Novel evidence for natural formation of dioxins in ball clay

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ARTICLE

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Distribution, Characteristics, and Worldwide Inventory of Dioxins in Kaolin Ball Clays

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Supporting Information

ABSTRACT: Distribution, characteristics, and global inventory of dioxins (polychlorinated dibenzo-*p*-dioxins [PCDDs] and dibenzofurans [PCDFs] and dioxin like polychlorinated biphenyls) in kaolin clays collected from 10 countries were investigated. Dioxins were found in all kaolin clay samples analyzed, at total concentrations ranging from 1.2 pg/g (Brazil) to 520,000 pg/g (USA). Dioxin concentrations in kaolin clays from a few countries (e.g., Brazil and UK) were lower than those reported for background soils in Japan. Dioxin profiles in kaolin clays were characterized by the domination of the congener octachlorodibenzo-*p*-dioxin (OCDD), and the concentrations of other congeners decreased in the order of reduction in the levels of chlorination. Furthermore, specific distribution of congeners, with predominant proportions of 1,4,6,9-substituted PCDDs within each homologue group, was found in most clay samples. The ratios of concentrations of PCDD to PCDF and 1,2,3,7,8,9-HxCDD to 1,2,3,6,7,8-HxCDD indicated differences in the profiles found for anthropogenic sources (including pentachlorophenol) and kaolin clays. Concentrations of PCDD/Fs in kaolin clays, except for American ball clays, did not exceed the environmental criteria set by the Law Concerning Special Measures against Dioxins in Japan. Based on the average concentrations measured in our study, inventories of PCDD/Fs from the production/usage of ball clays on a global scale were estimated to be 650 kg/yr; the corresponding value on a TEQ basis is 2400 g-TEQ/yr. More than 480 kg of OCDD is estimated to be released annually from the production of kaolin clays worldwide, suggesting that kaolin clays can be a major contributor for additional source of dioxins, especially OCDD, in the environment.

INTRODUCTION

Since the 1980s, many studies have suggested the natural formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) (hereafter referred to as dioxins).[1−3] Elevated concentrations and unique congener profiles of dioxins in sediment and soil from the Mississippi embayment in the USA were attributed to arise from the natural processes.[1] Several studies were conducted to elucidate the sources and mechanisms of formation of high concentrations of dioxins, particularly PCDDs (>450 ng/g dry weight (dw), and >1500 pg WHO-TEQ/g dw), in ball clays, which consisted primarily of kaolin, from the South-Central USA.[4−6] An estimated 1.1 million metric tons of American ball clay was mined in 2007, for use in the ceramic industry.[7] In the USA, ball clay is mainly mined in Tennessee, Texas, Kentucky, and Mississippi regions of the Mississippi Embayment. The ball clays are embedded in sediments laid down during the early to middle Eocene Epoch (approximately 40−45 Ma).[4] The presence of dioxins in such ancient clays presented an interesting scientific quandary. Dioxin profiles in ball clays are characterized by the domination of the congener octachlorodibenzo-*p*-dioxin (OCDD), and the concentrations of other congeners decrease with corresponding reduction in the levels of chlorination. Furthermore, concentrations of PCDFs in ball clay are low or nondetectable.[8] Ball clay is a type of kaolin clay with predominant proportion of kaolinite mineral. High concentrations of dioxins were found not only in the American ball clay but also in kaolin clay from Germany and Spain.[8,9] Moreover, the congener compositions of PCDDs were fairly consistent among the clays from the various geographical regions. Kaolin clay is an important industrial resource. In 2007, 38.5 million metric tons of kaolin was produced in the world. The

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production was the greatest in the USA (7.1 million tons), followed by Uzbekistan (5.5 million metric tons) and Germany (3.8 million metric tons).[10] In the past, dioxin contamination in various animal products, including chicken and cat fish, was attributed to the use of ball clay as an anticaking additive in feed.[11,12] Moreover, high levels of PCDDs were found in milk in The Netherlands, and this was traced back to the use of kaolin clay in the process of sorting of potatoes.[13] Franzblau et al.[14] reported human exposure to dioxins from ball clay through occupation/hobby in ceramics/pottery industry. Although previous studies reported high concentrations and contamination of dioxins in kaolin clays from the USA and Europe, no information was available on dioxins in kaolin clays from Asian countries.

In this study, concentrations of dioxins (including dioxin like polychlorinated biphenyls [DL-PCBs]) were determined in kaolin clay samples collected from 10 countries, mainly from Asia. This is the first study to measure dioxins in kaolin clays from Asian countries. For comparison, dioxins were also measured in the American ball clays. Global inventory of dioxins was estimated from the annual production of kaolin clays, based on the measured mean and median concentrations. This inventory was compared with annual emission of dioxins from anthropogenic sources, to enable an understanding of contributions of kaolin to dioxin emissions. To investigate any relationship between dioxin concentrations and mineral content of clays, element compositions of kaolin clays were determined. The process of natural formation of dioxins in kaolin clay was also discussed.

