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Long-Term Sampling Method for PCDD/Fs in Atmosphere by Adsorption onto Economical Materials

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A sampling method of dioxins in atmosphere by using economical materials as monitoring indicators was proposed. The materials used were polyurethane foam, newspaper, and activated carbon paper filter. Among the adsorbents, polyurethane adsorbed the most amounts of dioxins. The TEQ values in spring and autumn seasons were 0.13 and 0.027 pg cm^{-2}, respectively. The composition of dioxin congeners was compared with that obtained by the air-sampler one. As a result, the distribution pattern of dioxins approximately coincided with that of the air-sampler.

Combustion is an efficient way of disposing of waste materials; however, unfortunately, it is also a major source of dioxin emissions in the environment,[1,2] especially in the atmosphere. For instance, dioxins are formed from natural woods and waste woods by combustion.[3,4] They are also formed from sodium chloride (NaCl)-impregnated woods[3] and a mixture of wood and plastic wastes[5] during combustion.

When dioxins in the atmosphere are collected, high volume air-sampler, which is relatively expensive, is usually used. The disadvantage of dioxin collection by the air-sampler is to take sampling only in a day, that is, this method is unsuitable for long-term sampling for dioxins. Generally, dioxin emission is varying daily or even hourly. Therefore, it is worthwhile to develop the simple, economical, and long-term collection methods of dioxins. The passive sampler was originally designed to monitor elevated concentrations in working areas, and has been adapted to low-concentration monitoring. A passive sampler for air measurements at environmental concentrations was previously developed.[6] Collecting dust or biomonitoring using passive samplers is less expensive. From this point of view, several researchers estimated air pollution by polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) using spruce needle as an indicator.[7–9] On the other hand, Miyata et al.[10] revealed that Japanese black pine needle accumulates effectively atmospheric pollutants of PCDDs, PCDFs, and non-ortho chlorine-substituted coplanar PCBs. In addition, their accumulation levels were rather stable, showing the variation to be within 2 times during a period of 3 months. Furthermore, they applied to evaluate atmospheric pollution of dioxin analogues using the pine needle samples from various areas in Japan.[10,11] Biomonitoring reflects longer-term changes of environmental quality, because tree leaves or needles accumulate dioxins over several years. Therefore, this method is difficult to evaluate the present air pollution by dioxins.

Purpose of this study is to develop a simple and economical sampling method of particle-bound dioxins in atmosphere. Previously, collection of dioxins in atmosphere by adsorption with polyurethane foam was performed for 2 weeks.[12] In the present study, we carried out the sampling of particle-bound dioxins by using economical materials, such as polyurethane foam, newspaper, and activated carbon paper filter, as indicators from 1 day to 4 weeks. Furthermore, this evaluation method for air pollution by dioxins was established by comparing with the air-sampler method. The material samples were placed in Hisai City, Mie Prefecture, where are near incinerators. Samples collected were analyzed for dioxins by gas chromatography/mass spectrometry (GC–MS) in order to investigate the characterization of particle-bound dioxins adsorbed on the economical materials.

Table 1. Weather conditions on the sampling of dioxins in atmosphere

Spring season					
Sampling date	27 March–24 April,2002				
Temperature					
	5.6–27.2 °C				
Rainfall	1 day	1 week	2 weeks	3 weeks	4 weeks
	25.0 mm	21.5 mm	20.5 mm	19.5 mm	58.5 mm
Wind speed	5.6 m/s	9.8 m/s	5.7 m/s	3.1 m/s	4.5 m/s
Autumn season					
Sampling date	1 November–3 December,2002				
Temperature					
	4.5–18.5 °C				
Rainfall	1 day	1 week	2 weeks	3 weeks	4 weeks
	0.0 mm	2.0 mm	1.0 mm	0.0 mm	11.5 mm
Wind speed	6.2 m/s	5.2 m/s	3.8 m/s	3.3 m/s	2.2 m/s

