

DIOXIN SURROGATE STUDY UNDER STARTUP CONDITIONS OF MUNICIPAL WASTE INCINERATOR

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Abstract

Surrogates for dioxins (DXNs) from municipal waste incinerators (MWIs) were examined under startup conditions. Organic halogenated compounds (OHC), chlorobenzenes (CBs), and chlorophenols (CPs) were measured along with DXNs in flue gas at the inlet and outlet of the bag filter of two MWIs in 5 runs. The time course of OHC during startup corresponded to DXNs, and OHC correlated to DXNs in the range of 2–3 orders of magnitude in all bag filter outlet samples, while bag filter inlet data was separated due to considerable particulate DXNs. CBs and CPs also showed a correlation to DXNs in the runs. The level of DXNs at startup was higher than in the steady-state condition because of significant memory effects. An evident difference in memory effect between congeners was observed by the rate of concentration change: Cl₇ and Cl₈ congeners increased followed by a gradual decrease, whereas Cl₄, Cl₅ and Cl₆ congeners showed a consistent decrease. Considering the DXN formation mechanism involving macro carbon from incomplete combustion, chlorinating activity and post-combustion reaction, desirable surrogates are organic chlorinated compounds such as OHC, CBs and CPs, though the correlation is influenced by memory effects.

Introduction

An efficient and simple surrogate is needed for monitoring DXNs in waste combustion¹. The surrogate measurement should be low-cost and quick. Potential candidates are chlorobenzenes (CBs)^{2,3}, chlorophenols (CPs)⁴ and “total” organic halogen (TOX)⁵⁻⁸ which has been classified according to volatility. To examine applicability, continuous surrogate monitoring was performed using an organic halogen compound (OHC) analyzer by J-Power Systems, while CBs and CPs were examined by simultaneous sampling along with DXNs. The response, correlation and “memory effect” have been determined.

Materials and Methods

Sites and Conditions

Two stoker-type MWIs were selected. The gas treatment train and sampling location are presented in Fig. 1. Five runs were carried out: 3 runs in MWI “A” and 2 runs in “B”. To check the effect of particulate, samples were taken from the bag filter inlet in the 2nd run of “A”. In other runs, gas samples were taken at the bag filter outlet.

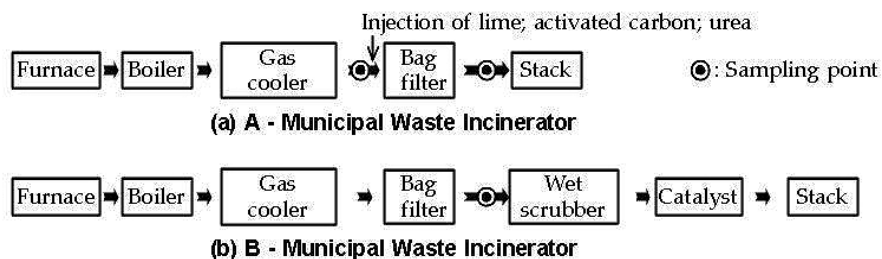


Fig. 1 DXNs, OHC, CBs and CPs were all sampled during startup at the bag filter inlet of MWI “A” (Oct 23–24, 2006: A2 series); at the bag filter outlet of “A” (Oct 9–10, 2006: A1; Oct 30–31, 2006: A3) and at the bag filter outlet of “B” (Dec 5–6, 2006: B1; Dec 26–27, 2006: B2).

At the startup of MWI, natural gas fuel was provided to heat the furnace, followed by municipal solid waste (MSW) input. It took about half a day for the temperature at the furnace top to reach 900°C. Gas sampling for DXNs, CBs and CPs was started a few hours after the temperature reached a steady state. Sampling was repeated 5 times, of which 4 times were at 2-hour intervals and the final 4-hour sampling was about 20 hours later. The OHC analyzer was continuously operated before and after the startup procedure.

