CHEMOSPHERE

Correlation of low-volatile organic chlorine (LVOCl) and PCDD/Fs in various municipal waste incinerators (MWIs)

Nobuhisa Watanabe [a,*], Akito Takakura [b,1], Yoshitaka Minami [a], Satoshi Mizutani [a], Hiroshi Takatsuki [a]

[a] *Kyoto University Environment Preservation Center, Kyoto 606-8501, Japan*
[b] *Osaka City Institute of Public Health and Environmental Sciences, Tohjoh-choh 8-34, Ten-nohji-ku, Osaka 543-0026, Japan*

Abstract

Medium- and low-volatile organic chlorine (M/LVOCl) and PCDD/Fs in flue gas from various municipal waste incinerators (MWIs) were monitored. The sample for M/LVOCl was collected in an adsorption tube which was thermally desorbed and the amount of chlorine was measured by atomic emission spectrometry (AES) detection using radiofrequency helium plasma. The helium plasma excited chlorine having an optical emission line of 837.6 nm was monitored. The MVOCl and LVOCl were organic chlorine groups whose boiling points (bp) ranged from 70–120 °C and 170–270 °C, respectively. The compounds having bp 120–170 °C were distributed in two tubes. LVOCl correlated well with PCDD/Fs (ng/Nm^3, $r = 0.81$) in a wide range of 0.01–100 ng/Nm^3 of PCDD/Fs, while the correlation of LVOCl vs. TEQ was less related ($r = 0.69$). These results agreed with the fact that LVOCl monitored the amount of organic chlorine without molecular structure information, which is critical to toxicity. Since the bp of LVOCl was not identical with that of PCDD/Fs, the regression was effected by the conditions of the gas treatment devices. Because most data of 2001 were collected just after the installation of PCDD/Fs in MWIs, the regression of 2001 was slightly different from that of 2002–2003. Eliminating these initial unsteady data, the regression of LVOCl vs. PCDD/Fs became better, giving $r = 0.86$. Besides having PCDD/Fs as surrogates, M/LVOCl is valuable as a versatile element-selective organic chlorine monitor to improve thermal process control.
© 2006 Elsevier Ltd. All rights reserved.

Keywords: Surrogates; LVOCl; Chlorine; Plasma; Incineration

1. Introduction

The formation of PCDD/Fs through combustion has been a matter of concern for a few decades. As research on the formation mechanism has advanced, it has been revealed that PCDD/Fs are only a limited fraction of the various organic chlorinated compounds. For this reason, the group parameter of "organic halogens" is considered

to be a good indicator or surrogate for PCDD/Fs (Kato et al., 2000; Kawamoto et al., 2002; Öberg et al., 2002).

However, the traditional method of halogen determination using combustion–coulometric titration is neither selective nor sensitive to the elements. This problem was overcome by the development of atomic emission spectrometry (AES) detection of halogens using radiofrequency helium plasma. This method was initially introduced by Rice et al. (1985) as a GC detector and improved by Pedersen-Bjergaard and Greibrokk (1993). Lepkojus et al. (1999) have first modified this plasma AES to the end-on monitoring. Watanabe et al. (2001) have accomplished in making this plasma a barrier discharge and simplified the optical detection. Gaseous organic chlorine was determined by

---
* Corresponding author. Present address: Osaka Institute of Technology, Osaka 535-8585, Japan. Tel.: +81 6 6954 4407; fax: +81 6 6957 2131.
  E-mail addresses: watanabe@env.oit.ac.jp (N. Watanabe), akito.takakura@iphes.city.osaka.jp (A. Takakura).
[1] Tel.: +81 6 6771 3389; fax: +81 6 6772 0676.

adsorptive collection and direct introduction of thermally desorbed sample to the plasma.

During 2001, the first examination of the correlation of organic chlorine and PCDD/Fs was conducted (Takakura et al., 2003), which denoted a good correlation between low-volatile organic chlorine (LVOCl) and PCDD/Fs, while medium-volatile organic chlorine (MVOCl) gave a poor correlation with PCDD/Fs. In 2002–2003, further studies were conducted. In this paper, the obtained results are first summarized, secondly the effect of PCDD/Fs-countermeasure is discussed, and finally the applicability of M/LVOCl to MWI control is explained.