Isotope-labeled dioxins for internal standards were obtained from Wellington Laboratories, Inc. The concentration of PCDD/Fs was determined by spiking ^{13}C-labeled compounds containing 2,3,7,8-PCDD/Fs homologues and 1,2,3,4-TCDD. All organic solvents for dioxin analysis were purchased from Wako Pure Chemicals Co., Inc. (Tokyo, Japan). All reagents used were of analytical grade and were used without further purification. Adsorbents used were polyurethane foam, newspaper, activated carbon paper filter, paper filter, aluminum foil, glass and polyphenol resin. The adsorbents used (100 cm^2) put on the wood board. The board was placed from one day to four weeks in previously reported site.[12] The details of sampling method was based on the previous report.[12] The weather conditions on the sampling of dioxins are summarized in Table 1. All adsorbents were washed by methanol and acetone prior to use to remove organic contaminations and then dried at room temperature. The adsorbent samples were extracted with toluene, and were cleaned with multilayer silica gel and alumina column chromatography. The volume of sample solutions was adjusted to exactly 50 μL under nitrogen flow. The PCDD/Fs analysis was performed using a Hewlett–Packard (HP) model 6890 GC interfaced with a JMS-700D double focus MS (JEOL, Japan). The GC was equipped a CP-Sil 88 capillary column (60 m × 0.25 mm i.d.) for $Cl_{4\text{–}6}$ dioxins or a CP-Sil 8 capillary column (30 m × 0.25 mm i.d.) for $Cl_{7,8}$ dioxins. In order to assess the proposed sampling method, an air-sampler (HV-500F, Sibata Scientific Technology Ltd., Japan) was used for the collection of dioxins in atmosphere. The dioxin sampling was performed for 6 h at a suction rate of 500 L min^{-1}. In blank experiments, PCDD/Fs onto all adsorbents were below detection limit. The sampling experiments were conducted in five replicates and the results showed at the mean values. The relative standard deviations were 9–18%. The results of recovery tests for 2,3,7,8-PCDD/F congeners were 83–105%.

Among the seven studied adsorbents, particle-bound dioxins hardly adsorbed onto aluminum foil, glass and polyphenol resin in sampling period for 4 weeks. Therefore, the results of dioxin sampling using other adsorbents were described.

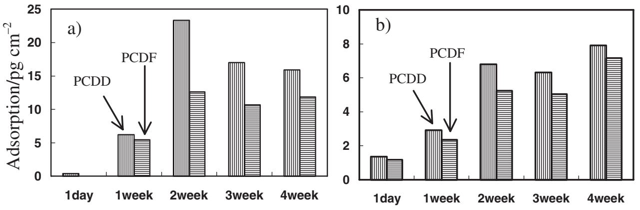

Figure 1. Adsorption amount of PCDD/Fs onto polyurethane foam on the various sampling period. (a), spring season; (b) autumn season.

Collection of dioxins using polyurethane foam was examined from 1 day to 4 weeks in spring and autumn seasons. These results are shown in Figure 1. It was expected that the adsorption amount of dioxins increased with increasing sampling period. However, in spring season, the adsorption amount of dioxins onto polyurethane foam increased with increasing the sampling period up to 2 weeks, and that of dioxins collected for 3 and 4 weeks decreased as shown in Figure 1. The sample collected for 2 weeks showed the maximum adsorption amount and the amount was 23 and 13 pg cm^{-2} for PCDD and PCDF, respectively. The TEQ value was 0.13 pg cm^{-2}. On the other hand, in autumn season, the adsorption amount increased with increasing sampling period. The maximum adsorption amount was 7.9 and 7.2 pg cm^{-2} for PCDD and PCDF, respectively (0.027 pg-TEQ cm^{-2}). As described above, the adsorption amount of dioxins decreased in the samples collected for 3 and 4 weeks in spring season. This might be mainly caused from deterioration of polyurethane foam[12] because of higher temperature of spring season. Therefore, 2 weeks would be suitable sampling period for the collection of dioxins in atmosphere using polyurethane foam.

