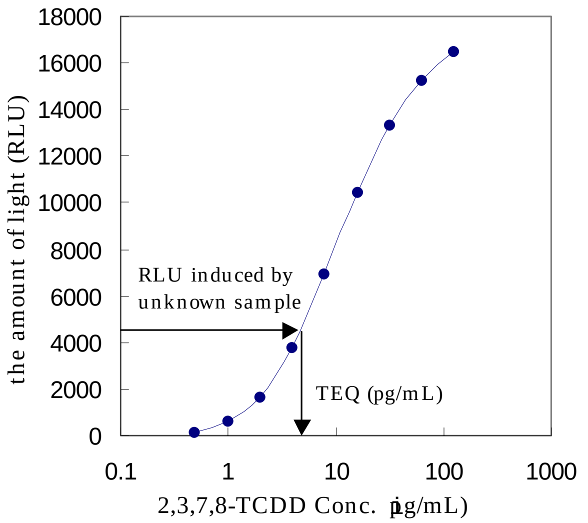

Figure 2. Typical calibration curve for determination of TEQ. An appropriate dilution of the sample was tested in the CALUX™ assay and TEQ was calculated from the RLU value.

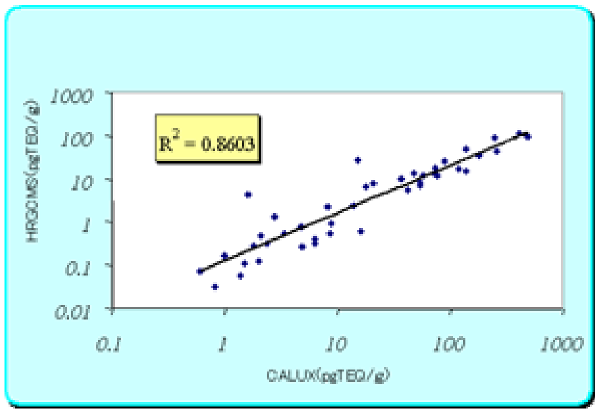

Figure 3. Correlation between TEQ determined by CALUX™ bio-assay and HRGC/HRMS for soil samples.

In this research, the CALUX™ (Chemically-Activated Luciferase Expression) assay method[2] was used to measure the dioxins TEQ (Toxic Equivalent Quantity) concentrations of samples. The CALUX™ assay is a bio-assay method that are faster, less expensive, and require smaller quantity of samples than HRGC/HRMS (High resolution Gas Chromatography with High Resolution Mass Spectrometer) method. The determination of TEQ by the CALUX™ assay has been described previously[3]. Briefly, the CALUX™ assay uses a modified mammalian cell (mouse hepatoma H1L6.1) which gene produces the firefly enzyme (luciferase) when Ah (Arylhydrogen)-receptor becomes active. The concentration of dioxins can be detected by measuring the amount of light emitted as the recombined cell discharges light in the proportion of one to one to the degree of activity of

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Ah-receptor (Figure 2). Furthermore, there is a good correlation between the values using HRGC/HRMS and those using CALUX™ as shown in Figure 3.

Results and Discussions

The relationships of the dioxins TEQ concentration and total organic content in surface soils from various land uses are shown in Figure 4. From Figure 4, it is found that the TEQ concentration of dioxins in forest is proportional to total organic content. This fact indicates the following two things:

The higher total organic content in forest soil is, the more can the soil sorb dioxins due to their extreme hydrophobicity[4]. The soil organic matter is typically made up of about a third to half carbon. Therefore, the high total an organic content involves increasing of non-polar moiety in soil organic matter where hydrophobic substances such as dioxins are transferred.

The same amounts of dioxins have been supplied to the forest soil. In other words, the only route of dioxins into the forest soil could be the supply through the atmospheric deposition that can be considered common in the river basin.

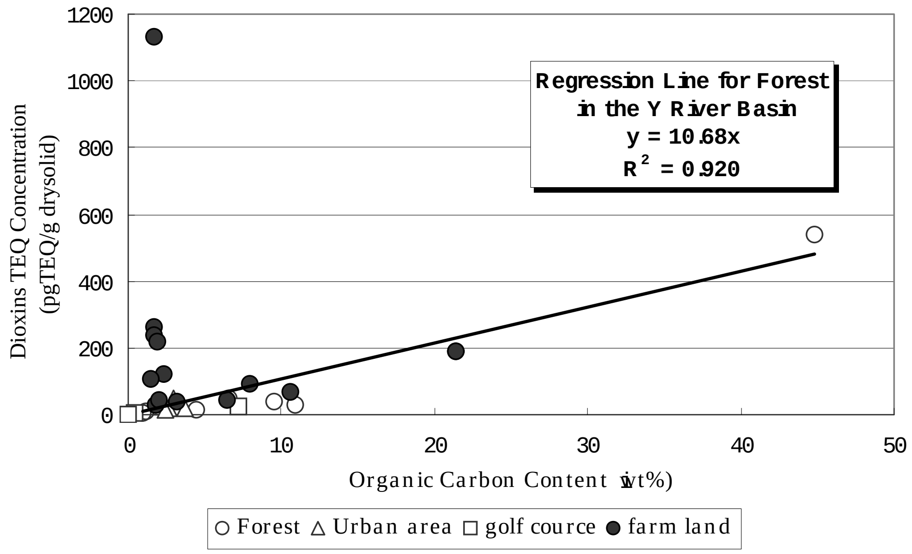

Figure 4. Relationship between dioxins TEQ concentration and organic carbon content of the surface soils.

