A Chemometric Approach for the Verification of the Formation Mechanism of Dioxin/Furan in Municipal Waste Incinerators

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Abstract

This paper presented a series of regression analysis for the verification of the formation mechanism of PCDDs/PCDFs in municipal incinerators. Such analysis is significant in several areas regarding to the evaluation of new combustion criteria, public regulations, and risk assessments in the incineration projects.

1. Introduction

The emissions of a full range of polychlorinated dibenzo-p-dioxins and furans (PCDDs/PCDFs) have become the most controversial issue in siting and building new municipal incinerators. Until last decade, several emission tests of municipal solid waste incineration were conducted. Besides, formation mechanism of PCDDs/PCDFs, new combustion criteria, public regulations, and risk assessments regarding to waste combustion have been widely discussed and excessively documented in the literature. However, only a few analyses of statistical prediction and control have been established, but none of them addressed statistical relationship directly associated with the proposed formation mechanism of PCDDs/PCDFs and related compounds. This paper presented a series of regression analysis, using the approach of single equation model or simultaneous equations system to statistically verify the proposed PCDDs/PCDFs formation mechanism for several types of incinerators.

The database used in this regression analysis was integrated from the famous National Incinerator Testing and Evaluation Program (NITEP), conducted by the Environment Canada during the period of 1984 and 1990. SAS® computer package was employed as a computer solver. Based on these regression results, further evaluation of emission prediction, combustion criteria, public regulations, and environmental and health risk assessment can then be expected.

2. Formation Mechanism

It is noted that the factors influencing dioxin formation in combustion include the presence of precursor, the low combustion temperature, wet refuse, large or discontinuous influxes of refuse, insufficient or too much oxygen, insufficient mixing, and insufficient residence time. It also appears that as particulate emissions increase there is a general increase in the total emissions of PCDDs/PCDFs. But the true influential factors regarding to the formation mechanism(s) of PCDDs/PCDFs in the incineration process are still unknown. At least four dioxin formation theories exist in literature : (a) emitted PCDDs/PCDFs enter the system as PCDDs/PCDFs; (b) emitted PCDDs/PCDFs formed from chlorinated precursors such as PVC, PCB's, and chlorophenols; (c) emitted PCDDs/PCDFs are formed from appropriate organic species which become chlorinated, such as lignin; or (d) PCDDs/PCDFs are formed as a result of incomplete combustion; the formation of PCDDs/PCDFs from condensation of organics and chlorine atoms on the surface of the particulates is catalyzed by heavy metals, possibly copper, in low temperature zone before the inlet of particulate removal process[1),2)]. Several kinetic studies of PCDDs/PCDFs formation were established and shown in literature[3)]. In general, the fourth mechanism regarding to the low temperature formation of PCDDs/PCDFs is relatively acceptable than the others and also raises much interesting in the current scientific community. Hence, the US Good Combustion Practice (GCP) criteria[4),5),6)] and Japan's incineration standards[5)] have suggested the minimum flue gas temperature at the inlet of fabric filter (FF) or electrostatic precipitator (ESP).

3. Statistical Verification

Many test programs were conducted in the Europe and North America[21),22)] in which several statistical regression analyses have been developed to detect the relationships between PCDDs/PCDFs emission prediction/control and its related design/operating parameters in the system[7),8),9),10),11),12),13),14),15),16),17),18),19),20)]. But the direct connections between the proposed formation mechanism of PCDDs/PCDFs and a specific statistical structure have not been explored yet. This multivariate statistical analysis covers several functional forms including single equation model, recursive equations system, and seemingly unrelated regression (SUR) system in order to verify the fourth formation mechanism of PCDDs/PCDFs in the literature. BASE and ETS subroutines in the SAS® computer package were combined as a computer solver. The data set obtained in the NITEP associated with different types of incinerators, including mass burn waterwall, modular, and refused-derived-fuel incinerators, were integrated as the regression database in this statistical analysis[19),20),23),24)]. All the data sets have to be normalized to the same basis of 8% O_2 standard condition at dry basis before the regression analysis was performed.

Since different types of incinerators and air pollution control systems may have totally different feature in forming PCDDs/PCDFs, independent regression analysis was needed for different types of incinerators. Each type of incinerator may present different statistical formulation due to the limitation of data availability and the performance in the regression results. Focus has been placed upon the chemometric association of PCDDs/PCDFs concentrations (i.e., dependent variable), measured at the inlet of electrostatic precipitator or spray dryer plus fabric filter process, with the suspected chemical species, such as possible precursor, heavy metal, particulate, and flue gas or combustion temperature, as delineated in the literature. The functional forms of single equation model, recursive equations system, and seemingly unrelated regression (SUR) system were then generated by using selected independent variables. These independent variables were added stepwise in an attempt to improve the model fitting according to the response of the coefficient of determination (R^2 values), F values, t-ratios, and sign convention of each estimator. The final choice of the best-fit model were based on the professional judgement of the authors.

