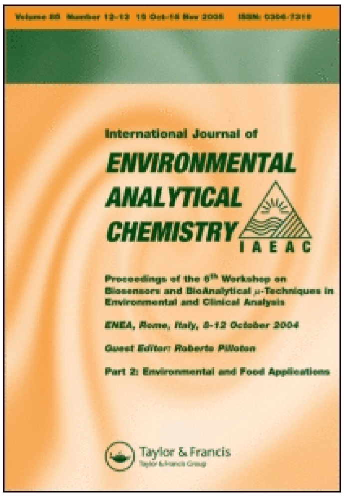

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Extractability of dioxins from soil: I. Extractability of dioxins from airborne particulates and humic acid fraction in soil

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The extractability of dioxins (polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, and coplanar polychlorinated biphenyls) from airborne particulates (APs) and humic acid (HA) in soil was evaluated. APs collected from ambient atmosphere and dioxins-associated precipitated HA fraction (PHA) were extracted by pressurized liquid extraction with either toluene or acetone. Native dioxins were equivalently extracted from APs with both solvents, whereas only acetone could satisfactorily recover the ^{13}C-labelled compounds from metal-free PHA. The recovery rates of dioxins by toluene extraction from metal-free PHA varied with the organic carbon content of the PHA. However, even with acetone, the recovery of dioxins from metal-bound HA was poor (11–40%). These results suggest that PHA prevented the solvents from accessing sequestered dioxins. This characteristic of solid HA may influence the extractability of dioxins from humus-rich soil.

Keywords: Dioxins; Extractability; Soil; Airborne particulates; Humic acid

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like coplanar polychlorinated biphenyls (CoPCBs) are highly toxic organic compounds that enter the environment from various sources (e.g. by emission as by-products of a variety of thermal processes [1], by waste disposal [2], or as impurities of certain pesticides [3–5]). Many studies of their formation mechanisms, toxicity, intake into biota, and environmental behaviour have been published. In Japan, recent research has generated data on the present levels of dioxin contamination in various environmental media (ambient air, soil, sediment, surface water, etc.) [6],

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and the environmental fate of dioxins has been estimated by means of the statistical analyses of the data [7].

Accurate estimation of dioxin levels in environmental media is essential for elucidation of their behaviour in the environment, their toxicological effects on organisms, and the sources of dioxin contamination. Accurate estimation of dioxin levels in soil is particularly important because soil plays an important role in the fate of dioxins entering the environment. If dioxins are to be accurately determined in soil, they must be efficiently extracted from the soil matrix. However, in determination of dioxins in soils extraction is the main bottleneck.

The effects of soil matrices on the extractability of dioxins must be understood if dioxins are to be effectively extracted from soil. The extractability of dioxins from airborne particulates (APs) should also be evaluated because atmospheric deposition is recognized to be the main source of dioxins in urban topsoil [8]. In addition, soil organic matter (OM) must also be considered. Numerous studies have shown that hydrophobic organic pollutants (HOPs) can bind to soil OM, which results in the formation of 'unextractable residues'. The American Institute of Biological Sciences Environmental Task Group proposed the definition of bound residues as 'unextractable and chemically unidentifiable residues remaining in the fulvic acid, humic acid (HA), and humin fractions after exhaustive sequential extraction with non-polar and polar organic solvent' [9]. Almost all the previous studies of unextractable residues have demonstrated their strong association with soil humus. Long-term aging experiments using isotope-labelled compounds have revealed the conversion of exogenous organic compounds (pesticides or polyaromatic hydrocarbons) to unextractable residues as a result of their strong association with soil humus [10–12]. In particular, various kinds of reversible and irreversible binding (e.g. covalent bonding, hydrogen bonding, chemisorption) with insoluble humin have been found to contribute strongly to the formation of unextractable residues [13].

On association of dioxins with humic substances, the association of 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin has been evaluated [14, 15]. It is safe to say that the associations between dioxins and humus do occur in OM-rich soil. Thus, the influence of humus on the extractability of dioxins as well as their extractability from particulate matter needs to be investigated.

In this study, we evaluated the extractability of dioxins from AP and HA, and found that the analytes associated with precipitated HA fraction (PHA) could not be efficiently extracted from the precipitate by the traditional toluene extraction method.