MATERIALS AND METHODS

Samples. Thirty-three kaolin clay samples were collected from 10 countries: USA ($n = 5$), Japan ($n = 11$), China ($n = 6$), South Korea ($n = 5$), India ($n = 1$), Indonesia ($n = 1$), Australia ($n = 1$), New Zealand ($n = 1$), Brazil ($n = 1$), and UK ($n = 1$). Most of the clay samples were either purchased from retail suppliers or obtained from the ceramic industries in Japan. The kaolin clays include raw clay originated from a mine without further processing and processed clay after elutriation. Two types of Japanese ball clays (sedimentary kaolinitic clay), *Gaerome* and *Kibushi*, which have been used as raw materials in ceramic wares, floor and wall tiles, and pottery, were obtained from ceramic industries in Japan. *Kibushi* and *Gaerome* deposits of Pliocene age in ancient lake are distributed near Nagoya in Aichi Prefecture, the Chubu region, and constitute the most productive kaolin-mining area in Japan.[15] The lower part of the lacustrine sediment is composed mainly of quartz sand and *Gaerome* clay, whereas the upper part is composed of *Kibushi* clay and silty clay. *Gaerome* is a plastic kaolin clay consisting of coarse quartz grains and occasional feldspar grains.[15] *Kibushi* is a dark-colored, plastic kaolin clay stained with organic substances and thus resembles the ball clay in the USA. American ball clays originating from the mines located in Tennessee and Kentucky were kindly provided by Joseph Ferrario at the U.S. Environmental Protection Agency. The Chinese kaolin was taken from kaolin outcrop located in Boshan, Shandong. Based on the origin, the kaolin clays analyzed in this study can be divided in two groups.[16] The first is 'primary' kaolin clay which is a weathering product of feldspar by hydrothermal metamorphism; this includes kaolin from Australia, Brazil, China, India, Indonesia, New Zealand, South Korea, and the UK. The second group is 'sedimentary' kaolin clay, which is eroded kaolin, transported and deposited in ancient lakes or marshes; this includes American and Japanese ball clays. The types of clay samples investigated in this study were nonbaked clays. Japanese bentonite clay ($n = 2$), which is a class of clay mineral, was analyzed as a reference sample. Sample information such as sample type and suppliers are available in the Supporting Information (Table S1).

Chemical Analysis. The analytical method was similar to that described earlier with minor modifications.[17] Briefly, 100 g of the samples (20 g for American ball clay) were extracted using toluene for 24 h in a Soxhlet apparatus. As for the internal standard, 0.5 to 1 ng of ^{13}C-labeled PCDD/Fs and DL-PCBs (Wellington Laboratories, Ontario, Canada) were spiked into half of the extract (one-twentieth of the extract for American ball clay), after extraction. The extracts were purified and fractionated using acidic silica-gel columns and active carbon column. Concentrations of dioxins were determined by gas chromatography-high resolution mass spectrometry (GC-HRMS; JMS-800D, JEOL, Tokyo, Japan). The detailed analytical procedure and instrument conditions are provided in the Supporting Information.

Quality Assurance/Quality Control. The recovery rates of internal standards for PCDD/Fs and DL-PCBs through the entire analytical procedure were in the acceptable range (50−120%). Procedural blanks ($n = 4$) were analyzed with every batch of samples, to monitor for any contamination. Trace levels of DL-PCBs and OCDD were detected in some procedural blanks, but those levels did not exceed our limits of quantification. Peaks in samples were identified as dioxins if the ratio between first and second ions was within ±15% of the theoretical ratio. Method detection limit (MDL) and quantification limit (MQL) values for dioxins were calculated from the variance associated with replicate analysis ($n = 5$). MDL and MQL were set to be 3 and 10 times of the standard deviation, respectively, from the replicate analysis of trace level of dioxins, divided by sample weight and multiplied by the injection volume. Concentration below the MDL and TEQ below the MQL were assigned a value of zero for data analysis. MDL and MQL values for each congener are available in the Supporting Information (Table SI2). The concentrations in kaolin clays are reported on a dry weight basis.

Element Analysis. Element compositions such as silica (Si), aluminum (Al), iron (Fe), potassium (K), titanium (Ti), magnesium (Mg), and copper (Cu) were determined in clays using energy dispersive X-ray spectroscopy (EDX; Horiba Co., Kyoto, Japan) equipped with scanning electron microscope (SEM; Hitachi High-Technologies Co., Tokyo, Japan).

