FACTORS INFLUENCING THE PARTITIONING OF PCDDs/PCDFs BETWEEN THE GAS AND SOLID PHASES OF CEMENT KILN EMISSIONS

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Introduction

Organic constituent partitioning between the gas and solid phases of cement kiln emissions is important from both a risk assessment and organic emissions control perspective. The extent to which organic constituents partition to either phase is highly dependent on the environment to which the constituents are exposed. From a theoretical standpoint, the partitioning of an organic constituent is dependent on variables such as vapor pressure, and particle surface area and activity. For risk assessments where mechanisms such as vapor phase transport and particle deposition rate are significant modeling variables, the fate and transport of organic constituents are evaluated at ambient air conditions. At stack conditions, particle characteristics will not be significantly different than at ambient conditions. However, vapor pressures of organic constituents, which are a function of temperature, may be significantly different at ambient versus stack conditions. As a result, the fraction of an organic constituent adsorbed to available particulate matter may approach one at ambient conditions, but may be closer to zero at stack conditions.

Vapor/Particle Partitioning of PCDDs/PCDFs

Several sources of data can be used to evaluate vapor/particle partitioning of PCDDs/PCDFs at stack and ambient conditions. These include data on organic concentrations in collected cement kiln dust, actual emissions test data (front and back-half sampling train analyses), ambient air sampling studies, and theoretical evaluations of organic constituent partitioning.

Various stack tests have been conducted to determine the vapor phase/particulate phase (V/P) partitioning of PCDDs/PCDFs. The fraction of PCDD/PCDF that partitions to the vapor and particulate phases can be determined by analyzing the sampling train's front-half and back-half separately. To collect sufficient mass of particulate for accurate analytical determination of the concentration of the recovered congener requires lengthy stack sampling times. However, longer sampling times may affect the V/P partitioning calculations because PCDD/PCDF may

move from one part of the train to the next through desorption or particulate blow-off. PCDD/PCDF emissions from the stack of tested incinerators indicate that PCDDs/PCDFs are predominantly in the vapor phase (1).

Using PCDD/PCDF 1994 emissions test data from a wet cement kiln, it can be shown that the quantity of adsorbed PCDD/PCDF on emitted particulate matter is a small fraction of the emitted PCDD/PCDF. Three test runs performed at two different test conditions illustrated the partitioning of PCDD/PCDF between the gas and adsorbed particulate phases. Based on the six test results, the percentage of emitted PCDD/PCDF adsorbed to particulate is expected to be less than 0.3 percent (95% confidence interval).

Analysis of PCDD/PCDF emissions test data from another wet cement kiln yielded similar conclusions. On a mass basis, PCDD/PCDF adsorbed to the particulate matter being emitted was on average less than 20% of total stack emissions. However, the test also demonstrated that at lower PCDD/PCDF stack emission rates (low APCD inlet temperature condition), the PCDD/PCDF concentration in the particulate matter did not increase. This suggests that gas-phase PCDD/PCDF is not transferring to the particulate phase at a greater rate, but rather PCDD/PCDF formation rates are decreased.

The measurement of PCDDs/PCDFs in air under ambient conditions has only been achieved since the late 1980s. Although there may be some variations, the ambient air sampler consists of a glass fiber filter followed by a polyurethane foam (PUF) plug (1). Unlike the stack sampling method, the particulate filter is not artificially heated, nor is there a condensing component where the sampled air is quickly cooled. Hence, this sampling method scheme should be more useful to the interpretation of the V/P partitioning of PCDDs/PCDFs under ambient conditions. PCDD/PCDF partitioning data at ambient air conditions indicate that PCDDs/PCDFs are predominantly in the vapor phase for lower chlorinated PCDDs/PCDFs and on the particulate phase for higher chlorinated PCDDs/PCDFs (1).

A theoretical evaluation can also be used to illustrate that at cement kiln stack gas conditions, PCDD/PCDF is not partitioned to the particulate phase to an appreciable extent. Vapor pressures are fundamental thermodynamic observables which give direct information on the change of the Gibbs free energy functions in the phase transition. They play an important role in the equilibria which determines the fate of substances in the stack and in the environment.