2. Methods and materials

2.1. Sampling

Flue gas from MWI was sampled as shown in Fig. 1. Drawn gas was introduced to a drain trap to remove moisture and sampled in two adsorption tubes. When the gas was sampled at the inlet of a flue gas precipitator, a thimble filter was equipped at the head of the sampling probe. The front adsorption tube contained 0.3 g of 20/40 mesh Carbotrap C, while the latter contained 0.3 g of 20/40 mesh Carbotrap B. The flow rate and the sampling time were 2 l/min and 5–20 min, respectively. The sample was collected in duplicate.

The distribution of organic compounds to the drain trap, the front tube and the latter tube was reported elsewhere (Watanabe et al., 2004) which is briefly described below. The passage efficiency of organic compounds through the drain trap depended on the boiling point (bp) and the pH of the drain trap water. If the compound was insoluble in water, those with a bp up to 250 °C, e.g., tetrachlorobenzene (tetra CB) could completely pass the drain trap at 4 °C. On the other hand, aqueous soluble compounds such as chlorophenols (CPs) did not pass effi-

ciently. If the drain trap was adjusted at pH 1, the passing efficiency of 20% was achieved for mono-, tri- and tetra CPs; however, no CPs could pass the alkali-adjusted drain trap due to ionic dissolution. The experiment with penta CP was interesting. This compound did not pass the drain trap at all pHs, the mechanism of which was thought to be condensation instead of ionic dissolution. Since the bp of penta CP was 310 °C, the boundary of the drain trap passage/capture was expected between 250 and 310 °C, which was nominally considered to be 270 °C.

After the passage from the drain trap, the volatile compounds distributed to the LVOCl and MVOCl tubes according to their bp. Di-, tri- and tetra CB were collected by the LVOCl tube, whereas mono CB and 1,1,2,2-tetrachloroethane were evenly distributed to the LVOCl and MVOCl tubes. Therefore, the bp range of LVOCl was determined as 170–270 °C, although compounds with a bp range of 120–170 °C were distributed to both tubes. The bp range of MVOCl was considered to be 70–120 °C, because 1,1,1-trichloroethane was completely collected, whereas dichloromethane was not collected at all. The tubes were brought to the laboratory and thermally desorbed chlorine was quantified by helium barrier discharge – AES.

2.2. Determination

The instrument is described in Fig. 2. The discharge tube was made by a 4×6 mm alumina tube (SSA-S, Nikkato, Japan) which had two copper film (Nitto Denko, Japan) electrodes. One electrode was earthed and the other was provided with radiofrequency bipolar high voltage (90 kHz, ±3 kV, 35 W) from a rf-power supplier (Haiden, Japan). Supplying helium gas at a rate of 400 ml/min, atmospheric helium plasma was built in the discharge tube between the electrodes. The optical emission from the discharge tube was end-on-gathered and transferred to a spectrometer USB 2000 (Ocean Optics, America) by an optical fiber.
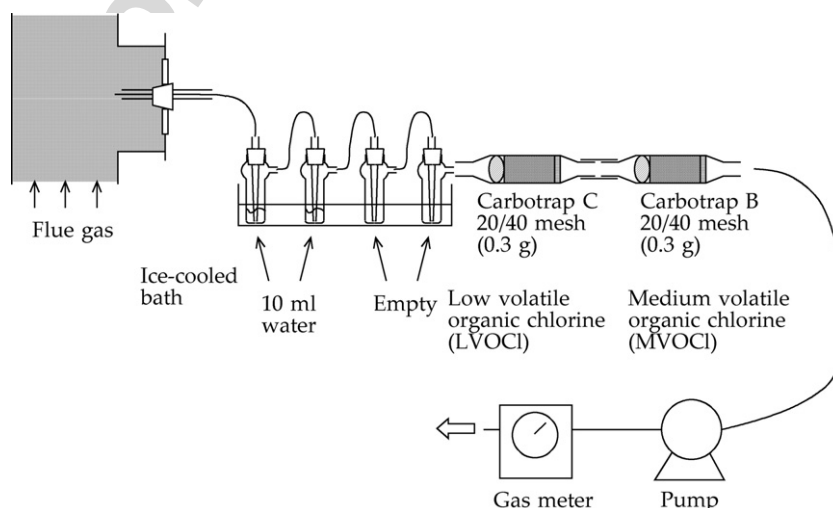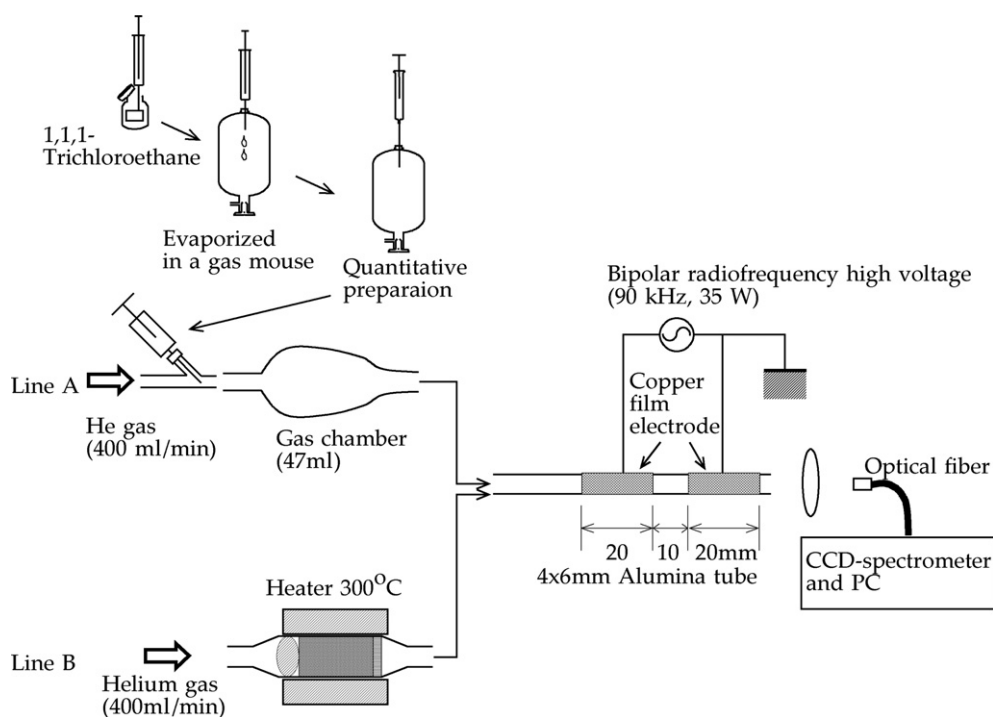