After a series of separate statistical runs, the best regression results of waterwall, modular, and RDF incinerators were directly listed as follows:

a) mass burn waterwall incinerator at Quebec city (single equation model):

PCDDs/PCDFs= 29344 - 0.85CU -75.43TEMP1+2018.97TSP-34.75HCl
(30.895) (-42.591) (-26.277) (33.873) (-26.459) R^2=0.9996

PCB= 1341.01 - 14.86TEMP1+7.19HCl
(0.365) (-1.054) (1.634) R^2=0.4835

PAH= 520534 -1494.96TEMP1+14915TSP-418.28HCl
(1.684) (-1.544) (0.957) (-1.146) R^2=0.7112

b) mass burn modular incinerator at Prince Edward Island (P.E.I.) (recursive equations system):

PCDDs/PCDFs= 211.28 + 0.083PAH +0.046PCB
(1.341) (0.726) (0.430) R^2=0.3916

PCB= -11384 +0.259PAH+13.599CU
(-0.507) (0.497) (0.531) R^2=0.2328

PAH= 58354-45.627TEMP3
(3.523) (-2.792) R^2=0.7958

c) Refused-derived-fuel (RDF) incinerator at Mid-connecticu,t Hartford (recursive equations system):

PCDDs/PCDFs= 1515.917 + 0.009PAH -2.053PCB - 7.338TEMP1
(1.019) (2.248) (-0.110) (-0.755) R^2=0.8388

PCB= -86.999 -0.00006PAH+0.327HCl+0.007CU-0.009TSP
(-2.294) (-0.941) (3.460) (1.236) (-2.162) R^2=0.9523

PAH= 499370+118.846CO-45.627TEMP3
(2.167) (6.356) (-2.137) R^2=0.9136

where :

- TSP (mg/Nm^3) = the concentration of total suspended solid in the flue gas before the inlet of FF or ESP.
- CU (µg/Nm^3) = the concentration of copper in the flue gas before the inlet of FF or ESP.

- CO (ppmv) = the concentration of carbon monoxide in the flue gas before the inlet of FF or ESP.
- TEMP1 and TEMP3 (°C)= flue gas temperature before the inlet of FF or ESP, and combustion temperature in the furnace, respectively.
- PCDDs/PCDFs (ng/Nm^3) = the concentration of dioxins and furans before the inlet of FF or ESP.
- PCB (ng/Nm^3) = the concentration of PCB before the inlet of FF or ESP.
- PAH (ng/Nm^3) = the concentration of PAH before the inlet of FF or ESP.

The units used in this analysis are all metric units. The statistical regression results for the interpretation of PCDDs/PCDFs production before the inlet of air pollution control devices show that single equation model is most suitable for the mass burn waterwall incinerators while the recursive equations system is a better choice for both the mass burn modular and refused-derived-fuel incinerators. In the latter case by solving the recursive equations system, two stage least square (2SLS) method was selected as the solution procedure, and the statistical formulation of recursive structure presumes that PCDDs/PCDFs formation is majorly dependent on the formation of PAH and PCB simultaneously while the formation of PCB is dependent on the formation of PAH and other related parameters. The numbers in these parenthesis as shown below each regression estimate are t-ratios in statistics.

A couple of observations can be made as follows:

- It is shown that the fourth proposed formation mechanism of PCDDs/PCDFs is verified in the cases of mass burn waterwall and RDF incinerators statistically. But the regression results in the case of mass burn modular incinerator are generally worse than the others probably due to the limited number of data sets available (i.e., only four data sets are collected in the NITEP reports in this case).

- Part of the t-ratios pass the inference test of the 5% level of significance in the cases of mass burn waterwall and RDF incinerators. R^2, $\bar{R}^2$, and F values are fairly good in several cases.

- Sign convention of each estimator in the first regression equation for mass burn waterwall incinerators reveals that the higher the concentrations of HCl and copper appear in the flue gas, the lower the possibility of copper attached in the particle surface reacts with free radical of related chlorinated hydrocarbon compounds in the low temperature environment. But it is not true in the case of RDF incinerator.

- Sign convention of each estimator in all of the three analyses reveals that the lower the temperature of flue gas and/or combustion temperature, the higher the concentrations of PCDDs/PCDFs, PCB, and PAH exist in the flue gas.

4. Conclusions

This study showed a statistical analysis of the proposed formation mechanism regarding to the production of the major chlorinating agents, including PCDDs/PCDFs, PCB, and PAH, in a low temperature environment associated with metal-catalyzed reaction of HCl in an excess oxygen condition in the flue gas. The formation mechanism in the downstream environment is partially verified in the mass burn waterwall and RDF incinerators. It can be concluded that the formation mechanisms of PCDDs/PCDFs, PCB, and PAH probably are different in different types of incinerators. Based on the regression results in this analytical framework, not only PCDDs/PCDFs but also PCB and PAH concentrations at the inlet of particulate removal process can be estimated for different types of incinerators.