2. Experimental

2.1 *Apparatus*

A high-volume air sampler (HV-700F, Shibata Science Technology, Tokyo) was used to sample ambient atmosphere. Dioxins were extracted from APs and from PHA by pressurized liquid extraction (PLE) with an ASE-200 (Dionex, Sunnyvale, CA) instrument. The conditions for each extraction were as follows: cell volume, 33 mL; cell temperature, 100°C or 200°C; cell pressure, 10 MPa (1500 psi); duration of static cycle, 7 min; solvent flush volume, 20 mL; duration of N_2 gas purge, 60 s; number of cycles, 2. Each sample was extracted once at 100°C and continuously twice at 200°C under the specified conditions, and both extracts were combined.

PCDD/Fs and CoPCBs were analysed by high-resolution gas chromatography–mass spectrometry (HRGC–HRMS) with an HP-6890 Plus (Agilent, Palo Alto, CA) gas chromatograph coupled to a JMS-700D mass spectrometer (JEOL, Tokyo). The analytes were determined with BPX-DXN (SGE, Austin, USA) and RH-12ms (InventX, Torrance, CA) capillary columns. Dissolved organic carbon (DOC) was determined using a TOC-5000A analyser (Shimadzu, Kyoto, Japan).

2.2 *Materials*

A QR-100 quartz fibre filter (0.3-µm particle retention, Shibata) was used for retention of APs. A GF-75 glass fibre filter (0.3-µm particle retention, Toyo Roshi, Tokyo) was used for filtration of PHA. All dioxin-analytical-grade solvents and adsorbents were purchased from either Wako Pure Chemical Industries (Osaka, Japan) or Kanto Chemicals (Tokyo). Analytical-grade hydrochloric acid, sodium hydroxide, $FeCl_3 \cdot 6H_2O$, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, *o*-phenanthroline hydrochloride, sodium acetate, acetic acid, and hydroxylammonium chloride were purchased from Kanto Chemicals. Hydrochloric acid and ammonia solution (25.0–27.9% as NH_3; poisonous metal analytical grade) were also obtained from Kanto.

PCDD/F and CoPCB standards, including ^{13}C-labelled homologues, were purchased from Wellington Laboratories (Ontario, Canada) or Cambridge Isotope Laboratories Inc. (Andover, MA). A surrogates solution (SS) was prepared in acetone. This solution contained 17 ^{13}C-labelled 2,3,7,8-substituted CDD/F congeners (2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF and OCDF) and 12 ^{13}C-labelled CoPCBs (IUPAC Nos. 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189), each at a concentration of $1.5\,\mu g\,L^{-1}$, with the exception of the ^{13}C-OCDD/F at $3.0\,\mu g\,L^{-1}$. A recovery standards solution (RSS) in nonane was prepared containing ^{13}C-labelled 1,2,7,8-TeCDF, 1,2,3,4,7-PeCDD, 1,2,3,4,6,9-HxCDF, 1,2,3,4,6,8,9-HpCDF, 2,3′,4′,5-TeCB (#70), 2,2′,3,4,4′-PeCB (#85), 2,2′,3,4,4′,5′-HxCB (#138) and 2,2′,3,3′,5,5′,6-HpCB (#178), each at a concentration of $10\,\mu g\,L^{-1}$.

2.3 *Airborne particulates and humic acid*

APs were collected at Tokorozawa, Saitama, Japan, using a high-volume air sampler. The commercial humic acid (CHA, 45% organic carbon content and 22% ash content in product) used in this study was purchased from Wako. A CHA solution was prepared by dissolving 1.5 g of CHA in 1 L of 0.1 M NaOH using sonication. A soil humic acid fraction (SHA, 57% organic carbon content and 9% ash content in acid precipitate) was prepared according to the preparation method of the International Humic Substances Society [16]. Briefly, a sample of suburban surface soil (collected in the city of Tokorozawa) was air-dried, crushed, and passed through a 1-mm-mesh sieve. Fifty grams of the sieved sample (4.5% organic carbon content) were suspended in 500 mL of 0.1 M NaOH. After being shaken for 16 h, the suspended solution was centrifuged at 2000 *g* for 10 min, and the supernatant was collected.

