Environmental behaviors of dioxins and their sources in Ishikawa

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Abstract

In order to clarify the environmental behavior and the characteristics of regional emission of dioxins, I measured the concentration of dioxins in the ambient air, soil and atmospheric deposition in Ishikawa.

Air samples were considered to be influenced by both soil/dust suspension and combustion, because the contribution of each toxic isomer to the total toxicity equivalency quantity (TEQ) in the air was intermediate between their contributions in the soil and cinder samples. Gas/particle partitioning of atmospheric dioxins were depend on the temperature. The gaseous phase ratio of each homologue in air samples, generally, decreased with level of chlorination. However, most of tetrachloro dibenzo-*p*-dioxins (TeCDDs), tetrachloro dibenzofurans (TeCDFs) and tetrachloro biphenyls (TeCBs) in the air samples were existed in gaseous phase (usually > 70%) regardless of the temperature. Furthermore, isomers with higher vapor pressure tend to have higher gaseous phase ratios. Atmospheric dioxins deposition flux in Kanazawa, Japan was the highest in winter. Moreover, difference between ambient air and soil in homologue profiles was considered to be effect of washout ratio (a measure of scavenging efficiency from air) on individual homologue. Deposition fluxes were significantly correlated with several meteorological parameters (temperature, atmospheric pressure and rainy days ratio).

Introduction

Dioxins have attracted much concern in recent years because of their extreme toxicity, persistence in the environment, and bio-accumulation. Today, dioxins emission from combustion sources (0.23 kg-TEQ/year in 2004) have been decreased to about one-thirtieth of the amount 7 years ago (7.7 kg-TEQ/year in 1997). However, the major emission source during 1960s and 1970s was from two herbicides, such as pentachlorophenol (PCP) and chloronitrofen (CNP), and total emissions from the use of these herbicides in Japan during the past 40 years (1955-1995) were estimated to be 690 kg-TEQ. Dioxins from natural and anthropogenic sources have been widely distributed in the environment. Almost every living creature, including humans, has been exposed to dioxins. Our daily intake amount of dioxins was estimated to be 2.6 pg-TEQ/kg/day, and dietary intake occupied 93% (2.4 pg-TEQ/kg/day) of the daily intake. Especially, fishery products (1.5 pg-TEQ/kg/day) in the diet were the major exposure source. As mentioned above, dioxins persist in the environment and accumulate easily in the food chain. However, source contribution of dioxins will differ from one region to another. Therefore, it is necessary to clarify the environmental behaviors of dioxins emission in each region.

In present thesis, I examine the homologue and several isomers composition of dioxins in ambient air, soil and atmospheric deposition, and discuss the relative contribution of the emission sources. Moreover, the causes of their yearly or seasonal changes are described.

Results and discussion

Comparison of Compositions of Polychlorinated dibenzo-*p*-dioxins (PCDDs) and Polychloro dibenzofurans (PCDFs) in Air and Soil

The concentrations of dioxins in ambient air and soil in Ishikawa, Japan were both extremely low by comparison with environmental quality standards of Japan. The soil in a shrine, in which a fire was built during religious ceremonies, tended to have high concentration of dioxins.

Isomers that mainly contribute to the total TEQ of the combustion–origin samples are different from those of the agrochemical-influenced samples. Therefore, it is useful to examine which isomers predominantly contribute to the TEQ. The contribution of each toxic isomer to the total TEQ in the air tended to be intermediate between their contributions to the TEQ in the soil and cinder samples (Figure 1). These result suggested that the air samples were influenced by both soil/dust suspension and combustion.

In winter, the contribution of soil/dust suspension, which is thought to contain dioxins from agrochemicals, to the atmospheric dioxins decreased, and the contribution of combustion relatively increased. Because snow covered ground surface, soil/dust suspension was considered to be suppressed.

