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Multiple linear regression based congener profile correlation to estimate the toxicity (TEQ) and dioxin concentration in atmospheric emissions

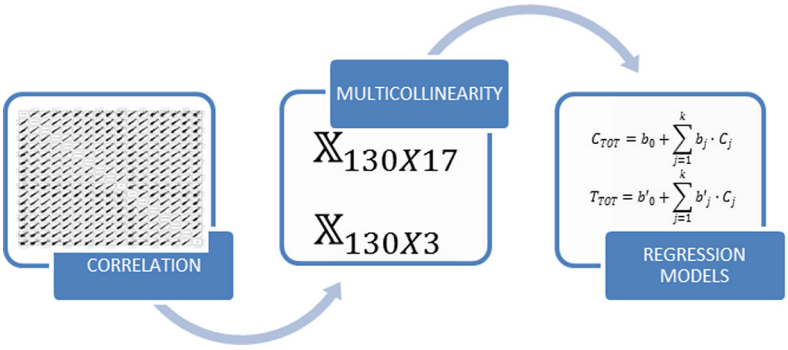
D. Palmer [a], J.O. Pou [a], L. Gonzalez-Sabaté [b], J. Díaz-Ferrero [c,*]

[a] Industrial Engineering Department, Institut Químic de Sarrià - Universitat Ramon Llull, Via Augusta, 390, Barcelona 08017, Spain
[b] Quantitative Methods Department, Institut Químic de Sarrià - Universitat Ramon Llull, Via Augusta, 390, Barcelona 08017, Spain
[c] Analytical and Applied Chemistry Department, Institut Químic de Sarrià - Universitat Ramon Llull, Via Augusta, 390, Barcelona 08017, Spain

HIGHLIGHTS

- PCDD/F congeners of emissions present multicollinearity, meaning that some of them can be predicted from the remaining as a linear combination
- Only the formation of 1,2,3,6,7,8-HxCDD, OCDF and 2,3,7,8-TCDF can be considered as linearly independent.
- A linear model is proposed to estimate the total concentration of PCDD/F in atmospheric emission using the selected congeners.

GRAPHICAL ABSTRACT



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ABSTRACT

The formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) is governed by complex chemical reactions with complex kinetic models. The simulation of Municipal Solid Waste incinerators, or other industrial thermal processes, is a powerful tool that can be used to optimize and control them, and reducing the number of components to simulate is mandatory for a proper use. In this study it has been determined that only the formation of 3 of the 17 main PCDD/F congeners can be considered as linearly independent. This fact has been used to establish linear regression models that are able to estimate properly the total amount and toxicity of a sample considering only the amount of 1,2,3,6,7,8-HxCDD, OCDF and 2,3,7,8-TCDF. All models have been validated using new samples performing a close approach to the real values provided by complete analytical studies. The average relative error is 3.5% and the maximum relative error is below 9% for these new testing samples. The main goal of our investigation is to build a dynamic simulation process of a MSW facility and include the dioxins formation on it using these models.

1. Introduction

Municipal Solid Waste (MSW) generation in most countries in the EU has been increasing in the last 20 years, so its management is certainly an important environmental challenge that society has to solve in the years to come. There are up to four widely-extended methods used for this purpose: recycling, landfilling, composting and incineration (EUROSTAT, 2017). Although the carbon footprint of MSW incinerators is less demanding for the environment than landfilling (Hogg et al., 2002), other environmental issues, like polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F)

* Corresponding author.
E-mail address: jordi.diaz@iqs.edu (J. Díaz-Ferrero).

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atmospheric emissions during combustion (McKay, 2002; Shaub and Tsang, 1983) and gasification processes (Lopes et al., 2015) should be taken into account. These products are regulated by the Stockholm Convention on Persistent Organic Pollutants since they present 4 main characteristics that define POPs: persistence, bio-accumulation, potential for long-range environmental transport and toxicity (The Stockholm Convention, 2001).

Dioxins are emitted during combustion processes as a mixture of up to 210 PCDD/Fs congeners. The relative composition of each one is named "fingerprint" and has been extensively used to identify possible sources or investigating the mechanisms that happen during its propagation through the atmosphere.

The quantity and the location of the chlorine atoms in the structure of a PCDD/F directly affects to its toxicity. Regarding this fact, only the toxicity of the 17 congeners with four or more chlorine atoms in the 2, 3, 7, and 8 positions are considered significant (Ahlborg et al., 1992). Therefore, the total concentration is calculated as the amount of toxic equivalents (TEQ), based on NATO/CCMS criteria (Kurtz and Bottimore, 1988), using toxicity conversion factors that rescale all the amounts of each congener considering as the factor of unity the most toxic congener: 2,3,7,8-tetrachlorodibenzo-p-dioxin. The International Toxicity Equivalency Factor (I-TEF) defined values (Kutz et al., 1990) remain as the internationally adopted criteria since all legislative issues for atmospheric emissions are still referred to it (European Parliament and of the Council, 2010).