Surrogates Monitored with DXNs

The instrumentation of the OHC analyzer⁹ (OHC-201, J-Power Systems, Japan) was as follows. Only gaseous samples were collected through a filter (used for bag filter inlet study). After eliminating moisture and HCl using a cooler and a silver column, OHC was adsorbed to Carbotrap B maintained at 100°C. Thermally desorbed OHC was introduced for Cl determination by combustion-coulometric analysis. The sampled gas volume was approx. 100–200 L by 1–2 hours sampling in most measurements. Detection range of Cl was 0.1 to several tens of µg.

CBs and CPs were sampled using a dioxin sampling train. In the analytical procedure, a portion of the extract was utilized to determine CBs and CPs.

Results and Discussion

Time Course of OHC and DXNs

The concentration change of OHC and DXNs during MWI startup is given in Fig. 2. In MWI “A”, OHC peaked just after ignition, and then gradually decreased. In MWI “B”, OHC consistently decreased throughout preheating and ignition. DXNs showed a decrease with time, which corresponded well with OHC. Note that the MWI “B” sample was collected before the wet scrubber and catalyst stages, after which DXNs and other pollutants were considerably reduced.

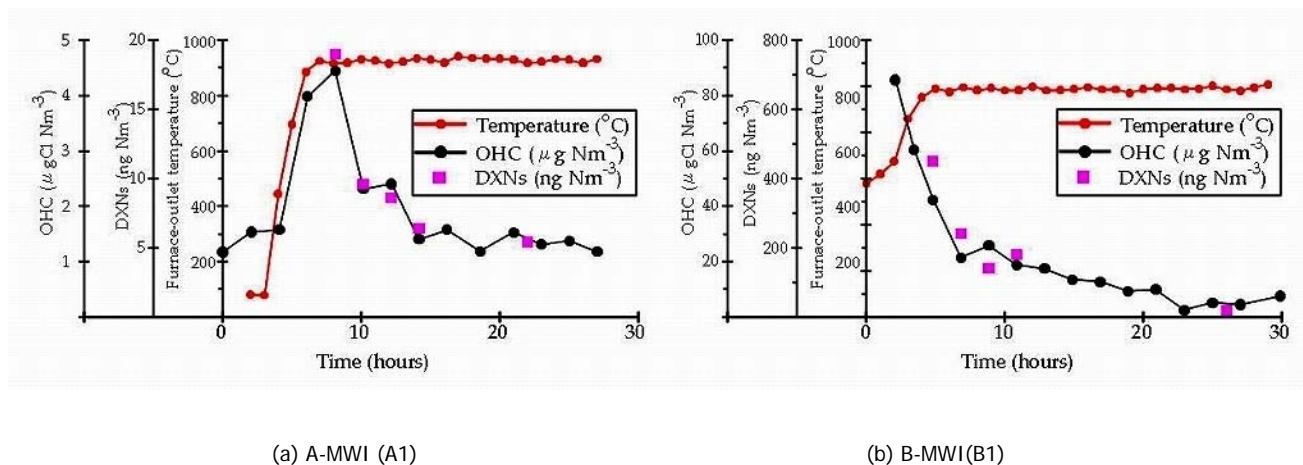


Fig. 2 Time course of DXNs and OHC was in good agreement under startup conditions (A1 and B1 series). DXN sampling was repeated 5 times, starting after the temperature at the furnace top reached 900°C.

Correlation of Surrogates versus DXNs

Collected data sets of OHC and DXNs from MWIs “A” and “B” are plotted in Fig 3. Good correlation was observed for both MWIs and for the range of 0.01–10 ng-TEQ Nm⁻³. The solid triangles located at distinctively high DXN areas reflect data from the bag filter inlet. This data includes considerable particulate DXNs, while the other data is mainly gaseous DXN, proving that OHC can predict DXN in gas phase instead of particulate phase.

CBs and CPs also showed good correlation with DXNs; however, the regression might be dependent on the MWI, sampling point and run. The response of CBs and CPs to DXNs is considered to give some information on the DXN formation mechanism.