Each of the obtained HA solutions (the CHA solution and the SHA solution) was adjusted to pH 7 and then filtered to remove the insoluble fraction. The filtrate was designated sol-1. Thereafter, 50 mL of the sol-1 was diluted to 500 mL with distilled water, and the resulting solution was designated sol-2.

2.4 *Analysis of dioxins in airborne particulates*

A flow chart for the complete sample treatment procedure is shown in figure 1. The ambient atmosphere was sampled in duplicate using two samplers. Ambient atmosphere (1000 m^3) was drawn through a quartz fibre filter, and the AP retained on the filter were air-dried and subjected to PLE with toluene or acetone.

Each extract was spiked with 0.3 mL of SS, redissolved in *n*-hexane, and cleaned up by means of column chromatography on a multilayer silica gel column and an active-carbon-impregnated silica gel column according to the procedure outlined in figure 1. Each eluate was concentrated to about 2 mL on a rotary evaporator

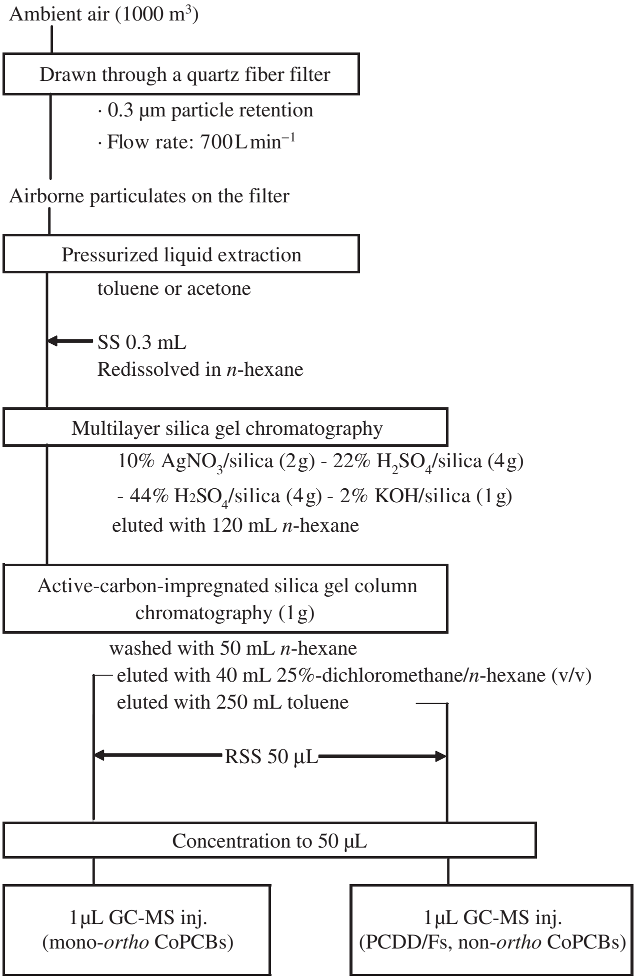

Figure 1. Analytical protocol for determination of PCDD/Fs and CoPCBs in airborne particulates.

at 40°C (for *n*-hexane or dichloromethane) or 60°C (for toluene) under reduced pressure. The concentrate was transferred to a 10 mL centrifuge tube with *n*-hexane and spiked with 50 µL RSS. Thereafter, the solvent was removed by purging under a nitrogen stream, and the sample was finally dissolved in 50 µL of *n*-nonane.

2.5 *Recovery of dioxins from precipitated humic acid fraction*

A flow chart for the complete sample treatment procedure is shown in figure 2. The HA solutions were spiked with SS and then shaken for 30 min so that the added compounds