RESULTS AND DISCUSSION

Raw Clay versus Processed Clay. In general, raw clay is mined and then is processed by elutriation (<2 μm of particle size), dried, and homogenized, for use as a material in ceramic industry. The concentrations of dioxins determined in raw *Kibushi* and processed *Kibushi* clays were compared in order to examine distribution of dioxins during clay preparation processes. The concentrations of total dioxins in raw *Kibushi* ranged widely from 950 to 16000 pg/g, (mean: 5990 pg/g), which were similar to the concentrations found in processed *Kibushi* (Figure 1). In the case of *Gaerome*, dioxin concentrations in processed clays were 2−3 times higher than the concentrations found in raw clay. It has been reported that PCDD/F concentrations between raw and processed American ball clays were remarkably different.[4] In general, the processed clay exhibited

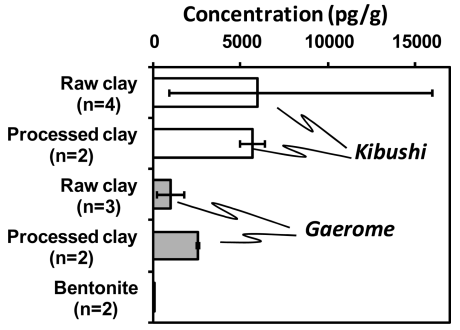

Figure 1. Mean and range of concentrations (pg/g) of sum of PCDD/Fs and DL-PCBs in raw and processed clays of *Kibushi* and *Gaerome*, Japan, compared with the concentrations in bentonite clay (as a reference).

higher concentrations of dioxins than the raw clay. This difference might be related to the differences in the amount of impurities (such as quartz and organic substances) found before and after elutriation. Even in a same sediment layer, thickness, particle size, and types of impurities can differ depending on the distance from the clay sources and water current during sediment formation processes. This can be the reason for the wide range of concentrations found in raw *Kibushi* clays. We also measured dioxins in bentonite clays as a reference material. Trace level of dioxins (at 2.8 pg/g) was detected in raw and processed bentonite. This suggested that sample contamination with dioxins during the clay preparation processes is lower than that found in the bentonite itself. Therefore, the measured concentrations of dioxins in clay are purely derived from kaolin clays, not from production/preparation processes.

Concentrations. The mean concentrations of individual toxic (2,3,7,8-substituted) PCDD/F congeners and sum of 12 DL-PCBs in the kaolin samples from each country, along with their TEQs are summarized in Table 1. Dioxins were found in all samples analyzed, at total concentrations ranging widely from 1.2 pg/g (Brazil) to 520000 pg/g (USA) (Table 1). As reported in earlier studies,[4,5] the highest concentrations of dioxins were detected in the American ball clays. The *Kibushi* and *Gaerome* (Japan) and the Australian kaolin had relatively high concentrations of dioxins, at ppb (ng/g) level. Trace levels of dioxins were found in the kaolin from New Zealand, Brazil, and the UK. It should be noted that only a limited number of samples were analyzed from these countries. However, the concentrations of dioxins in the limited number of samples were low and comparable to those found in bentonite reference material. Concentrations of dioxins in Chinese kaolin ranged from 3.1 to 1500 pg/g (mean: 300 pg/g), which were 3−8 times higher than the concentrations in kaolin from South Korea, Indonesia, and India. Concentrations of DL-PCBs in kaolin clays varied from 0.19 to 100 pg/g, which were up to 4 orders of magnitude lower than those of PCDDs (Table 1 and Table SI3).

Recently, Schmitz et al.[16] investigated the distribution of dioxins in primary and sedimentary kaolin clay (similar to ball clay). Ten to thousand times higher concentrations of dioxins were found in sedimentary kaolin clay than primary kaolin, supporting the natural formation of dioxins in ancient clay sediment. Similarly, based on the origin, the kaolin clays analyzed in this study are categorized as primary kaolin clays and sedimentary kaolinitic clays. Relatively high concentrations of dioxins were found in sedimentary kaolinitic clays, whereas primary kaolin clays contained trace levels of dioxins.

TEQ Levels. Toxic equivalents (TEQs) were calculated based on the WHO-TEF2006. The TEQ concentrations in the kaolin clay samples ranged widely from 0.0011 pg-TEQ/g to 1600 pg-TEQ/g (Table 1). The highest TEQs were found in the American ball clays, which were comparable to the average TEQ values determined previously (1500 pg-TEQ/g),[4,5] followed by Japanese *Kibushi* (21 pg-TEQ/g) and *Gaerome* (6.7 pg-TEQ/g). None of the kaolin clays, except for the American ball clays, exceeded environmental criteria for soil (1000 pg-TEQ/g) and for sediment (150 pg-TEQ/g) set by the Law Concerning Special Measures against Dioxins in Japan. However, the TEQs found in *Kibushi* (mean: 21 pg-TEQ/g; maximum: 47 pg-TEQ/g) were 10 times higher than the values reported for background soils in Japan (2.1 pg-TEQ/g, $n = 717$).[18]