Fig. 1. Sampling apparatus.

Fig. 2. Instrument of helium barrier discharge-AES.

A chlorine emission line of 837.6 nm and a background of 837.0 nm were recorded.

Calibration of chlorine was carried out by the injection of 1,1,1-trichloroethane from line A in Fig. 2. The gas chamber between the injection port and the discharge tube had a role of peak shape smoother against quick injection. An analytical chart is presented in Fig. 3. After several standard injections and calibrations, the sample tube was connected to the discharge tube followed by the supplying helium gas and rf. The tube was gradually heated to 300 °C, taking 100 s and maintained while the Cl emission line was monitored. The amount of chlorine was quantified by peak area using the 1,1,1-trichloroethane calibration. The detection limit determined by "3 times of S/N" was 4 ngCl; hence, the detection limit of M/LVOCl was 0.1 μgCl/Nm^3 for the sampled volume of 40 l.
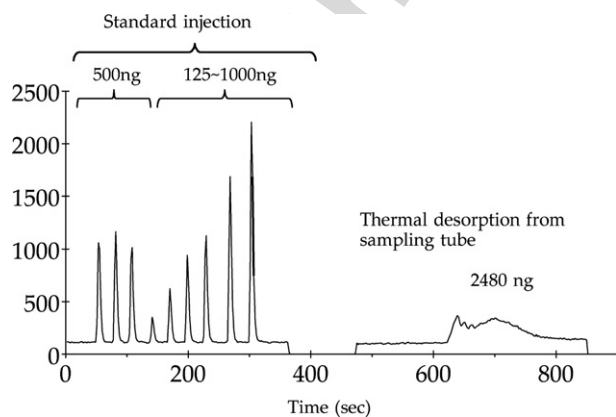

Fig. 3. Analytical chart.

2.3. Municipal waste incinerators

In conjunction with legislated periodical PCDD/Fs inspections of gas emitted from MWI stacks, LVOCl and MVOCl were measured in 2001, 2002 and 2003. Eleven stoker-furnace MWIs (Nos. 1–11) were studied, but the gas treatment lines were categorized into five types, A–E (Fig. 4).