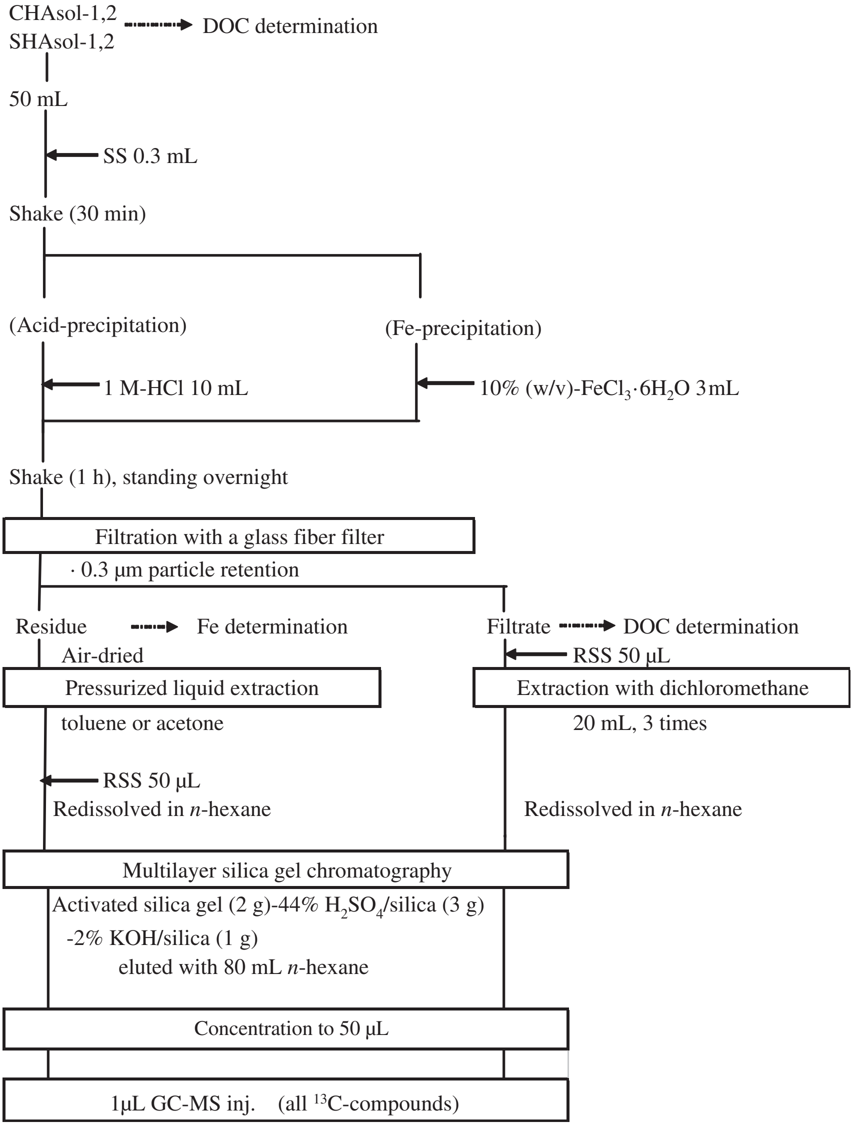

Figure 2. Analytical protocol for recovery of ^{13}C-labelled dioxins from precipitated humic acid fraction.

could be adsorbed by HA. Thereafter, precipitates of HA-^{13}C compounds associates were produced by the addition of 1 M HCl or 10% (w/v) $FeCl_3 \cdot 6H_2O$. The fraction of the ^{13}C compounds detached from PHA was estimated by determining the compounds in the filtrate (recovered by liquid–liquid extraction with dichloromethane) and those adsorbed on the walls of the glass materials (recovered by rinsing the walls with acetone and dichloromethane). In all recovery experiments, the amount of ^{13}C compounds detached from PHA was negligible ($<3\%$), proving that 30 min of shaking after addition of SS is sufficient for association of the added compounds with HA.

The OC content in the PHA was calculated by subtracting the DOC content in the filtrate of PHA suspension from the DOC content in the HA solution before precipitation. Iron in the PHA was determined colorimetrically using *o*-phenanthroline [17] after thermal digestion of OM (by heating at 500°C for 12 h).

2.6 *Quantification of dioxin concentrations by HRGC–HRMS*

An aliquot (1 µL) of the resulting solution was injected into the GC, which was equipped with a BPX-DXN column for analysis of PCDD/Fs (60 m × 0.25 mm i.d.) and an RH-12 ms column for analysis of CoPCBs (60 m × 0.25 mm i.d.). The detailed conditions for GC–MS analysis and the quantification procedure have been described elsewhere [18]. Recovery of the surrogate was calculated by using the ratio between the peak area of it against that of the corresponding recovery standard and by using the corresponding relative response factor.