Dioxin Profiles. The toxic congener distribution and profiles were remarkably similar among all kaolin samples analyzed. OCDD (85%) was the predominant congener in all samples, followed in abundance by 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (HpCDD) (9.7%) (Figure 2). Concentrations of 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (HxCDD) were 2−5 times higher than those of other toxic HxCDDs. PCDFs and DL-PCBs were not detected in samples or were found at the ultra trace level. The congener profiles of DL-PCBs were similar to those reported in technical PCBs, which has predominant levels of CB118 and CB105.[19] The PCDD/F congener profiles were remarkably similar to those reported for the American ball clays.[4,8] The composition profiles of toxic PCDD/Fs in kaolin (American and Japanese ball clays in this case, as a representative for clays) compared with those for several anthropogenic dioxin sources, pentachlorophenol (PCP, agrochemical formulation), chloronitrophen (CNP),[20] technical PCB mixture,[21] flue gas, and fly ash,[22] are shown in Figure 2. The characteristic profile of predominance of OCDD, with a limited number of toxic congeners found in the kaolin clays, resembles that for PCP but was remarkably different from the profiles reported for other anthropogenic sources of dioxins. PCP contains trace levels of octachlorodibenzofuran (OCDF), whereas OCDF was near the detection limit in all kaolin clay samples. To distinguish dioxins in kaolin from anthropogenic dioxin sources, a ratio analysis of PCDD to PCDF (PCDD:PCDF) and 1,2,3,7,8,9-HxCDD to 1,2,3,6,7,8-HxCDD (1,2,3,7,8,9-HxCDD:1,2,3,6,7,8-HxCDD) was performed for selected dioxin sources (Table 2). For this analysis, PCDD/F congener concentrations determined in American and Japanese ball clays were selected as representatives. The PCDD:PCDF ratio in the kaolin (mean: 4580, range: 1040−8600) was much higher than the ratios found in anthropogenic sources including PCP (mean: 33, range: 0.7−200). The PCDD:PCDF ratio analysis has been conducted for American ball clays previously.[4] PCDD:PCDF ratios for raw and processed ball clays were 957 and 2672, respectively: this is similar to the range found in our study. In general, the ratios of 1,2,3,7,8,9-HxCDD:1,2,3,6,7,8-HxCDD were >1 in the kaolin clays, whereas the ratios were <1 in anthropogenic dioxin sources such as pesticides and combustion. The ratios of 1,2,3,7,8,9-HxCDD:1,2,3,6,7,8-HxCDD reported for ball clays (4.6 for raw clays and 2.7 for processed clay) were in the range of what was found in our study. The ratio of 1,2,3,7,8,9-HxCDD:1,2,3,6,7,8-HxCDD could be a useful indicator to distinguish dioxins in kaolin including Japanese clay from anthropogenic sources.

Few studies have reported concentrations of non-2,3,7,8-substituted congeners and DL-PCBs in ball clays. In this study, non-2,3,7,8-substituted congeners and DL-PCBs were also

Table 1. Concentrations (Mean and Median in Parentheses; pg/g) of Dioxins and TEQ Values (pg-TEQ/g) in the Kaolin Clays from 10 Countries