Seasonal Change of Gas/Particle Partitioning of Atmospheric Dioxins

The gaseous phase ratios of both TeCDD/DFs and TeCBs in the air samples remained high regardless of the temperature. However, the ratios of penta-, hexa- and hepta-chlorodibenzo-p-dioxin and chloro dibenzofuran (CDD/DF) homologues varied widely with temperature. Each of the gaseous phase ratios of penta-hepta chloro biphenyls (CBs) homologues were much higher than those of penta-hepta CDD/DF, which have the same number of substituted chlorines (Figure 2).

The gaseous phase ratio of each homologue in air samples, generally, decreased with level of chlorination. Furthermore, among of isomers in same homologue, those with short retention time in chromatogram were tended to be distributed in gaseous phase. In general, the elutability of isomers from GC column reflects molecular polarity, which is related vapor pressure. Therefore, isomers with higher vapor pressure tend to have higher gaseous phase ratios. This phenomenon was remarkable in the lower chlorinated DD/DFs, because the relative difference in molecular polarity between isomers is small for higher chlorinated DD/DFs.

Atmospheric Deposition of PCDDs and PCDFs

Yearly average of atmospheric PCDD/DFs deposition flux in Kanazawa, Japan was estimated to be 7.7 pg-TEQ/m^2/day (360 pg/m^2/day), and the seasons with the highest and next highest deposition fluxes were winter and spring, respectively. TeCDDs is dominantly congener in ambient air dominated, while octachloro dibenzo-*p*-dioxin (OCDD) dominates in soil. Difference between ambient air and soil in homologue profiles was considered to be effect of washout ratio (a measure of scavenging efficiency from air to deposition) on individual homologue. Washout ratio was increased with level of chlorination, therefore high chlorinated dibenzo-p-dioxins and dibenzofurans (i.e. heptachloro dibenzo-*p*-dioxins (HpCDDs), OCDD, heptachloro dibenzofurans (HpCDFs) and octachloro dibenzofurans (OCDF)) were removed from ambient air efficiently. OCDD is secondary dominant congener in ambient air but its washout ratio is high. Thus, this is consistent with soil which dominates

OCDD. Such as deposition process explained one of reasons for difference in homologue profile between the air and soil (Figure 3).

Deposition fluxes were significantly correlated with several meteorological parameters (surface temperature, atmospheric pressure and rainy days ratio). Possible explanations for their correlations are a change in gas/particle partitioning of atmospheric PCDD/DFs, a reducing dilution of pollutant due to the presence of an inverse layer and a dependence of scavenging efficiency on frequency of rain. However, HpCDDs and OCDD had weakly or no correlation with most of meteorological factors, possibly because HpCDDs and OCDD are generated by photochemical reactions of PCP in the air.