1. Type A: the MWI was equipped with an activated carbon (AC) injected electrostatic precipitator (ESP), a catalyst and a wet scrubber. The sampling points were the inlet of ESP (after AC injection, A1), the outlet of ESP (A2) and the stack (A3). The relevant MWI was only No. 1.
2. Type B: the MWI was equipped with an activated carbon (AC) injected electrostatic precipitator (ESP) and a wet scrubber. The sampling points were the outlet of ESP (B1) and the stack (B2). The MWI No. 2 was relevant; however, this MWI was closed at the end of 2002.
3. Type C: the MWIs had an ESP, a wet scrubber and a bag filter in which AC was circulated for PCDD/Fs removal. Most samples were collected at the stack (C3). The inlet (C1) and the outlet (C2) of ESP were examined only once. The MWIs were Nos. 3–7.
4. Types D: the MWIs were equipped with a lime-injected bag filter, a catalyst and a wet scrubber. Only stack gas (D1) was studied. The MWIs were Nos. 8 and 9.
5. Types E: the MWIs were equipped with a bag filter, a wet scrubber and a catalyst. The inlet (E1) and the outlet (E2) of the bag filter, and the stack (E3) were examined. The MWIs were Nos. 10 and 11.
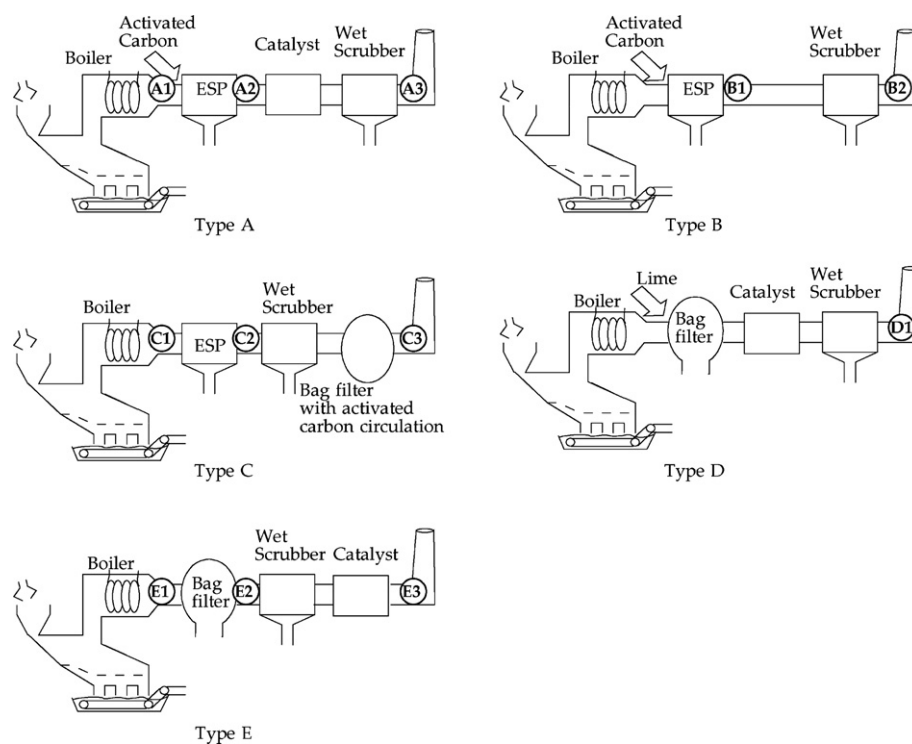
Fig. 4. Gas treatment lines and sampling points of studied municipal waste incinerators (MWIs).

The legislative PCDD/Fs inspection was conducted by government-registered institutes. The protocol of sampling and analysis was of Japan Industrial Standards (JIS) K0311, which involved a sampling train of a thimble filter cooled drain trap, XAD-2 adsorption and diethylene glycol absorption, and an analytical protocol involving internal standard spike, clean-up and HRGC-MS quantification.

3. Results and discussion

3.1. Correlation between M/LVOCl and PCDD/Fs

The collected data are tabulated in Table 1. As the sample was measured in duplicate whose variation was within several decades percentage, the average was taken as the result. Sets of data numbering 57 involving M/LVOCl, gas phase and total (gas and particulate phases) PCDD/Fs (ng/Nm^3), and gas phase and total TEQ (ngTEQ/Nm^3) were collected from 17 points of 11 MWIs. All data were plotted in eight ways in Fig. 5, namely, MVOCl and LVOCl as the X-axis, while gas phase PCDD/Fs, total PCDD/Fs, gas phase TEQ and total TEQ as the Y-axis. Data from the study in 2001 are plotted with blank circles, which are discussed later.