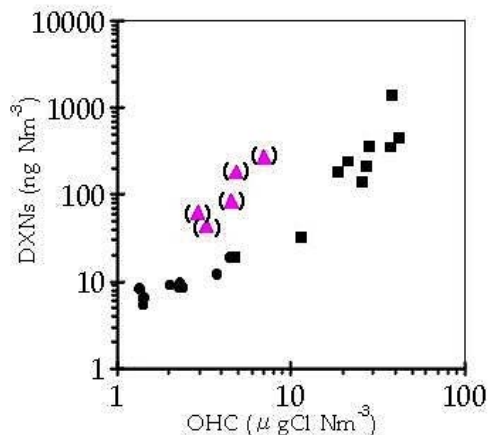


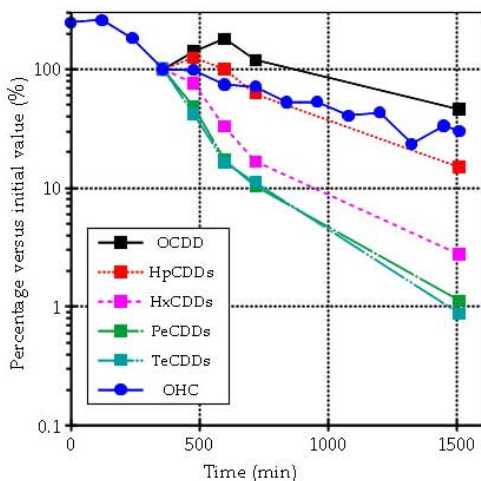
Fig. 3 Data sets of OHC-DXNs showed good correlation. The regression of OHC-DXNs ranged from 2 to 3 orders of magnitude and showed no dependence on facilities. The solid triangles in parentheses reflect data from the bag filter inlet(A2), and which includes considerable particulate DXNs.

Memory Effect

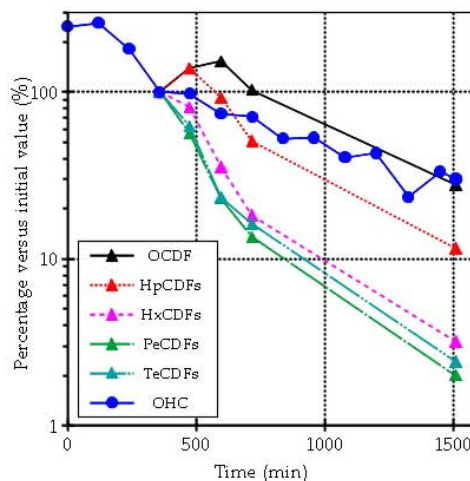
The correlation of OHC and DXNs in Fig. 3 was satisfactory; however, it was found that the level of DXNs under startup conditions was higher than that at steady state when compared with the same OHC level. The reason is presumably due to the significant memory effect of semi-volatile DXNs.¹⁰ High- or medium-volatile compounds, e.g. low-chlorinated CBs, would be volatilized just after formation, while semi-volatile compounds such as DXNs could remain in the solid phase or be adsorptively captured on any cooled surface of the gas duct, from which they would be released according to temperature increase.

The time course of OHC and each PCDD/F congener in the B2 series revealed a significant difference of memory effect (Fig. 4 (a) for PCDDs; (b) for PCDFs). Each congener concentration was normalized by dividing the initial value and is expressed in percentage:

$$(\text{Normalized concentration}) = (\text{Measured concentration}) / (\text{Initial concentration}) \times 100 \quad (\%)$$



(a) PCDD congeners and OHC



(b) PCDF congeners and OHC

Fig. 4 A difference in memory effect between low- and semi-volatile compounds was observed in startup monitoring (B2). Time course of PCDD and PCDF congeners with OHC is depicted in (a) and (b), respectively. The concentration of each congener and OHC was normalized by the initial value. Low-volatile compounds such as OHC and Cl₄-Cl₆ congeners presented a consistent decrease (little memory effect), while Cl₇ - Cl₈ congeners showed a significant increase even after the furnace temperature reached 900°C. The concentration increase was presumably due to gradual desorption of these semi-volatile compounds from the gas ducts, with which were slowly heated by flue gas.