2.7 *Accuracy control*

For the recovery experiments, RSS was added before multilayer silica gel cleanup to evaluate recovery of ^{13}C-compounds only by PLE. The recovery for the recovery standard was roughly evaluated by comparing its peak area with that of a standard injection. Minor analyte loss during the cleanup was confirmed in every experiment by confirming sufficient recoveries of the recovery standards ($>70\%$).

Variations of HRGC–HRMS analysis were estimated by multiple determinations of an identical resulting solution of a soil sample, and the relative standard deviations (RSD) of every PCDD/F homologues and CoPCB congeners were confirmed to be less than 5%.

An instrumental blank was measured prior to every GC-MS analysis by injecting clean *n*-nonane, and it was confirmed that no analyte was detected. Analysis of a method blank was run in each sample batch to demonstrate freedom from contamination. In this study, the quantities of all the method blanks were negligible for all PCDD/F homologues and CoPCBs congeners (below 2% of the quantities in the soil samples).

3. Results and discussion

3.1 *Extractability of dioxins from airborne particulates*

As stated in the introduction, atmospheric deposition is considered to be the main source of dioxins in topsoil. Particulate matter, which is emitted from various

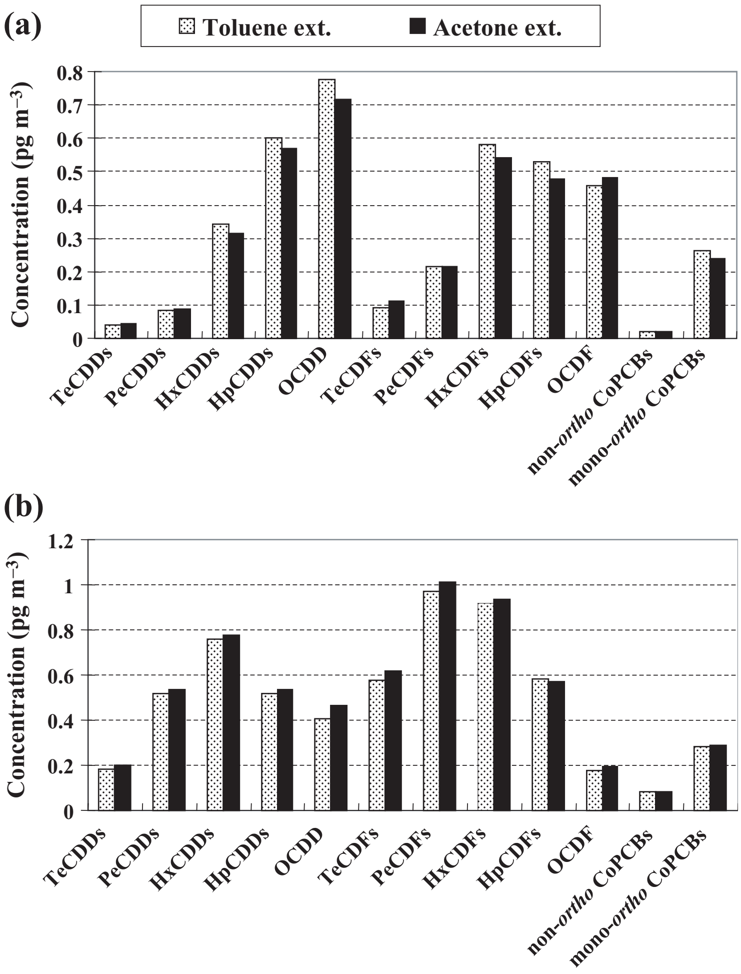

Figure 3. Comparison of the dioxin homologue profiles obtained by toluene and acetone extraction of airborne particulates collected in (a) summer and (b) winter.

combustion processes and is rich in dioxins, can be deposited on the ground by dry and wet deposition processes. Therefore, it is necessary first to estimate the extractability of dioxins from APs in soil.