	USA (ball clay) $n = 5$	Japan (*Kibushi*) $n = 6$	Japan (*Gaerome*) $n = 5$	China $n = 6$	South Korea $n = 5$	Indonesia $n = 1$	India $n = 1$	Australia $n = 1$	New Zealand $n = 1$	Brazil $n = 1$	UK $n = 1$
Congeners											
2,3,7,8-TeCDD	170	1.1	0.50	0.068	<0.02	<0.02	0.020	0.070	<0.02	<0.02	<0.02
	(110)	(1.2)	(0.54)	(<0.02)	(<0.02)						
1,2,3,7,8-PeCDD	680	5.6	2.1	0.43	<0.01	<0.01	0.10	0.56	<0.01	<0.01	<0.01
	(680)	(5.9)	2.6)	(<0.01)	(<0.01)						
1,2,3,4,7,8-HxCDD	660	7.6	3.3	1.2	<0.02	<0.02	0.11	0.79	<0.02	<0.02	<0.02
	(670)	(8.0)	(4.0)	(<0.02)	(<0.02)						
1,2,3,6,7,8-HxCDD	980	15	5.4	1.7	0.009	<0.009	0.42	1.8	0.040	<0.009	0.010
	(980)	(15)	(6.2)	(<0.009)	(<0.009)						
1,2,3,7,8,9-HxCDD	2900	66	16	2.2	0.0060	<0.02	0.20	3.7	0.090	<0.02	<0.02
	(2900)	(72)	(18)	(0.075)	(<0.02)						
1,2,3,4,6,7,8-HpCDD	18000	480	130	36	0.37	0.47	6.6	61	0.21	0.080	0.35
	(19000)	(460)	(140)	(0.53)	(0.32)						
OCDD	440000	2800	890	190	15	31	33	2900	0.80	0.83	1.8
	(430000)	(2700)	(950)	(42)	(4.2)						
2,3,7,8-TeCDF	<0.5	<0.009	0.0020	<0.009	0.026	<0.009	0.15	<0.009	<0.009	<0.009	<0.009
	(<0.5)	(<0.009)	(<0.009)	(<0.009)	(<0.009)						
1,2,3,7,8-PeCDF[a]	<1	<0.02	<0.02	<0.02	0.026	<0.02	0.14	0.030	<0.02	<0.02	<0.02
	(<1)	(<0.02)	(<0.02)	(<0.02)	(<0.02)						
2,3,4,7,8-PeCDF	<0.5	0.022	<0.009	<0.009	0.020	<0.009	0.15	0.013	<0.009	<0.009	<0.009
	(<0.5)	(<0.009)	(<0.009)	(<0.009)	(<0.009)						
1,2,3,4,7,8-HxCDF[b]	<0.5	0.033	<0.01	<0.01	0.038	<0.01	0.17	<0.01	<0.01	<0.01	<0.01
	(<0.5)	(<0.01)	(<0.01)	(<0.01)	(<0.01)						
1,2,3,6,7,8-HxCDF	<0.5	0.020	<0.01	<0.01	0.028	<0.01	0.12	0.43	<0.01	<0.01	<0.01
	(<0.5)	(<0.01)	(<0.01)	(<0.01)	(<0.01)						
1,2,3,7,8,9-HxCDF	<0.5	<0.01	<0.01	<0.01	<0.01	<0.01	0.17	0.070	<0.01	<0.01	<0.01
	(<0.5)	(<0.01)	(<0.01)	(<0.01)	(<0.01)						
2,3,4,6,7,8-HxCDF	<0.5	<0.01	<0.01	0.015	0.016	<0.01	0.11	<0.01	<0.01	<0.01	<0.01
	(<0.5)	(<0.01)	(<0.01)	(<0.01)	(<0.01)						
1,2,3,4,6,7,8-HpCDF	2.5	0.12	0.058	0.020	0.12	<0.01	1.9	<0.01	0.11	<0.01	0.020
	(2.4)	(0.12)	(0.050)	(<0.01)	(0.020)						
1,2,3,4,7,8,9-HpCDF	0.56	0.022	<0.01	<0.01	0.010	<0.01	0.20	<0.01	0.040	<0.01	<0.01
	(0.60)	(0.015)	(<0.01)	(<0.01)	(<0.01)						
OCDF	53	0.11	0.056	0.037	0.090	<0.02	4.9	0.030	<0.02	<0.02	<0.02
	(44)	(0.12)	(<0.02)	(<0.02)	(<0.02)						
Total PCDDs	520000	5900	1600	280	16	34	86	3100	2.3	1.0	3.0
	(520000)	(5500)	(1800)	(44)	(5.2)						
Total PCDFs	69	2.4	0.52	0.48	1.4	<0.009	19	0.74	0.87	<0.009	0.33
	(63)	(2.2)	(0.49)	(0.24)	(0.25)						
Total DL-PCBs	5.3	5.8	9.3	1.6	22	1.1	3.5	0.40	2.3	0.19	0.63
	(5.1)	(6.8)	(3.8)	(1.4)	(3.9)						
Total PCDD/Fs and DL-PCBs	520000	5900	1600	300	41	35	110	3100	5.4	1.2	3.9
	(520000)	(5500)	(1800)	(48)	(10)						
Total TEQ	1600	21	6.7	1.4	0.031	0.014	0.40	2.8	0.0093	0.0011	0.0041
	(1600)	(22)	(5.7)	(0.025)	(0.0046)						

[a] Coelute with 1,2,3,4,8-PeCDF. [b] Coelute with1,2,3,4,7,9-HxCDF.

measured. The concentrations are reported in the Supporting Information (Table SI3). Congener compositions (%) of tetra- to hepta-CDDs in the kaolin clays from several countries are shown in Figure 3. Interestingly, specific congener profiles with predominant 1,4,6,9-substitutions, were found in the kaolin clays. For example, 1,4,6,9-TeCDD and 1,2,4,6,9-PeCDD (coelute with 1,2,3,4,7-PeCDD) were the most predominant congeners in the corresponding homologues. The compositions of PCDD

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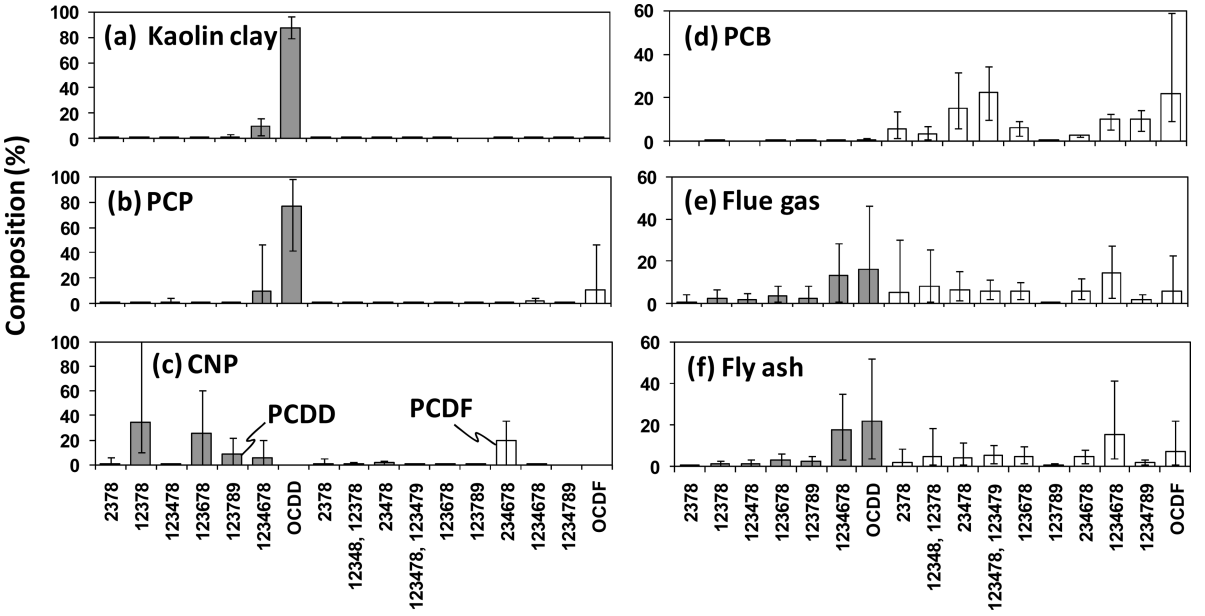