Effect of sampling period on the adsorption of particle-bound dioxins onto newspaper was carried out in the range of 1 day to 4 weeks in spring and autumn seasons. The results are shown in Figure 2. In both seasons, the adsorption amount of dioxins onto newspaper increased with increasing the sampling period up to 3 weeks. In the sample of 3 weeks, the adsorption amounts were 4.7 (PCDD) and 4.2 pg cm^{-2} (PCDF) for spring, and 2.7 (PCDD) and 3.5 pg cm^{-2} (PCDF) for autumn, respectively. The TEQ values in spring and autumn seasons were 0.023 and 0.012 pg cm^{-2}, respectively. In the case of autumn season, the adsorption amount decreased in 4 weeks extremely. Although the weather conditions seem to be a cause on this fact, the clear casual relation could not be found. The adsorption amount in spring was higher than that in autumn. This trend was also observed upon polyurethane foam. It would reflect that air pollution level by dioxins in spring season was higher than that in autumn or the adsorption efficiency would be affected the temperature of sampling period. When collection of dioxins is performed by using newspaper, sampling period of 3 weeks would be suitable. The adsorption tendencies were different from polyurethane foam and newspaper. This would originate from the materials of adsorbents.

Effect of sampling period on the adsorption of particle-bound dioxins onto activated carbon filter paper in autumn season was examined. In analogy with trend of newspaper, the adsorption amount increased with increasing the sampling period up to 3 weeks.

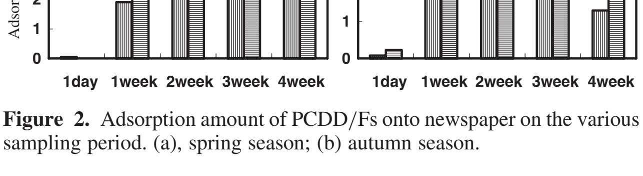

Figure 2. Adsorption amount of PCDD/Fs onto newspaper on the various sampling period. (a), spring season; (b) autumn season.

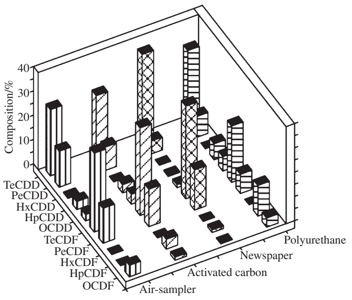

Figure 3. Composition ratio of PCDD/F congeners onto the various materials.

Amount of dioxins adsorbed onto activated carbon filter paper was 2.4 and 3.1 pg cm^{-2} for PCDD and PCDF, respectively, in the 3 week sample (0.017 pg-TEQ cm^{-2}). It is well known that activated carbon is good adsorbent for dioxins.[13,14] However, the adsorption amount of dioxins onto activated carbon filter paper was similar to that of newspaper. This cause might be because the main component of the activated carbon filter paper is paper. This consideration would be supported by the results of 3 week sampling using paper filter (2.9 pg cm^{-2} for PCDD and 3.0 pg cm^{-2} for PCDF, 0.0089 pg-TEQ cm^{-2}).

In order to assess the present method, dioxins in atmosphere were collected by air-sampler. The collection of the dioxins by the air sampler was carried out in the weekly Monday in the sampling period in the autumn season. The results of air-sampler were shown in mean values. The composition ratio of dioxin congeners obtained by the air-sampler method was compared with that obtained by the present method (polyurethane foam, newspaper and activated carbon paper filter). The results are shown in Figure 3. The results are approximately in good agreement with those obtained by the air-sampler method although HpCDF was detected by the present method because of longer sampling period. In the 2,3,7,8-PCDD/F congeners, 2,3,7,8-TeCDF was the highest amount in all the system, and the distribution of the congeners in the present method was also in accordance with the air-sampler method. Therefore, it could be considered that the composition of dioxin congeners adsorbed on the adsorbents reflected that in the atmosphere of the sampling site.

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