The highest correlation coefficient (r) was obtained in LVOCl vs. total PCDD/Fs regression giving 0.81 (Fig. 5d), followed by LVOCl vs. gas phase PCDD/Fs ($r = 0.715$, Fig. 5b). LVOCl monitored only the gas phase compound; however, the correlation was better with total PCDD/Fs than with gas phase PCDD/Fs. This arose from the fact

that the data range of total PCDD/Fs was wider than that of gas phase PCDD/Fs.

As expected from the former study, MVOCl did not correlate with PCDD/Fs or TEQ as well as LVOCl (Fig. 5a, c, e, and g). Moreover, the prediction of PCDD/Fs from LVOCl (Fig. 5d) was better than that of TEQ from LVOCl (Fig. 5h). This was reasonable, because LVOCl only quantified the amount of organic chlorine without molecular structure information. As noted above, because LVOCl monitored gas phase compounds, the correlation of LVOCl vs. total PCDD/Fs and total TEQ became worse in a lower concentration range i.e., less than 1 ng/Nm^3 and 0.001 ngTEQ/Nm^3, respectively. In these levels, the contribution of gas phase to the total was 33% and 35% in arithmetic mean for PCDD/Fs and TEQ, which were consistently lower than 60% and 61% in the range above 1 ng/Nm^3 and 0.001 ngTEQ/Nm^3.

In summary, LVOCl could be considered as the function of gas phase PCDD/Fs, which correlated with total PCDD/Fs and TEQ with some variation in their molecular structure spectrum and in the contribution rate of the gas phase.

3.2. Time course changes after PCDD/Fs-countermeasure installation

The blank circles in Fig. 5 were the data collected in 2001, most of which were located in the left-high area compared to the regression line. In other words, the correlation of LVOCl vs. PCDD/Fs or TEQ in 2001 was different from