Dioxins were extracted from collected APs with either toluene or acetone. Toluene is traditionally used as the extraction solvent for dioxin analysis. However, it has been found that, when PLE is used for complex matrices such as soils or sediments, HOP extraction efficiency with acetone is generally better than that with toluene [19–21].

Figure 3 shows the quantitative results of PCDD/F homologues and CoPCBs (non-*ortho*- and mono-*ortho*-) in APs collected in the summer and winter. As shown in figure 3, toluene and acetone extraction gave similar quantitative values for all the homologues, which indicates that the two solvents have equivalent extraction efficiencies with respect to dioxins in APs. An additional extraction at 200°C was performed for the residual APs, and a negligible amount of the analytes was detected. These results suggest that dioxins exist in an easily extractable form on the particles.

3.2 *Extractability of dioxins associated with humic acid*

On the basis of the high affinity of HA for HOPs, we assumed that some portion of the dioxins would occur in an HA-bound form and that the extractability of these bound forms would influence their extraction from OM-rich soil. Therefore, we needed to evaluate the extractability of dioxins associated with solid HA. HA in soil can occur either in a metal-free form (in which all acidic groups are undissociated) or in a metal-bound form (in which some acidic groups are dissociated and coordinated with metal atoms) [22, 23]. The presence of metals may influence the extractability of dioxins from HA. Thus, we conducted recovery experiments using both types of HA. In this study, PHA formed by acidification (to pH ~ 1) and by the addition of $FeCl_3$ are designated metal-free PHA and metal-bound PHA, respectively.

Recovery of ^{13}C compounds from PHA is shown in figures 4 and 5. (The recovery results are presented for only one isomer of each homologue series because no differences in the recovery rates were observed for the various isomers in each series.) In addition, the OC and Fe contents for the PHA are presented in table 1.

When sol-1, the more concentrated solution of HA, was used, the OC contents in the metal-free PHA of CHA and SHA were 30.5 and 33.3 mg, respectively. In this case, toluene extraction gave a poor recovery of ^{13}C compounds (below 15%), whereas acetone extraction gave a sufficient recovery (60–98%) from both PHA (figures 4a and 5a). These results indicate that toluene, which is traditionally used for dioxin analysis, cannot efficiently extract dioxins associated with HA and that acetone extraction is therefore better for extraction of dioxins from humic-rich soil. In addition, recovery using the more dilute sol-2 (2.7–2.8 mg OC in the acid-PHA) was also evaluated. In this case, as shown in figures 4(b) and 5(b), even toluene extraction gave a moderate recovery of dioxins from both PHA (39–73% for CHA and 44–66% for SHA). Toluene is known to be an effective extraction solvent for aromatic compounds owing to its π–π interactions with such compounds [24, 25]. Therefore, the results imply that the difficulty in extracting dioxins with toluene may be caused not by its weak extraction power but by its inability to permeate into the sites in HA at which the dioxins are sorbed.

Dioxin recovery from Fe-bound PHA was evaluated only for sol-2 of both CHA and SHA, and the results are shown in figures 4(b) and 5(b). As shown in table 1, the metal-free PHA and the Fe-bound PHA had similar OC contents for both HA types. The Fe contents in the Fe-bound PHA of CHA and SHA were 0.19 mg/mg OC and 0.48 mg/mg OC, respectively, whereas Fe was not detected (< 0.01 mg/mg OC) in either of the metal-free PHAs. Thus, the only apparent difference between the metal-free and Fe-bound PHA was the Fe content. For toluene extraction, the recovery of dioxins from the Fe-bound PHA was clearly lower than that from the metal-free PHA (11–20% for CHA and 11–25% for SHA). Moreover, the recovery was still poor even for acetone extraction (15–37% for CHA and 28–41% for SHA).