5. References

1) Dickson, L. C., et al. (1989) : Surface-catalyzed Formation of Chlorinated Dibenzo-dioxins and Dibenzo-furans During Incineration. *Chemosphere*, 19 (1-6):277-282.
2) Gullett, B. K., Bruce, K. R., and Beach, L. O. (1990) : The Effect of Metal Catalysts on the Formation of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofuran Precursors. *Chemosphere*, 20 (10-12):1945-1952..
3) Altwicker, E. R. & Rappe, C. (1992) : Mechanism of PCDD/PCDF Formation in Incinerators : A US/Sweden Collaborative Study. Final Report, The New York State Solid Waste Combustion Institute, Cornell University, U.S.A..
4) Schindler, P. (1987) : Municipal Waste Combustion Study : Emissions Data Base for Municipal Waste Combustor. *EPA/530.SW.87.021B*, Midwest Research Institute, Cary, NC, U.S.A..
5) Hiraoka, M., Sakai, S., & Yoshida, H. (1992) : Japan's Guidelines for Controlling Dioxins and Dibenzofurans in Municipal Waste Treatment. *Chemosphere*, **25**, Nos. 7/10, 1393-1398.
6) Federal Register (Feb. 11, 1991) U. S. 40 CFR Parts 51, 52, and 60, Standards of Performance for New Stationary Sources and Final Emission Guidelines; Final Rules, Washington D.C., U.S.A..
7) Hasselriis, F. (1986) : Minimizing Trace Organic Emissions from Combustion of Municipal Solid Waste by the Use of Carbon Monoxide Monitors. *Preceedings of National Waste Processing Conference*, Denver, CO, U.S.A.. 31- 37.
8) Hasselriis, F. (1986) : Effects of Burning Municipal Waste on Environment and Health. presented at the *joint. ASME/IEEE Power Generation Conference*, Portland, Oregon, U.S.A., 19- 23.
9) Visalli, J. R. (1987) : A Comparison of Dioxin, Furan and Combustion Gas Data from Test Programs at Three MSW Incinerators. *Journal of Air Pollution Control Association* **37**, No. 12, 1451-1463.
10) Neulicht, R. (1987) : *Results of the Combustion and Emissions Research Project at the Vicon Incinerator Facility in Pittsfield, Massachusetts.* Final Report, prepared by *Midwest Research Institute*, for the New York State Energy Research and Development Authority, New York, U.S.A..
11) Hasselriis, F. (1987) : Optimization of Combustion Condition to Minimize Dioxin Emissions. *Waste Management & Research* **5**, 311-325.
12) Tillman, D. A. et al. (1989) : *Incineration of Municipal and Hazardous Solid Wastes.* Academic Press Inc., San Diego, California, U.S.A., 92-95.
13) Miller, H., Marklund, S., Bjerle, I., & Rappe, C. (1989) : Correlation of Incineration Parameters for the Destruction of Polychlorinated Dibenzo-p-dioxins. *Chemosphere* **18**, Nos. 7-8, 1485-1494.

13) Miller, H., Marklund, S., Bjerle, I., & Rappe, C. (1989) : Correlation of Incineration Parameters for the Destruction of Polychlorinated Dibenzo-p-dioxins. *Chemosphere* **18**, Nos. 7-8, 1485-1494.
14) Miles, A. J. (1989) : *Combustion and Emissions Testing at the Westchester County Solid Waste Incinerator.* prepared by Radian Corporation, for the New York State Energy Research and Development Authority, New York, U.S.A..
15) Horaguchi, M., Ogawa, H., Ose, K., Tomisawa, S., & Matsuura, S. (1989) : PCDDs & PCDFs from the MSW Incinerator. *Chemosphere* **18**, Nos. 9/10, 1785-1797.
16) Kelly, W. (1990) : *Results from the Analysis of MSW Incinerator Testing at Oswego County, New York.* prepared by Radian Corporation, for the New York State Energy Research and Development Authority, New York, U.S.A..
17) Kilgroe, J. D., Brna, T. G., & et al. (1990) : Control of PCDD/PCDF Emissions from Refuse-Derived Fuel Combustors.*Chemosphere* **21**, Nos. 12, 1809-1815.
18) Chang, N. B. and Huang, S. H. (1994) : Statistical Modelling for Prediction and Control of PCDDs/PCDFs Emissions from Municipal Solid Waste Incinerators. *Waste Management & research,* accepted.
19) Environment Canada (1988) : The National Incinerator Testing and Evaluation Program : Environmental Characterization of Mass Burning Incinerator Technology at Quebec City. Summary Report, EPS3/UP/5, Ottawa, Canada.
20) Environment Canada (1992) : The National Incinerator Testing and Evaluation Program : the Environmental Characteristics of Refuse-derived-fuel Combustion Technology. Summary Report, Vol. I, Ottawa, Canada.
21) Beychok, M. R. (1987) A Data Base of Dioxin and Furan Emissions from Municipal Refuse Incinerators. *Atmospheric Environment* **21**, No. 1, 29-36.
22) Environment Canada (1991) : The National Incinerator Testing and Evaluation Program (NITEP). 91-05747, Ottawa, Canada.
23) Environment Canada (1985) : The National Incinerator Testing and Evaluation Program : Two-stage Combustion (Prince Edward Island). EPS3/UP/1, Ottawa, Canada.
24) Environment Canada (1986) : The National Incinerator Testing and Evaluation Program : Air Pollution Control Technology. Summary Report, EPS3/UP/2, Ottawa, Canada.