Table 1
M/LVOCl, PCDD/Fs and TEQ measured in flue gas from MWIs

MWI type[a]	MWI ID	Sampled date (Y/M/D)	Sampled point[a]	MVOCl (µgCl/Nm^3)	LVOCl (µgCl/Nm^3)	Gas phase PCDD/Fs (ng/Nm^3)	Total PCDD/Fs (ng/Nm^3)	Gas phase TEQ (ngTEQ/Nm^3)	Total TEQ (ngTEQ/Nm^3)
Type A	1	2001/8/31	A2	7.3	6.1	5.7	38.7	0.0081	0.3581
	1	2001/8/31	A2	30.2	12.8	6.9	58.9	0.031	0.591
	1	2001/8/31	A2	71.5	13.4	10	140	0.15	1
	1	2001/8/31	A3	17.9	5.6	7.3	15.7	0.014	0.154
	1	2002/12/10	A2	92	626	3.3	263	0.032	1.6
	1	2002/12/10	A3	13	138	5.4	10.8	0.045	0.13
	1	2003/7/2	A2	36.6	1059	27.9	510.4	0.38	4.7
	1	2003/7/2	A3	31.1	98	3.168	8.168	0.027	0.13
	1	2003/12/09,10	A1	2576	3816	13	873	0.11	7.61
	1	2003/12/09,10	A2	703	588	4.1	364.1	0.056	1.756
Type B	2	2001/8/10	B2	6.6	15.1	22	30.7	0.046	0.081
	2	2002/7/25	B1	33	31	16	51	0.23	0.51
	2	2002/7/25	B2	262	418	35	63	0.51	0.72
Type C	3	2001/12/12	C3	6.4	9.8	9.6	10.45	0.22	0.2226
	3	2001/12/12	C3	26.5	3.7	3.5	5.9	0.055	0.0642
	3	2002/8/2	C3	19	nd[b]	0.12	0.18	0.000085	0.000088
	3	2002/8/2	C3	35	15	0.12	0.93	0.0000059	0.0031
	3	2003/9/2	C3	1.5	0.5	0.085	0.823	0.0000006	0.0082
	3	2003/9/2	C3	15	23	0.278	31.558	0.00023	0.25
	4	2002/9/11	C3	8.1	2.7	0.18	0.23	0.00012	0.00012
	4	2002/9/11	C3	1.8	0.95	0.075	1.3	0.0000054	0.00015
	4	2003/9/30	C3	14.2	0.2	0.0104	0.0234	0	0
	4	2003/9/30	C3	5	0.8	0.019	0.195	0	0.00042
	5	2002/7/9	C3	12	4	0.34	0.64	0.00015	0.00017
	5	2002/7/9	C3	20	7.2	0.14	0.5	0.0000051	0.000031
	5	2003/7/9	C3	2.5	0.56	0.075	0.316	0.0000017	0.0011
	5	2003/7/9	C3	2.1	1.4	0.202	0.216	0.0011	0.0011
	5	2004/01/14,15	C1	6165	4147	170	198	1.6	3.6
	5	2004/01/14,15	C2	302	231	140	149.3	0.25	0.37
	6	2001/9/7	C3	7.8	2.9	7	9.2	0.0047	0.00489
	6	2001/9/7	C3	9.6	4	7.5	9.8	0.00063	0.0008
	6	2002/7/16	C3	13	6.3	0.31	5.31	0.00028	0.0024
	6	2002/7/16	C3	45	13	0.15	0.44	0.00011	0.00017
	6	2003/7/16	C3	2.3	0.36	0.113	0.245	0.00013	0.00025
	6	2003/7/16	C3	2.4	0.4	0.088	0.2	0.0001	0.00015
	7	2002/9/5	C3	38	5.5	0.22	1.5	0.00073	0.013
	7	2002/9/5	C3	7.4	2.9	0.066	0.29	0.0000047	0.00018
	7	2003/9/5	C3	1.7	1.1	0.034	1.593	0.0000005	0.025
	7	2003/9/5	C3	1.2	0.8	0.021	2.219	0	0.036
Type D	8	2001/7/27	D1	6.8	24.5	18	90	0.12	0.173
	8	2001/7/27	D1	5.2	10.3	10	11.8	0.16	0.16025
	8	2002/7/18	D1	7.7	26	4.4	4.5	0.068	0.068
	8	2002/7/18	D1	15	20	2.7	2.8	0.045	0.045
	8	2003/7/18	D1	1.7	1.8	3.01	3.229	0.057	0.057
	8	2003/7/18	D1	1.2	4.6	3.799	4.026	0.068	0.068
	9	2002/10/8	D1	5.5	3.5	2.9	3	0.05	0.05
	9	2002/10/8	D1	4.7	2.7	2.7	2.8	0.036	0.036
	9	2003/10/8	D1	1.6	2.3	4.036	4.103	0.06	0.06
	9	2003/10/8	D1	2.1	15	6.796	6.906	0.098	0.098
Type E	10	2002/9/13	E3	2.2	3.3	0.49	0.53	0.0022	0.0022
	10	2002/9/13	E3	24	13	0.25	0.51	0.00084	0.00086
	10	2003/7/31	E3	3	6.4	0.379	0.381	0.0067	0.0067
	10	2003/7/31	E3	1	11.9	0.121	0.1244	0.001	0.001
	10	2003/12/16,17	E1	1276	774	23	673	0.24	6.34
	10	2003/12/16,17	E2	42	11.3	7.5	11.1	0.044	0.069
	11	2003/7/25	E3	0.87	0.98	0.061	0.0673	0.0000017	0.0000017
	11	2003/7/25	E3	0.72	1	0.156	0.1618	0.000063	0.000063