If the OM% of SHA is calculated using the conventional formula, OC% × 1.724 [26], then the Fe concentration in the Fe–HA complex of SHA is calculated to be 5.0 $\mathrm{mmol\,g^{-1}}$ OM. Tsutsuki and Kuwatsuka estimated the total acidity of common soil HA as 6–8 $\mathrm{mmol\,g^{-1}}$ [27]. These figures indicate that the Fe-bound PHA of SHA has an iron–acidic group ratio of 1 : 1 to 1 : 2. Schnitzer and Skinner found that iron in Fe–HA complexes can occur as $Fe(OH)^{2+}$ or $Fe(OH)_2^+$ at pH 2.5 [26]. One reason for the lower recovery from Fe–HA complexes compared with that from

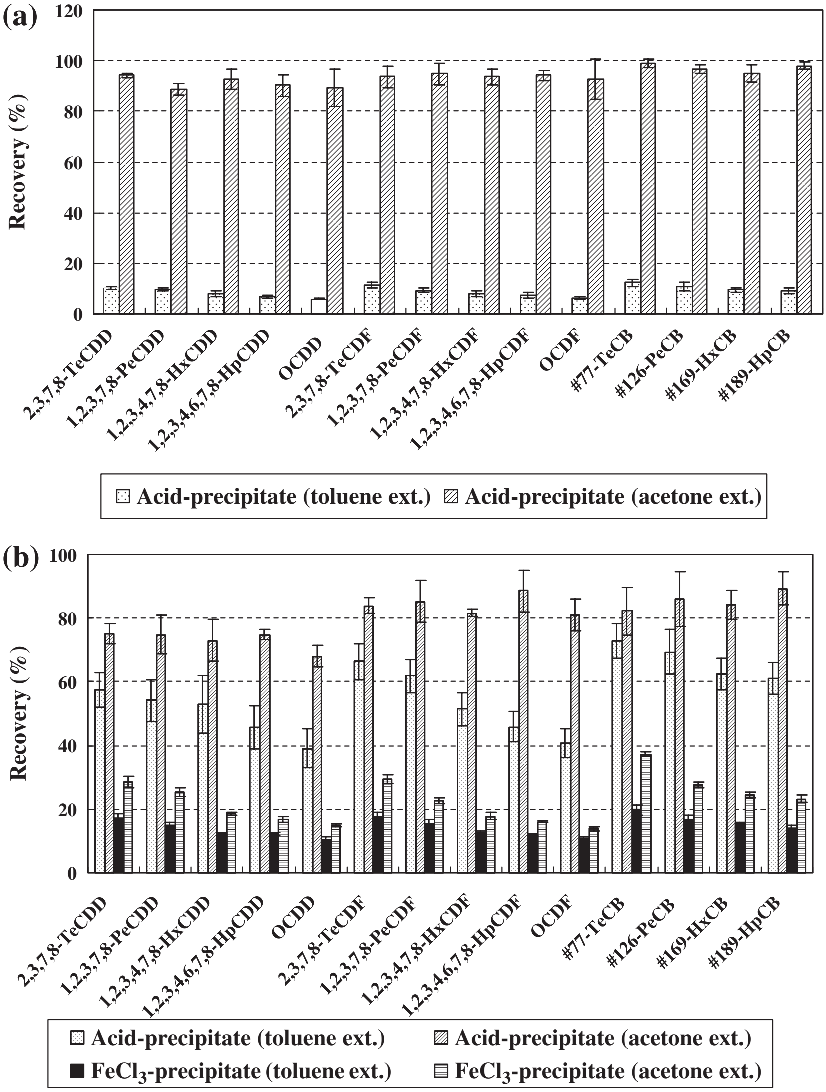

Figure 4. Recovery of ^{13}C-labelled dioxins from CHA precipitate derived from (a) sol-1 and (b) sol-2. The confidence interval at the top of each bar indicates the mean standard deviation for triplicate determinations.

the metal-free PHA may be that the polar ferric hydroxide substituents bound to acidic group(s) may lower the permeability of apolar organic solvents into the complexes. Grathwohl suggested that an increase in the overall polarity of HA results in a lower affinity for non-ionic compounds [28], which supports our suggestion that the poor recovery of dioxins from the Fe-bound PHA was not caused by their strong affinity for Fe–HA complexes. In addition, we assumed that polyvalent ferric ions may form cross-linkages between acidic groups in a HA molecule and that, therefore, the molecule may adopt a more compact conformation that can lower the permeability of organic solvents to sorbed sites of dioxins, as proposed by Jones and Tiller [29].

