Emission characteristics of PCDDs/Fs and a major congener from various emission sources in industrial complex

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Abstract

The emission characteristics of PCDDs/Fs and a major congener from emission sources in industrial complex located west from capital were investigated. The facilities for sampling were classified based on the Stockholm Convention for POPs. PCDDs/Fs were sampled 3 times in each stack from selected facilities and all congeners of PCDDs/Fs were analyzed. The emission ratio of total concentration from waste incinerators was the highest followed by nonferrous metals industries and that from chemical industries was the lowest, and the emission ratio of TEQ concentration from waste incinerators (large & small scale waste & industrial waste incinerators) was the highest followed by waste-pulp and -paper incinerators and that from chemical industries was the lowest. The distribution of each homology in the various industries was very different. Usually, Te-HpCDD/F were main emitted homologies for the municipal solid waste incinerators and waste-pulp and -paper incinerators and Mo-TrCDD/F for other facilities. The distribution of isomers in each homology in the various industries showed a little similar, although the distribution of each homology in the various industries was very different. The major emission source of PCDDs/Fs was waste incinerator and the major congener having influence on ambient air in industrial complex emitted from various emission sources was 2,3,4,7,8- PeCDF.

Introduction

After the Stockholm Convention for POPs in 2001, the control of POPs started worldwide and the countries ratifying the Stockholm Convention should submit NIP (National Implementation Plan). Korea has enacted the Administration Law for POPs in January and ratified the Stockholm Convention in February this year. For the Administration Law for POPs and ratification of Stockholm Convention many investigations are carried out. In Korea, the problem of PCDDs/Fs from municipal solid waste incinerators appeared in 1996, after then, since 1997 the concentration of PCDDs/Fs from municipal solid waste incinerators are regulated and the regulation was enforced in 2006. We are preparing the regulation act for the various industries (steel industry, nonferrous metal industry, chemical and oil industry, energy industry) except incinerators. The draft report for enactment was presented in 2006 and from 2008 the concentration of PCDDs/Fs from various industries will be regulated. For enactment of the regulation for various industries and the standard of environment for ambient air, water and soil, the many investigations were carried out already and many results were submitted. In this study, the emission characteristics and the major emission sources of PCDDs/Fs were investigated in a large industrial complex, which shows the high concentration of PCDDs/Fs since 2001, and a major congener having influence on ambient air in industrial complex emitted from each emission sources were examined to find a main emission source of PCDDs/Fs and a major toxic congeners affected in ambient air. However, in this study, the total amount of off gas from each emission source was not considered, but is based on the concentration.

Materials and Methods

The industries under investigation were classified as waste incinerator, chemical and oil industry, steel industry, nonferrous metal industry, and selected 17 waste incineration facilities (9 industrial waste incineration facilities, 3 large scale municipal solid waste incineration facilities, 5 small scale waste incineration facilities), 6 waste-pulp and –paper incinerators, 10 chemical and oil industry facilities, 7 steel industry facilities and 5 nonferrous metal industry facilities. The stack sampler and gas probe were used as sampling devices and the samples were collected by Q/F, XAD-2 resin and absorbed in impingers. For the particles phase of sample, isokinetic method was used and the sampling amount was above $3Sm^3$ during 4hrs. All congeners of PCDDs/Fs (210 congeners) were analyzed according to Korean Standard Testing Method (KSTM) for Dioxins and Furans to analyze TeCDDs/Fs-OCDD/F and in addition reference are taken from previous papers to analyze MoCDDs/Fs-TrCDDs/Fs. To analyze MoCDDs/Fs-TrCDDs/Fs, we used labeled standards of $^{13}C_{12}$- MoCDD, DiCDD and TrCDD to clean up and prepared calibration standard with native standards of MoCDD, DiCDD and TrCDD and labeled standards of $^{13}C_{12}$- MoCDD, DiCDD and TrCDD. The concentrated elute of each phase of the PCDDs/Fs samples was also separately analyzed by high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS). The HRGC/HRMS setup consisted of a Hewlett Packard 6890 GC coupled with Jeol 700D. Selected ion monitoring with electron impact of 38 eV was performed above a resolution of 10,000 with an SP-2331 column of 60m × 0.32mm ID × 0.20um. Samples were introduced in splitless mode with a flow rate of 1 $ml \cdot min^{-1}$ helium, and the temperatures of injector and ion source were 265°C. The oven temperature to analyze MoCDDs/Fs- TrCDDs/Fs was 120°C(1min) → 30°C min^{-1} → 200°C → 20°C min^{-1} → 260°C(1min), and to analyze TeCDDs/Fs-OCDDs/Fs was 100°C(1min) → 20C min^{-1} → 200°C → 20°C min^{-1} → 265°C(19.5min). Toxic equivalents were calculated by using the international toxicity equivalency factor (I-TEF), and the results were calculated only by concentration, not considered the total amount of off gas from each emission.