Figure 2. Profiles of individual 2,3,7,8-substituted PCDD/F congeners to total concentrations in selected dioxin sources: (a) kaolin clay, data from this study; (b) pentachlorophenol (PCP), data from ref 20; (c) chloronitrophen (CNP), data from ref 20; (d) PCB, data from ref 21; (e) flue gas, data from 22; (f) fly ash, data from ref 22. Gray and white bars represent PCDD and PCDF congeners, respectively.

Table 2. Concentration Ratios (Mean and Range) of PCDD to PCDF and 1,2,3,7,8,9-HxCDD to 1,2,3,6,7,8-HxCDD Found in Selected Dioxin Sources

	selected dioxin sources				
	kaolin[a] $n = 16$	PCP[b] $n = 10$	CNP[b] $n = 20$	flue gas[c] $n = 48$	PCB[d] $n = 27$
PCDD:PCDF	4580 (1040−8600)	33 (0.7−200)	629 (6.8−5730)	1.1 (0.13−6.5)	0.01 (0.001−0.016)
1,2,3,7,8,9-HxCDD:1,2,3,6,7,8-HxCDD	3.3 (1.4−6.1)	0.33 (0.02−1.2)	0.38 (0.33−0.57)	0.72 (0.38−1.3)	NA[e]

[a] Data from American and Japanese ball clays (this study). [b] Data from ref 20. [c] Data from ref 22. [d] Data from ref 21. [e] NA: not available, 1,2,3,7,8,9-HxCDD and/or 1,2,3,6,7,8-HxCDD were not detected.

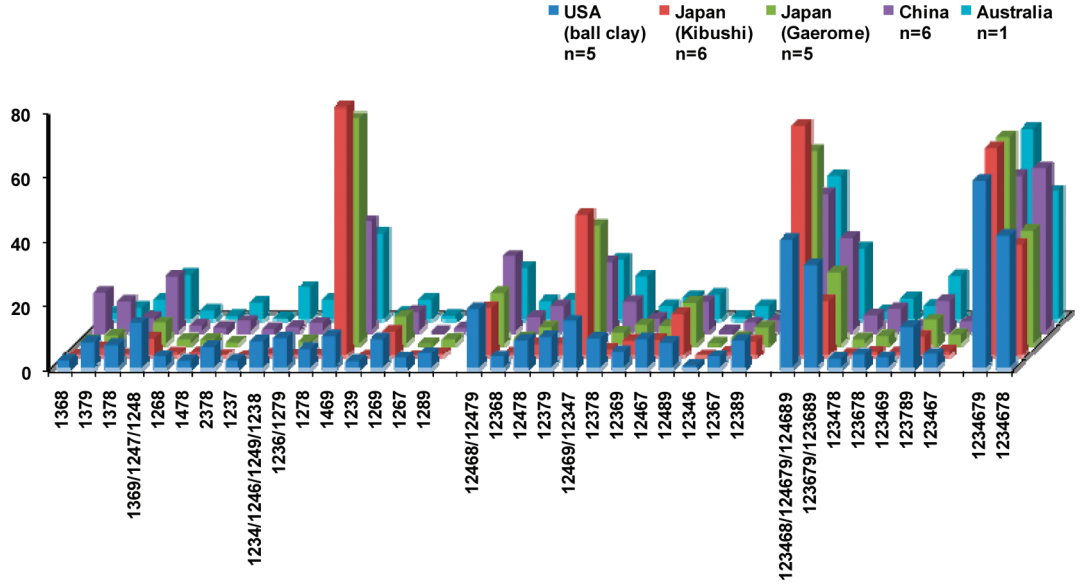

Figure 3. Congener compositions (%) of tetra- to heptachlorodibenzo-*p*-dioxins in kaolin clays from several countries. Congener compositions were calculated from corresponding homologues.