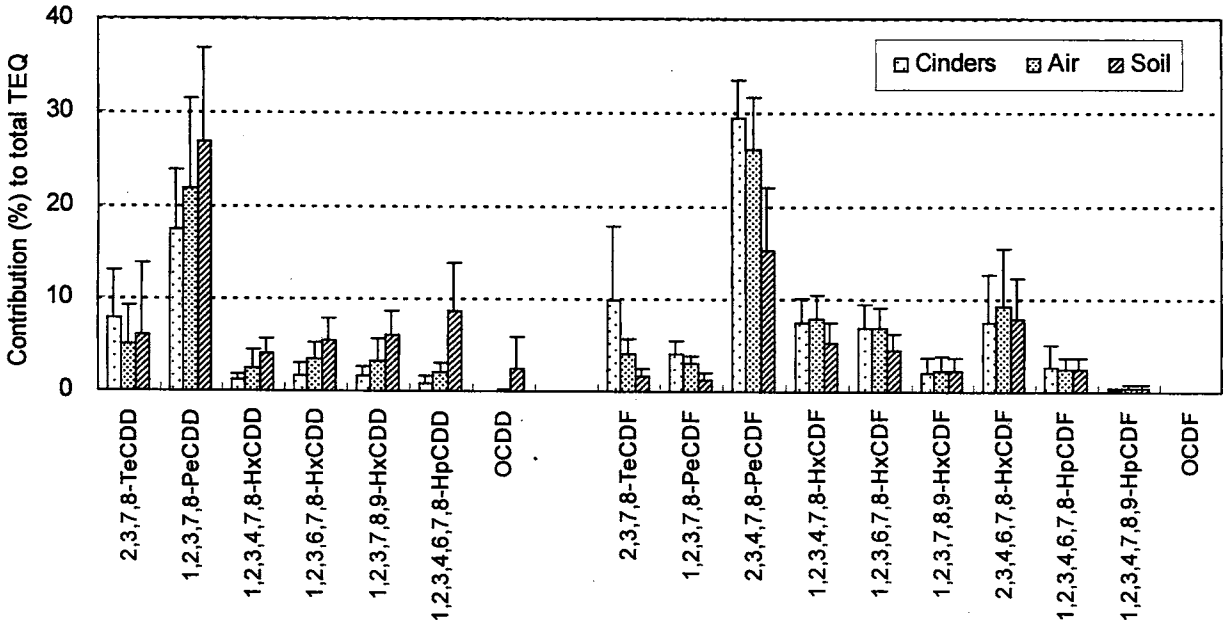

Figure 1. Contribution of 2,3,7,8-Chlorine Substituted Isomers to TEQ

Each box and vertical bar represent mean and S.D., respectively.

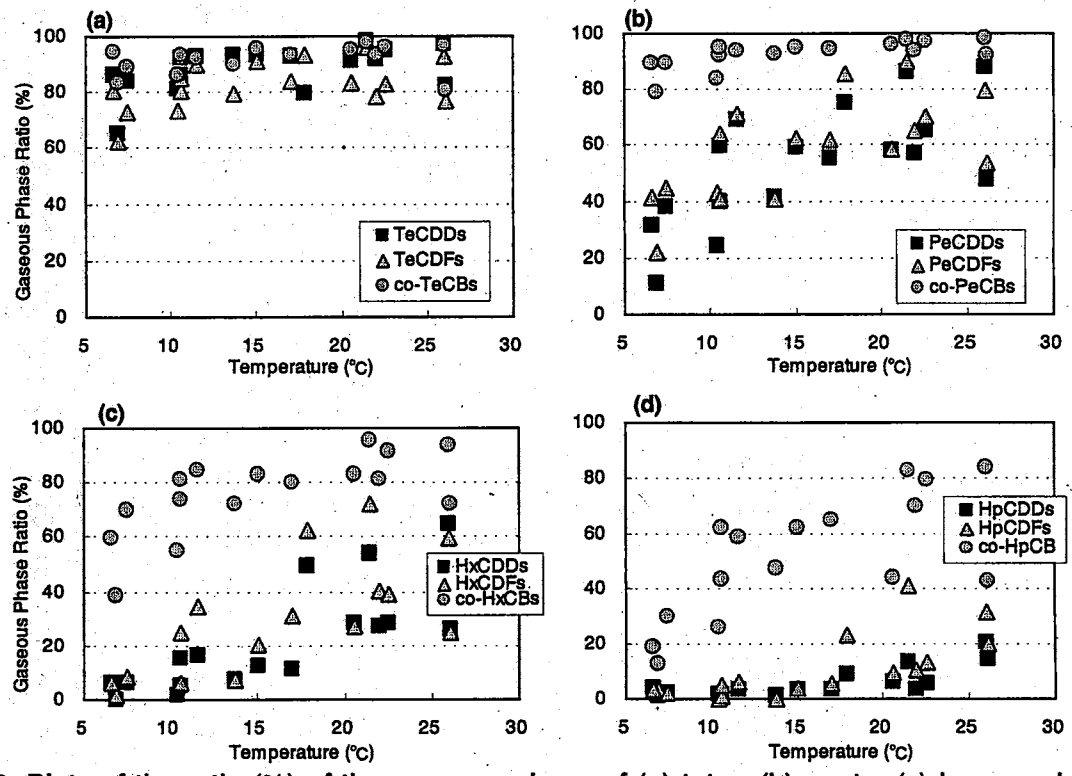

Figure 2. Plots of the ratio (%) of the gaseous phase of (a) tetra, (b) penta, (c) hexa and (d) hepta CDD/DFs and co-PCBs homologues vs. temperature.