[a] Described in Fig. 4.
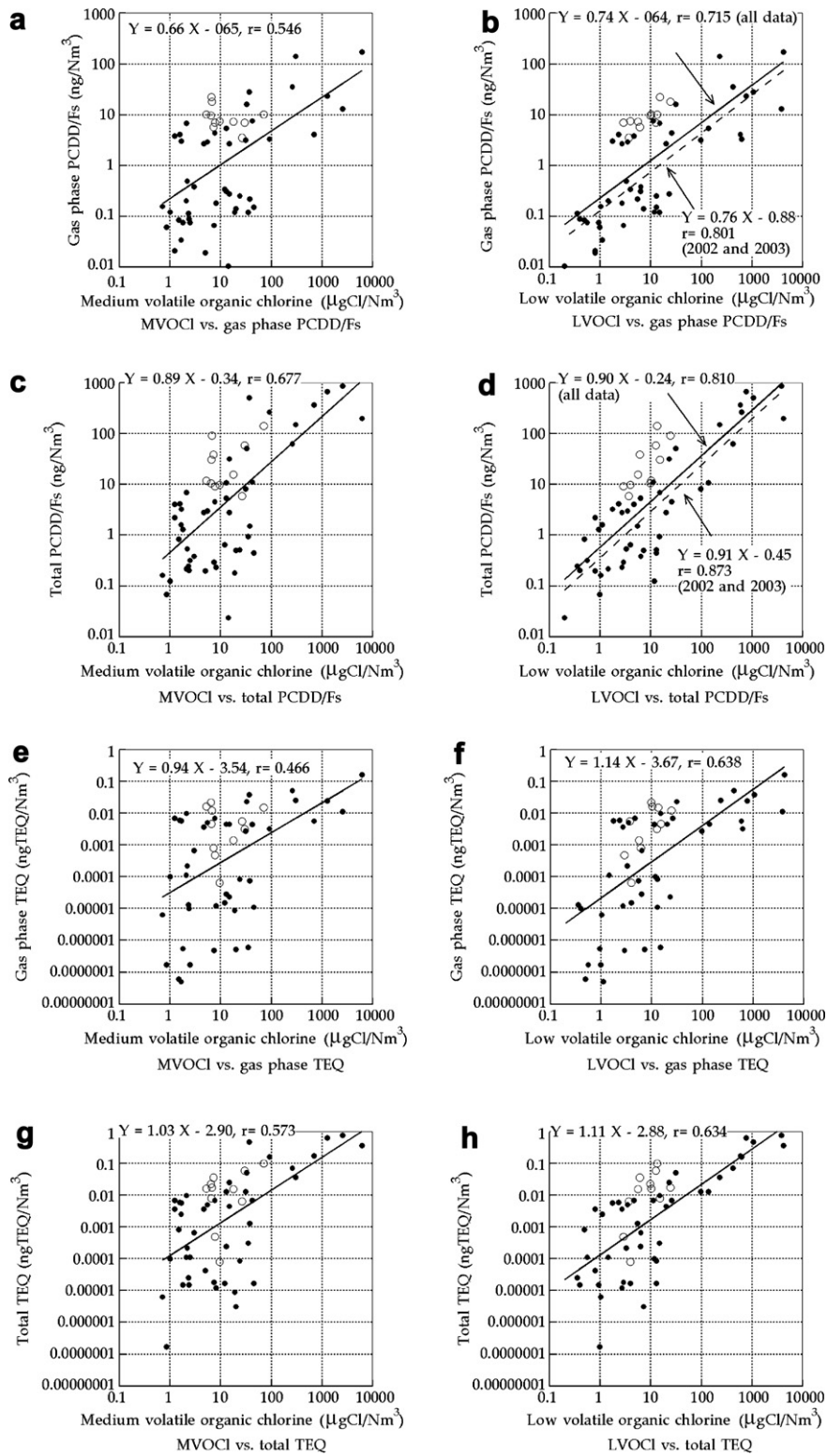[b] Quantification limit: 0.1 µgCl/Nm^3 for gas sampling volume of 40 l.

Fig. 5. Plots and regression lines of M/LVOCl vs. PCDD/Fs or TEQ.

that in 2002–2003. It must be noted that PCDD/Fs-countermeasure in MWIs was conducted to types A, B, and C during 2001; in addition, the sampling was just after these installations. Two eminent correlation changes are observed in Fig. 1:

1. In types A and B MWIs, LVOCl increased greatly in 2002–2003 compared with 2001, even though the PCDD/Fs level hardly changed.
2. In type C MWIs, the PCDD/Fs of 2001 were consistently higher than the regression estimate from the

relevant LVOCl values. The feasible reasons for the above are discussed below.

In types A and B MWIs, the injection of AC before the ESP was started in 2001. The temperature and the injected AC were controlled at 200–220 °C and 100 mg/Nm^3, respectively, throughout 2001–2003. However, since the purchase contract of AC was determined by bidding, the quality of AC in 2002–2003 was presumably normal, while that of 2001 was thought to be of a ''recommended'' grade. In other words, the high performance AC used in 2001 could capture more LVOCl than in 2002–2003, while the adsorbing performance against semi- and non-volatile organic chlorine (SNVOCl) including PCDD/Fs was thought to be the same between AC of 2001 and 2002–2003.