The “initial concentration” in the above equation was the value obtained at $T = 357$ min (sampling period: 297–417 min) for every congener and OHC. After ignition, OHC decreased with a slight peak at $T = 120$ min (furnace temperature = 860–950°C), whereas Cl_7 and Cl_8 PCDD/Fs peaked at $T = 476$ min (952–976°C) and 597 min (976–983°C) min, respectively. Namely, such high-chlorinated PCDD/Fs were gradually released into the flue gas even after the furnace temperature reached 900°C. The medium-chlorinated congeners such as Cl_4 – Cl_6 PCDD/Fs showed a consistent decrease. It was found that the OHC decrease rate was slower than that of Cl_4 – Cl_6 PCDD/Fs. The OHC value was nearly constant, namely, OHC was continuously provided from the combustion.

Comparison of surrogates considering DXN formation mechanism

An overview of the role of surrogates in DXN formation¹¹ is illustrated in Fig. 5. Carbon oxide (CO) is viewed as the indicator for incomplete combustion, while hydrogen chloride or chlorine (HCl/Cl_2) as that of chlorinating activity. However, they are considered to be “single pass monitoring”, because organic chlorinated compounds are the yield from macro carbon and chlorinating agents. Moreover, the secondary formation, known as *de novo* synthesis, in post-combustion zones must be taken into account. Surrogates from organic chlorinated compounds, e.g. OHC, CBs, CPs, etc. can be “tracers” of DXNs.

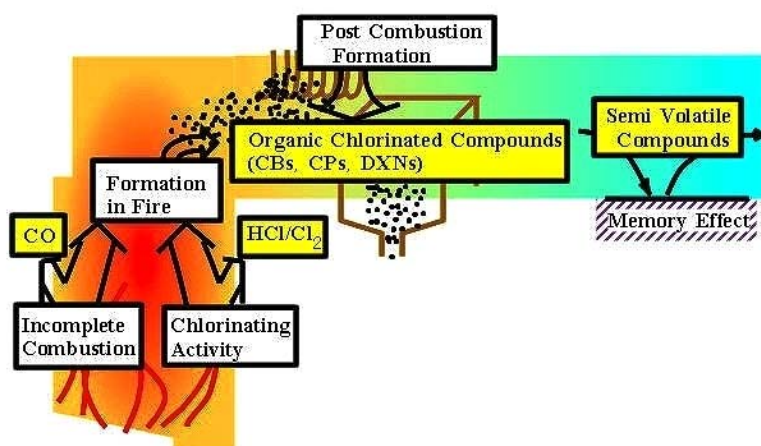


Fig. 5 Surrogates are evaluated based on the DXN formation mechanism. Both macro carbon from incomplete combustion and chlorinating agents are needed for organic chlorinated compound formation. The former factor is indicated by CO, the latter by HCl/Cl_2 ; therefore, they are considered “single pass monitoring”. On the other hand, surrogates from organic chlorinated compounds, such as CBs, CPs and OHC, are considered as by-products of DXN formation and hence, can be used as “tracers”. It should be noted that the memory effect of semi-volatile compounds such as DXNs can influence the correlation between surrogates and DXN.

Correlation studies on surrogates and DXNs have clarified that low-volatile surrogates are more suitable than medium-volatile compounds⁸. However, an appropriately volatile surrogate is able to warn of DXN formation without the effect of memory, although its correlation with DXNs is not expected to be high¹⁰. OHC in this study is positioned between medium and low volatility, namely, warning ability could be expected, although it suffered slightly from the memory effect.

Acknowledgment

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