Results and Discussions

The emission ratio of total concentration of PCDDs/Fs (as 210 congeners) according to industries were 37.4% for large & small scale waste and industrial waste incineration, 35.0% for nonferrous metal industry, 16.1% for waste-pulp and -paper incineration, 10.9% for steel industry, 0.6% for chemical and oil industry. The trend in this study was not similar with the trend known usually, that the emission ratio of total concentration of PCDDs/Fs from steel industry is higher than that of nonferrous industry, because the sintering process known as major emission source of PCDDs/Fs from steel industry do not existed in this area. For waste incineration facilities, the emission ratio of total concentration of PCDDs/Fs from small scale waste incineration facilities was 58.9% and 39.5% for industrial waste incineration facilities, 1.6% for large scale municipal solid waste incineration facilities. The emission difference between large and small incineration facilities was not only because of scale but also the application of regulation. PCDDs/Fs from the large scale waste incineration facilities are regulated since 1997, and after then the incineration condition and air pollution control devices were developed to control PCDDs/Fs. So, at present PCDDs/Fs from large scale waste incineration facilities are emitted very low. However, the small scale waste incineration facilities are not good controlled yet. The emission ratio of TEQ concentration of PCDDs/Fs (as 17 congeners) according to industries were not similar with the emission ratio of total concentration; 53.7% for incineration and 37.4% for pulp and paper manufacturing industries, 6.4% for the nonferrous metal industries, 2.0% for the steel industries, 0.5% for the chemical and oil industries. Comparing the emission ratio of total concentration and that of TEQ concentration of PCDDs/Fs, the emission ratio of TEQ concentration was 1.5 times higher than that of total concentration for the municipal solid waste incineration and 2.3 times higher for the waste-pulp and -paper incineration. But for nonferrous metal and steel industries, the emission ratio of TEQ concentration was 5.5 times lower than that of total concentration and 1.2 times lower for chemical and oil industries. The result shows that the emission characteristics of PCDDs/Fs from each emission source were different. The emission ratio of PCDFs was very higher than that of PCDDs from all facilities. Especially, the emission ration of PCDFs from the waste-pulp and -paper incineration and the steel industries were above 90%. The emission ratio of 2,3,7,8-substituted PCDFs was also higher than that of 2,3,7,8-substituted PCDDs from all facilities. Especially, the emission ratio of 2,3,7,8-substituted PCDFs from the small scale waste incineration facilities and the steel industries increased about 3-7 times. This result also shows that the emission characteristics of PCDDs/Fs from each emission source were different. For the correct examination of emission characteristics of PCDDs/Fs from each emission source, the emission ratio of each homology according to the emission sources was investigated. For the homologies of PCDDs, the emission ratio of MoCDD-TeCDD was higher than that of PeCDD-OCDD from industrial waste incineration facilities and that of MoCDD-TrCDD was lower than that of TeCDD-HpCDD from municipal solid waste incinerators. For the small scale waste incineration facilities, MoCDD and HxCDD-OCDD were low and DiCDD-PeCDD were high, and also TeCDD-HxCDD were higher for the waste-pulp and -paper incineration.

MoCDD was above 70% for chemical and oil industries and for nonferrous metal industries, MoCDD was about 60% and DiCDD was about 30%. For steel industries, the emission ratio of MoCDD-TeCDD was high. For the homologies of PCDFs, the emission ratio of TeCDF-HxCDF were higher than of MoCDF-TreCDF for municipal solid waste and small scale waste incineration facilities and that of TeCDF-HxCDF was high for the waste-pulp and -paper incineration. For the chemical and oil, steel and nonferrous metal industries, the emission ratio of MoCDF was above 50-60%. The distribution of isomers in each homology in the various industries showed a little similar, although the distribution of each homology in the various industries was very different. Especially, with increased number of substituted chlor the distribution of isomers in homologies became similar and the distribution of isomers in homologies of PCDF became more similar than that of PCDD. Only by concentration, the distribution of 2,3,7,8-substituted congeners in the various industries showed not own obviously characteristics according to the type of industry, and 2,3,4,7,8-PeCDF was a major congener emitted from incineration and industrial facilities. Therefore, we found that the major emission source of PCDDs/PCDFs was waste incineration facilities and the major congener having influence on ambient air in industrial complex emitted from various emission sources was 2,3,4,7,8- PeCDF.

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