The soils from other land uses can be divided into two groups. One is composed of the soils that are within the regression line for the forest mentioned above. Urban area and a portion of the farmland are in this group. Another group is composed of the soils that deviate from the regression line for the forest, which means high dioxins TEQ concentration despite of low total organic carbon content. Regarding the former group, it is said that the COP contained dioxins were not sprinkled or there is no influence of dioxins supplied as the byproduct in terms of the toxicity perspective. Results of the latter group mean that a large quantity of COP containing dioxins were supplied artificially in the past and still remained there. Regarding golf courses, no significant tendency was observed due to the small number of samples.

As stated above, the surface soils of high total organic carbon can sorb relatively large amount of dioxins, while the surface soils of low total organic carbon act poorly as reservoir of dioxins. Figure 4 indicates that the particles of smaller size tend to have the higher total organic carbon for all kinds of land use. The organic carbon content of the surface soils and sediemnts are greater than 0.01%. Therefore, the contribution of mineral surfaces on the Dioxins adsorption is considered to be negligible[5]. From the results shown in Figures 4 and 5, it is deduced that the smaller particles could sorb more dioxins. These small particles of high dioxins TEQ concentrations tend to be eroded from the land surface and transported to the aquatic environment (e.g., river). However, the smaller particles, due to their high mobility, are further carried away from the river (Figure 6) and ended up reaching the Lake Biwa sediments.

This research provides rationale information to estimate the origins of dioxins in a watershed. We may judge the origin of the existing dioxins even in other watersheds by obtaining the results similar to Figure 5.

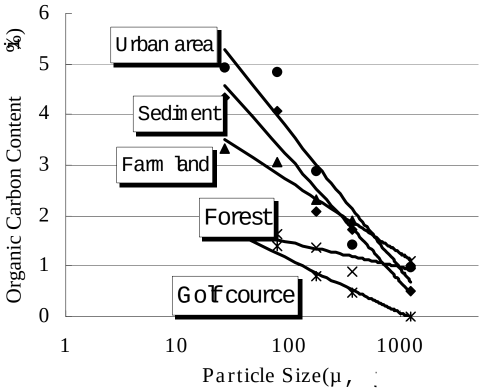

Figure 5. Relationship between organic carbon content and particle size.

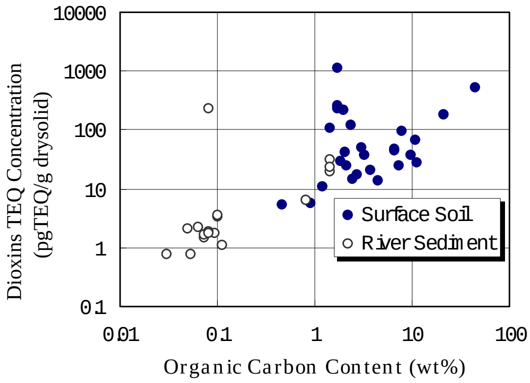

Figure 6. Relationship between dioxins TEQ concentration and organic carbon content of surface soils and river sediments.

Conclusions

Where the transportation through the atmospheric depositions is the only route for dioxins, such as forest and urban areas, the dioxins TEQ concentrations are directly proportional to the total organic carbon content of the soils. Also the results obtained from different watersheds indicated the similar tendency (data not shown). In agricultural fields, the excess dioxins in the applied COPs are still remained. The dioxins TEQ concentrations in river sediments are lower than those in surface soils, since small particles that sorb the large amount of dioxins due to its organic carbon affinity are hardly deposited in the river sediments and easily transported into the lake.

References

1 Kishimoto, A. Oka, T. Yoshida, K. and Nakanishi, J., Cost Effectiveness of Reducing Dioxin Emissions from Municipal Solid Waste Incinerators in Japan. *ES&T*, **35**(14), 2861-2866, 2001.
2 Denison, M., Brouwer, A. and Clark, G., U.S Patent#5, 854, 010,1998.
3 Tsutsumi, T., Amakura, Y., Nakamura, M., Brown, D., Clark, G., Sasaki, K., Toyoda, M., and Maitani, T., Validation of the CALUX bioassay for the screening of PCDD/Fs and dioxin-like PCBs in retail fish. *Analyst*, **128**, 486-492, 2003
4 Karickhoff, S.W, Brown, D.S. & Scott, T.A. Sorption of Hydrophobic Pollutants on Natural Sediments. Water Research, 1979, 13, 241-248.
5 McCarty, P.L., Reinhard, M. & Rittmann, B.E. Trace Organics in Groundwater. ES&T, 1981,

15, 40-51.