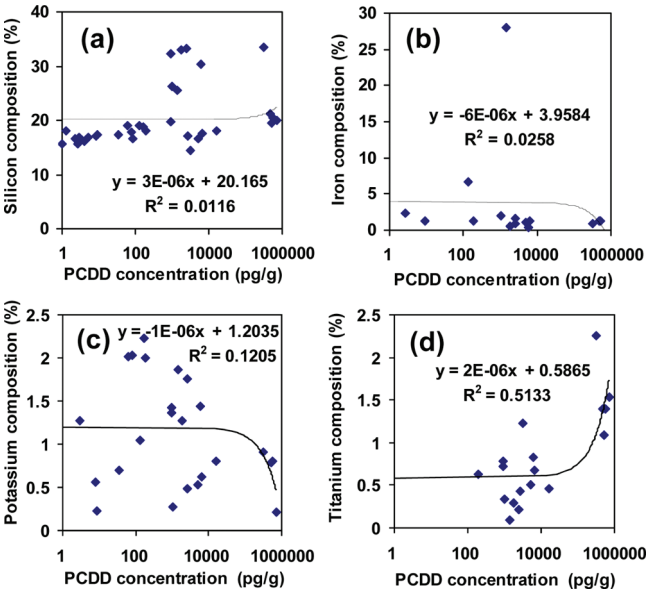

Figure 4. Relationships between PCDD concentrations (pg/g) and element compositions (%) in the kaolin clays: (a) silicon, (b) iron, (c) potassium, and (d) titanium.

congeners were also compared between raw and processed *Kibushi* clays (Figure SI2). The compositions of PCDD congeners in raw and processed *Kibushi* clays were similar: 1,4,6,9-TeCDD was the most predominant congener among the tetra-CDD, whereas 1,4,6,9-TeCDD was not the dominant congener in processed American ball clay (Figure 3). In general, the 1,4,6,9-substitution patterns were found for all homologues from tetra- to hepta-CDDs; this pattern resembles the one reported for sediment from Queensland (Australia), Lake Kasumigaura (Japan),[23] and Hong Kong.[24] The congener distribution indicates that peri-lateral and peri-dechlorination of OCDD.[23] Hepta- and other lower chlorinated PCDDs found in the kaolin clays could be the dechlorination products from OCDD. Mass chromatograms of PCDDs in the *Kibushi* clay are available in the Supporting Information (Figure SI1).

Clay Minerals and Dioxins. Clay minerals display many surface charge related activities such as ion exchange, adsorption, and catalysis. It has been hypothesized that the natural formation of dioxins in kaolin was a result of *in situ* mineral-catalyzed synthesis.[8] Studies have documented *in situ* OCDD formation in soils and geologic clay deposits.[25,26] These studies demonstrated the formation of OCDD in naturally occurring and widely distributed clay mineral, montmorillonite, under environmentally relevant conditions. OCDD was rapidly formed from PCP mixed with Fe(III)-montmorillonite. We determined element compositions in the kaolin clays investigated here. The relationships between PCDD concentrations and selected element compositions are shown in Figure 4. We found significant correlation between PCDD concentrations and Ti levels in kaolin clays (Spearman rank correlation coefficient, $r = 0.63$, $p < 0.01$), whereas a poor correlation was observed between PCDDs and Fe. Magnesium (Mg), calcium (Ca), and copper (Cu) were detected in the clays, but these were minor components. Poor correlations were observed between Si, Al, K, and PCDDs. It is known that Ti(IV)-montmorillonite is a strong acid catalyst. This element might assist mineral-catalyzed synthesis of dioxins in geologic clay deposits.

Inventory Estimation. We calculated inventory of PCDD/Fs from kaolin production worldwide, based on the average and median PCDD/F concentration and TEQs measured and those reported in previous studies (Table 3). It should be noted that DL-PCBs are not included in the estimation of inventories here, to enable comparison with previous studies, although DL-PCBs account for <0.5% of the sum of PCDD/Fs and DL-PCBs in kaolin clays. TEQ values reported in previous studies were based on the WHO-TEF1998.[8,9] In total, 21 million tons of primary kaolin clay from 12 countries were taken for this estimation, which account for >50% of the world production of 38.5 million tons.[10] Kaolin production in China was estimated to be 2 million tons annually.[27] For American and Japanese ball clays, the production was 1.1 million tons and 0.37 million tons, respectively.[7,28] On a mass basis, total global inventory of dioxins from kaolin clay production was estimated to be 650 kg/yr, based on the average concentrations. The highest value was found from the American ball clay at 550 kg/yr, followed by the Spanish kaolin at 61 kg/yr and the German kaolin at 29 kg/yr. On a TEQ basis, total global inventory was estimated to be 2400 g-TEQ/yr based on the average concentrations. The American ball clay contributed to high proportion of the total global inventories because of the high production volume and TEQs. The total dioxin inventory from the Japanese ball clay productions was estimated to be 3.3 g-TEQ/yr for *Kibushi* and 1.4 g-TEQ/yr for *Gaerome*. In this study, relatively high concentrations of dioxins were found in American ball clays and *Kibushi* clays. Dioxin inventory based on median concentrations were estimated to be 560 kg/yr for American ball clay and 0.86 kg/yr for Kibushi clay, which were close to those based on average concentrations. It should be noted that PCDD/F concentrations in several countries were derived from one sample (e.g., New Zealand, Brazil, and UK). Although dioxin inventories from the countries were estimated to be low and ranged from 0.000043 to 0.78 kg/yr, further analysis is necessary for those countries. In the production of ceramics, dioxins present in kaolin can be destroyed or volatilized at high temperatures (typically exceed 1000 °C in kilns). Assuming all of the dioxins present in the Japanese clays are discharged into the environment, the resulting total TEQs of dioxins released from ceramic industries was estimated to be 4.8 g-TEQ. This would represent 2.9% of the total release of dioxins to the environment in Japan, which was estimated to be 158−161 g-TEQ in 2009.[29] In the case of the American ball clay, release from the ceramic industries (1700 g-TEQ/yr) would represent an additional 130% of dioxins released in the USA.[30] Ball clays were mined not only in the US but also in the UK, Germany, and Ukraine.[27] This can be additional sources of dioxins and may augment the global inventory from kaolin clays.