The fraction of a chemical that is adsorbed to particles can be estimated using a theoretical model presented by Junge (2), whereby:

$$\phi = \frac{c \times S_T}{p^o + (c \times S_T)} \tag{1}$$

where:

ϕ = fraction of organic chemical adsorbed to particles, unitless

S_T = particle surface area per unit volume of air, cm^2/cm^3

p^o = vapor pressure, atm

c = molecular weight and heat of condensation factor, atm-cm

The particle surface area per unit volume of air is assumed to be 1.097×10^{-4} cm^2/cm^3 (based on a 180 mg/dscm particulate matter emissions rate and an average particle diameter of 10 μm). The molecular weight and heat of condensation factor does not vary much between compounds and is estimated to be 1.7×10^{-4} atm-cm (2,3).

It has been common practice in the literature to use the saturated vapor pressure $p_L°$ of a liquid organic compound as a predictor for the adsorption from the gas phase to a given surface. Although this procedure is actually not easily justified since the liquid vapor pressure of a compound depends solely on the internal interactions in the pure liquid, while adsorption depends on interactions with a surface which may represent a completely different material. However, for nonpolar substances (i.e., substances with no acid-base interaction) such as PCDDs/PCDFs, the liquid vapor pressure can be used as a prediction for the ability of compounds to engage in van der Waals interactions with like or dislike molecules.

Liquid vapor pressures for 2,3,7,8-TCDD, the most toxic PCDD/PCDF, were obtained from Schroy (4). Because stack gas temperatures in a cement kiln may vary from 300 to 600 °F, the fraction of 2,3,7,8-TCDD adsorbed to particulate matter was calculated at 300, 400, 500 and 600 °F, and the data were compared with partition fractions calculated at 68 and 100 °F (See Table 1).

Another gas/particle partitioning model has been presented by Pankow (5). This model was developed to describe gas/particle partitioning under urban conditions. The equation used to parameterize partitioning in the urban environment is:

$$K_p = \frac{F / TSP}{A} \tag{2}$$

where K_p (m^3/μg) is a compound and temperature dependent partitioning constant; F (ng/m^3) and A (ng/m^3) are the particle-associated and gaseous concentrations, respectively; TSP (μg/m^3) is the level of total suspended particulate matter in the air. Because (F/TSP) gives the concentration on/in the particulate matter, the constant K_p represents the sorbed/gaseous concentration ratio. The sorbed/gaseous concentration ratio for a compound can be written in terms of its vapor pressure according to the following equation:

$$\log K_p = m_r \log p_L^* + b_r \tag{3}$$

where $m_r = -1.02$ and $b_r = -8.09$. The values for the constants were derived using gas/particle partitioning data of polycyclic aromatic hydrocarbons on urban particulate matter (6). Using Equation 3, the fraction of 2,3,7,8-TCDD that would partition to the particulate phase was again evaluated using liquid vapor pressure data from Schroy (4). The results are presented in Table 1.

Results and Discussion

The fraction of PCDDs/PCDFs partitioned to the particulate phase is very dependent on vapor pressure, and subsequently temperature. At ambient conditions, partitioning to the particulate phase may be important where the fraction of PCDDs/PCDFs partitioned to the particulate phase is near 1.0. However, at the elevated temperatures of the flue gas exiting the cement kiln stack, the fraction of adsorbed PCDDs/PCDFs approaches zero.

References

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Table 1: Fraction of 2,3,7,8-TCDD Partitioned to the Particulate Phase

Temperature (°F)	ϕ using Junge Model	ϕ using Pankow Model
68	0.9999	1.0
100	0.9991	1.0
300	0.0036	0.295
400	8.75×10^{-5}	0.0093
500	2.53×10^{-6}	2.52×10^{-4}
600	1.49×10^{-7}	1.41×10^{-5}