In type C MWIs, since PCDD/Fs removal was expected not only on flying AC particles but also in the AC filtration layer built on the bag filter surface, the PCDD/Fs removal efficiency was expected to be higher than that for AC injected ESP. Moreover, the operation temperature of 150–170 °C, relatively lower than types A and B, was favorable for PCDD/Fs capture. The AC-circulated bag filter was installed in 2001 and the measurement of M/LVOCl and PCDD/Fs levels was conducted just after the installation. The measurement in 2002 was conducted one year later. The PCDD/Fs removal efficiency in 2002 seemed higher than in 2001, although the M/LVOCl level did not change. The difference could occur from the bag filter's performance elevation because of the formation of a layer of AC through usage.

Removing these initial unsteady date, more promising regression lines were achieved, which are given as dashed lines in Fig. 5b ($r = 0.801$) and in Fig. 5d ($r = 0.87$).

3.3. Monitoring of organic halogenated compounds by S/LVOX

LVOCl measurement only monitors the amount of gaseous organic chlorine without toxicity information; therefore, it is agreeable that the correlation of LVOCl vs. PCDD/Fs (ng/Nm^3), as presented in Fig. 5, is better than that with total TEQ (ngTEQ/Nm^3).

The other drawback of LVOCl as an indicator to PCDD/Fs is the fact that LVOCl measures organic chlorine whose bp is the range 170 to 270 °C, while the boiling point of most PCDD/Fs is higher than 300 °C, namely, the bp of ''measured'' and ''predicted'' are not identical. In this context, semi- and non-volatile organic halogens (SNVOX) discussed by Kato et al. (2000) is more appropriate as PCDD/Fs surrogates. However, the present study employing adsorption–thermal desorption-He plasma AES has an advantage of quick determination and feasibility to on-line monitoring.

Furthermore, the versatility of M/LVOCl as an element-selective organic halogen monitor is noteworthy. PCDD/Fs were the first organic halogenated compounds which gained public attention in MWIs flue gas. However, tremendous varieties of organic halogenated compounds are emitted from thermal processes through both de novo synthesis and incomplete decomposition of organic halogenated compounds. The method using helium barrier discharge-AES is now being developed for further investigation of organic fluorinated, chlorinated, brominated and iodinated compounds.

References

Kato, M., Urano, K., Tasaki, T., 2000. Development of semi- and non-volatile organic halogen as a new hazardous index of flue gas. Environ. Sci. Technol. 34, 4071–4075.

Kawamoto, K., Imaizumi, T., Fujiyoshi, H., Tanaka, M., 2002. Application of concentration of organohalogen compounds in flue gas for the measurement of dioxins. Organohalogen Compd. 59, 53–56.

Lepkojus, F., Watanabe, N., Buscher, W., Cammann, K., Boehm, G., 1999. A simple radiofrequency helium discharge plasma (RFP) for spectroscopic purposes. J. Anal. Atom. Spectrom. 14, 1511–1513.

Öberg, T., Neuer-Etscheidt, K., Nordsieck, H., Zimmermann, R., 2002. Dioxin surrogates – a comparison of approaches. Organohalogen Compounds 59, 37–44, Revised version with the corrected reference list is available in www.tomasoberg.com/pdf/surrogates.pdf.

Pedersen-Bjergaard, S., Greibrokk, T., 1993. On-column bromine- and chlorine-selective detector for capillary gas chromatography using a radio frequency plasma. Anal. Chem. 65, 1998–2002.

Rice, G.W., D'Silva, A.P., Fassel, V.A., 1985. A new discharge afterglow and its application as a gas chromatographic detector. Spectrochim. Acta 40B, 1573–1584.

Takakura, A., Watanabe, N., Fukuyama, J., 2003. Monitoring study of semi and low volatile organic halogen as the indicator of PCDD/Fs in the stack gas at a municipal waste incineration plant. Organohalogen Compd. 60, 501–504.

Watanabe, N., Buscher, W., Boehm, G., 2001. Determination of fluorine, chlorine, bromine and iodine by barrier discharge radiofrequency helium plasma. Anal. Sci. 17, i971–i972, Suppl.

Watanabe, N., Minami, Y., Mizutani, S., Takatsuki, H., Takakura, A., 2004. Collection efficiency and determination equivalency on the measurement of semi and low volatile organic chlorine (SLVOCl) in flue gas. J. Environ. Chem. 14, 597–604 (in Japanese, with English Abstr.).