The fingerprint of the emissions during MSW incineration at various atomic ratios of C:H:Cl has been studied (Yoshihara et al., 2002). These dioxin fingerprints from different thermal industrial processes have also been analysed by principal component analysis and hierarchical cluster analysis. In sum it appears that there are similarities between the dioxin fingerprints from some industrial metallurgical processes and MSW incinerators, producing more P_5CDF (Buekens et al., 2000). Other studies on the emissions of a cement plant (Conesa et al., 2016) and furniture incineration (Moreno et al., 2016) concluded that, with respect to the congener distribution, there were not significant differences in the emissions due to the fuel that was combusted. The emissions of dioxins from waste combustion show a close correlation with precursors like chlorinated benzenes or phenols (Lacatus et al., 2002). This correlation was used to model the formation of dioxins' precursors during combustion with the aim of establish an on-line measurer and even predict the formation of dioxins (Lavric et al., 2005). Similar models have also been used to predict tropospheric ozone concentrations (Abdul-Wahab et al., 2005; Sousa et al., 2007).

The fingerprint pattern of dioxin congener profiles of several samples from the emission of a similar combustion process have been analysed (Chen et al., 2012) and used in several environmental studies in order to identify a possible Occurrence/Source correlation (Cappelletti et al., 2016; Floret et al., 2007; Swerev and Ballschmiter, 1989; Xu et al., 2009).

Although extensive research has been done to study the formation of PCDD/F in combustion processes (McKay, 2002), the attribution of which mechanisms dominate it and which parameters are more important, there are still uncertainties concerning some aspects like the effect of chlorine or some emission factors and activity rates (Lavric et al., 2005). Once the thermodynamic properties of these molecules were calculated, it was found that the thermodynamic equilibrium constants of the main formation pathways for PCDD/F strongly favour its production (Dorofeeva et al., 1999, 2001; Dorofeeva and Yungman, 2003; Ritter and Bozzelli, 1994). It was also observed that the distribution of congeners obtained using the calculated equilibrium constants did not correspond to the experimental distribution published (Addink et al., 1998). This fact suggests that other routes, in addition to the gas phase reactions, should occur. The experimental distribution shows that the amount of PCDD/F obtained during combustions is noticeably lower than the predicted by the equilibrium constants; hence, the maximum thermodynamic conversion in the main formation pathways is never reached. Thus, the formation of PCDD/F could be controlled by kinetic mechanisms rather than by thermodynamics mechanisms. This kinetic control has also been studied and described focusing on the decomposition of the fuel during thermal decomposition (Conesa and Rey, 2015; Conesa and Soler, 2017).

The importance of the kinetic mechanisms supports the idea that the formations of all PCDD/F congeners are connected to each other (Shao et al., 2012). This kinetic dependence should provoke a correlation between the amounts of each congener that is produced during combustion.

There are three main mechanistic pathways to PCDD/F formation: gas-phase reactions, reactions between precursors catalysed by fly ash, and *de novo synthesis* reactions (Environment Australia, 1999).

Considering gas-phase reactions (a), the analyses of major pathways have been studied extensively (Babushok and Tsang, 2003). Main precursor routes formation from chlorinated phenols, from oxidation of benzene and from other precursors like hydroquinone also have been described (Altarawneh et al., 2009). It should be noted that PCDD/F formation using gas-phase reactions only occur at temperatures higher than 600 °C (Tuppurainen et al., 1998).

Many authors claim that fly-ash catalysed precursor (b) is the principal pathway for PCDD/F formation (Tuppurainen et al., 1998). The precursors are formed at high temperatures, as incomplete combustion products, and in the post-combustion zone the PCDD/F are formed by its reaction at lower temperatures (Froese and Hutzinger, 1996). Some precursors can be found as a part of the combustible. The precursor molecules react using elements in the fly ash as a catalyst to produce PCDD/F. Main processes of adsorption/desorption (Milligan and Altwicker, 1996a) and global kinetics (Milligan and Altwicker, 1996b) have been studied. The yield of formation of PCDD/F from dibenzofuran and benzonaphtofuran as precursors using model fly ash have been also described (Hajizadeh et al., 2011), as well as the reaction of formation of PCDD/F from polychlorinated diphenyl ethers (Altarawneh and Dlugogorski, 2014).

Studying the fly-ash catalysed *de novo synthesis* pathway (c), it is believed that in the fly ash of incinerated MSW still remains a small amount of carbon that can produce complete aromatic rings in lack of oxygen. It is also believed that chlorine is transferred from the ash surface to the carbon rings producing PCDD/F (Stieglitz and Vogg, 1987). Also kinetic models for *de novo synthesis* in surface catalysed reactions have been published (Huang and Buekens, 2001). The influence of catalysts and some additions on these pathways have also been studied (Wielgosiński et al., 2016). Model fly ash is used in several publications to determine the influence of catalysts (Verhulst et al., 2014), oxygen concentration (Yang et al., 2015), and other parameters. All these publications related to PCDD/F formation support the main idea that kinetics controls the production processes over thermodynamic equilibrium, which means that some correlation between all the congeners produced during combustion could be determined.

The main goal of our investigation is to build a dynamic simulation process of a MSW facility and include the dioxins formation on it. Reducing the number of simulated components in the model is an important factor to consider during its optimization. Specifically, the aim of this study is to determine a model that estimates the total amount and toxicity in a sample containing PCDD/F using less than the amount of the 17 PCDD/F as regressors. This result would considerably decrease the calculation effort by reducing the number of congeners to simulate in the heat and material balance. For this end it is proposed to determine the amount of some congeners as a lineal combination of those congeners identified as independents.

Other authors have proposed some correlation between the total concentration of two groups of congeners (highly or lowly chlorinated) and the TEQ, producing an average correlation coefficient of 0.8603 for tetra- to octachlorinated (highly chlorinated) PCDD/F, depending on the selected group of congeners and related to year season (summer or winter) (Song et al., 2007). Data on PCDD/F emissions analytics are