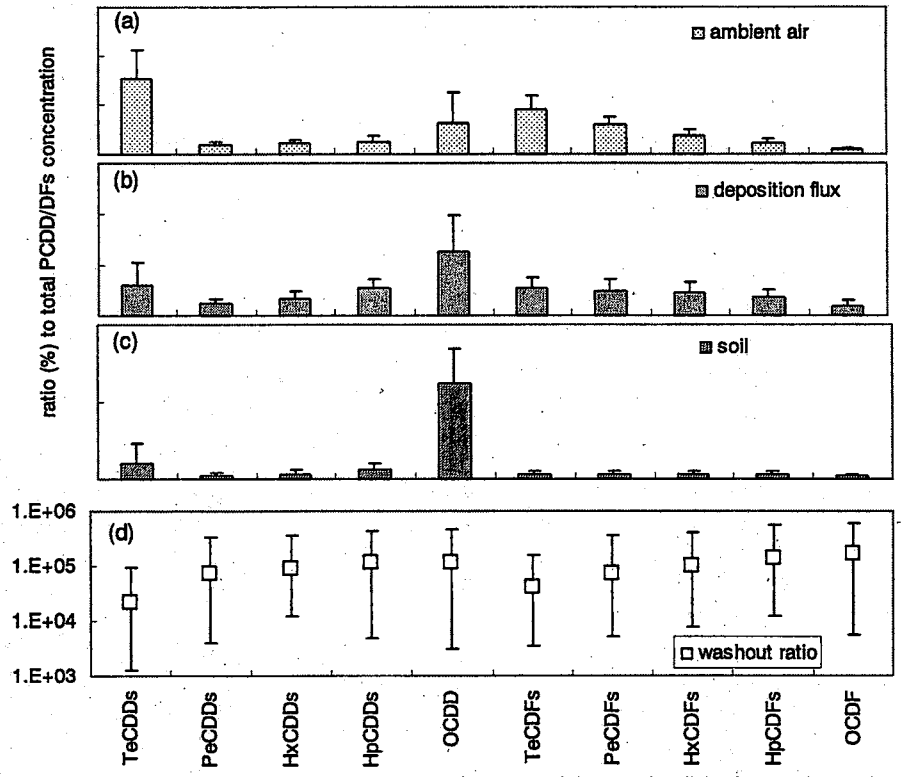

Figure3. Concentration ratio of homologues of (a) ambient air, (b) deposition flux, (c) soil and (d) washout ratio

In (a), (b) and (c), bar represents S.D.. In (d), each box and bar represents mean and range, respectively.

学位論文審査結果の要旨

［審査経過］審査方針従い、基礎学力を確認し、各委員による面接と諮問を行った。２月１日に口頭発表（最終試験）を行い、終了後に開催した最終審査委員会において協議の結果、次のように判定した。

［審査結果］ダイオキシン類に汚染された環境の実態把握と浄化は、わが国の環境施策の大きな課題である。これまでのダイオキシン類の動態研究は大都市域とその周辺など一部に限られ、地方における挙動については不明な点が多い。本研究は石川県を対象に、環境大気、土壌および大気降下物中のダイオキシン類を分析してその挙動を解析し、次のことを明らかにした。（１）大気は燃焼由来のダイオキシン類だけではなく、土壌巻き上げの影響も受けるが、冬季における後者の寄与は降雪により減少する。（２）ダイオキシン類の大気中ガス状／粒子状存在比は気温に依存して増加し、蒸気圧の高い異性体ほどガス状の割合が大きい傾向にある。（３）ダイオキシン類の大気降下フラックスは冬が最も大きい。その理由として、降下フラックスは地表温度、大気圧および降雨日数と相関が見られたことより、ガス状／粒子状存在比の低下、逆転層形成による汚染物質の希釈効果の抑制、および降水・雪による洗い出し効果の増大を推定した。以上のように、本論文は、降雪地方に特徴的なダイオキシン類の挙動の詳細を、石川県を対象として初めて明らかにしており、審査委員会は博士（薬学）に値すると判定した。