Baker and Hites[31] summarized PCDD/Fs sources and sinks to and from the atmosphere. They indicated that the majority of the discrepancy in the estimation of global emissions and depositions was due to the OCDD congener. The global depositions were roughly two times greater than the global emissions of dioxins, suggesting the additional missing dioxin sources (especially OCDD) in the environment.[31] OCDD is the dominant congener in the kaolin clay and half of the world's kaolin production contains >480 kg of OCDD annually, suggesting that the kaolin clay is the major contributor for additional source of dioxins in the environment. We are currently investigating the fate of dioxins in ceramic industries. This would enable the accurate estimation of emission rate and discharge of dioxins to atmosphere from ceramic industries. Very trace levels of dioxins were

Table 3. Summary of PCDD/F Inventories Based on Mean and Median (in Parentheses) Concentrations from the Production of Kaolin Clays from 12 Countries

	production (1000 t)	PCDD/Fs (μg/kg)	TEQ (ng-TEQ/kg)	inventory (kg/yr)	inventory (g-TEQ/yr)
Australia	250[a]	3.1	2.8	0.78	0.70
Brazil	2527[a]	0.0010	0.0010	0.0025	0.0025
China	2000[b]	0.29	1.42	0.59	2.8
		(0.045)	(0.025)	(0.090)	(0.050)
Germany	3843[a]	7.5[c]	130[c]	29	490
		(5.0)	(33)	(19)	(127)
India	770[a]	0.11	0.39	0.085	0.30
Indonesia	15[a]	0.034	0.014	0.00051	0.00021
Japan (Gaerome)	214[d]	1.6	6.7	0.34	1.4
		(1.8)	(5.7)	(0.39)	(1.2)
Japan (Kibushi)	156[d]	5.9	21	0.92	3.3
		(5.5)	(22)	(0.86)	(3.4)
New Zealand	14[a]	0.0031	0.0092	0.000043	0.00013
South Korea	2630[a]	0.018	0.016	0.046	0.042
		(0.0057)	(0.0046)	(0.015)	(0.012)
Spain	465[a]	130[e]	350[e]	61	160
UK	1800[a]	0.0033	0.0040	0.0059	0.0072
USA (ball clay)	1070[f]	520	1600	550	1700
		(520)	(1600)	(560)	(1700)
USA (kaolin)	7110[a]	0.57[c]	0.35[c]	4.0	2.5
		(0.048)	(0.32)	(0.34)	(2.3)
Total	22864	NA[g]	NA[g]	650	2400

[a] Data from ref 10. [b] Data from ref 27. [c] Data from ref 8. TEQ was based on WHO-TEF1998. [d] Data from ref 28. [e] Data from ref 9. TEQ was based on WHO-TEF1998, OCDD concentration was used as PCDD/Fs concentration. [f] Data from ref 7. [g] NA: not available.

reported in residual ball clay after high temperature kilning process.[32]

Holt et al.[33] reported that pesticides and their impurities are important sources of dioxin contamination of Australian soils and sediments. Several studies have suggested anthropogenic sources (e.g., PCP) of dioxin contamination in sediment and soils.[23,33] In the kaolin clays, natural formation is thought to be the major source of dioxins. Our previous study reported stable carbon isotope ratios of OCDD in the American and Japanese ball clays and in several anthropogenic sources, by congener specific isotope analysis.[34] The δ^{13}C-OCDD values in ball clays were 6‰ different from δ^{13}C-OCDD values in PCP, strongly suggesting a different carbon origin for OCDD between kaolin clay and PCP.

As proposed in previous studies, high levels of dioxins with a specific congener profiles are not limited to the kaolin clays from the Mississippi Embayment. Dioxins are ubiquitous in kaolin, especially in sedimentary kaolinitic clays, and they are found in samples from 10 countries located in North and South Americas, Europe, South Pacific, and Asia. This is the first study to report dioxins in Asian kaolin clays. Further studies should focus on the analysis of dioxins in the mother rock (granite), related weathering products, and sedimentary deposits in ancient lakes and marshes to reveal the origin of dioxins and their natural formation mechanisms. Release of dioxins from ceramic industries needs further investigations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed chemical analysis, concentrations of PCDD/F and DL-PCB congeners and homologues in kaolin clays, element compositions of kaolin clays, mass chromatograms of PCDDs in kaolin clay, and profiles of PCDD congeners in raw and processed *Kibushi* clays. This material is available free of charge via the Internet at http://pubs.acs.org.

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