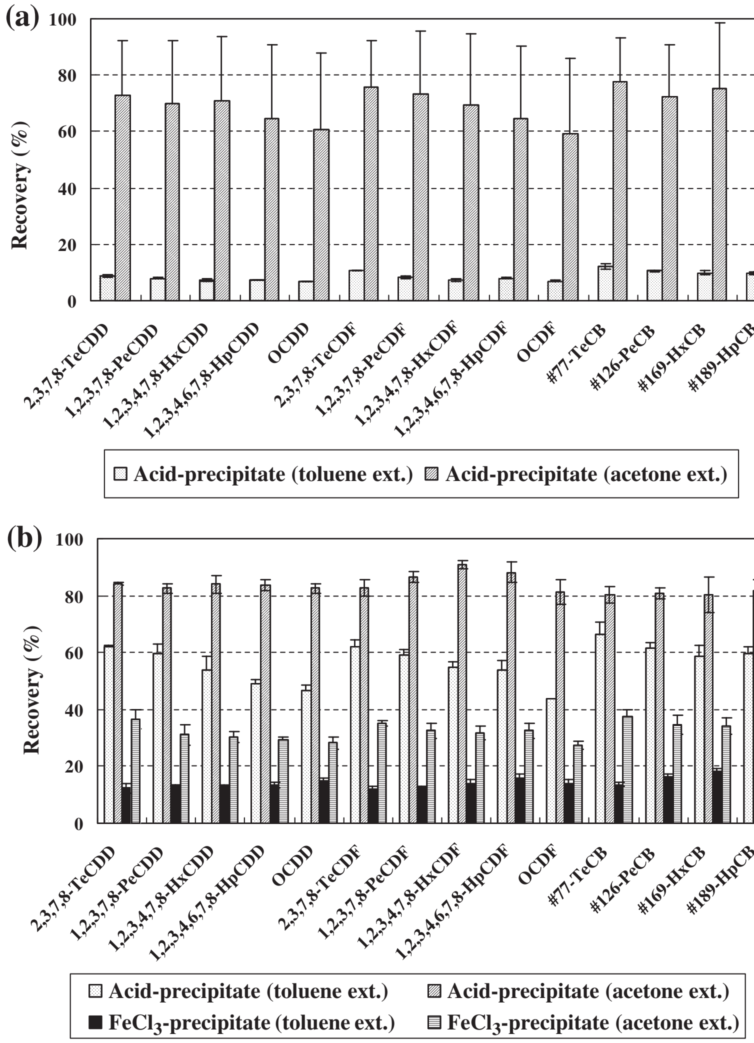

Figure 5. Mean recovery of ^{13}C-labelled dioxins from SHA precipitate derived from (a) sol-1 and (b) sol-2. The confidence interval at the top of each bar indicates the mean standard deviation for triplicate determinations.

We found in our preliminary experiments that other forms of metal-bound HA (precipitates obtained by the addition of Al^{3+}, Mn^{2+}, or Cu^{2+}) also gave a poor recovery of associated ^{13}C compounds. Although we cannot elucidate the detailed binding form of metals with soil humus, it seems apparent from our results that the presence of metals bound to HA will influence the extractability of sorbed dioxins.

In conclusion, the extractability of AP-borne dioxins with toluene was equivalent to that with acetone, whereas only acetone could effectively extract dioxins from the metal-free PHA. Moreover, the recovery of dioxins from the Fe-PHA was lower than that from the metal-free PHA. The insufficient recovery observed in this study was probably due to the low permeability of the solvents into the solid HA,

Table 1. Organic carbon and iron contents in humic acid aggregate.

	CHA				SHA			
	Sol-1		Sol-2		Sol-1		Sol-2	
Aggregation	Acid	$FeCl_3$	Acid	$FeCl_3$	Acid	$FeCl_3$	Acid	$FeCl_3$
OC in aggregate (mg)	30.5	30.1	2.7	2.7	33.3	44.4	2.8	4.0
Fe in aggregate (mg/mg OC)	n.a.[a]	n.a.	< 0.01	0.19	n.a.	n.a.	< 0.01	0.48

[a] Not analysed.

that is, to low accessibility of the sites of dioxin sorption to the solvents. The extractability of dioxins from soil components carrying them could be the dominant factor in their overall extractability from soil samples.

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