

CONSIDERATION OF THE VOLATILIZATION OF PCDD AND PCDF FROM DEPOSITED
PARTICULATES IN COMBUSTION SOURCE RISK ASSESSMENTS

Theodore D. Goldfarb and Stuart J. Harrad

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794-3400

ABSTRACT

Current risk assessments of waste incinerators and other combustion sources of PCDDs and PCDFs may seriously underestimate ambient levels of these toxins by using only stack emission transport models while ignoring volatilization from deposited particulates.

INTRODUCTION

The well-established toxicity of specific isomers of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), coupled with their detection in varying concentrations in the stack gases from municipal waste incinerators and other combustion facilities, has led to their inclusion in many recent health risk assessments for proposed incineration facilities. These assessments use air dispersion models that are designed to predict ground level ambient concentrations of PCDDs and PCDFs based on predicted (or measured) stack effluent levels and historical meteorological data in the vicinity of the incinerators. Predictions of deposition rates of particulate-bound PCDDs and PCDFs are also frequently included in such assessments.

The maximum potential cancer risk associated with inhalation of PCDDs and PCDFs is quite frequently determined to be a major component of the small overall human health risk that results from these assessments. The contribution to the ambient dioxin concentration due to the volatilization of PCDDs and PCDFs is invariably ignored or assumed to be negligible in the models that are used. We believe that this is a serious error that may result in a very significant underestimation of the ambient levels - and therefore the associated risks.

DISCUSSION

There are several observations and premises upon which this belief is founded. First is the fact that measured and estimated vapor pressures of pure PCDDs and PCDFs at 25°C far exceed the maximum ground-level concentrations that are estimated on the basis of stack effluent dispersion models. In Table 1 we list the predicted average annual ambient ground level concentrations of the 2,3,7,8-chlorinated tetrachloro- and pentachlorodioxins and furans at the point of maximum impact, based on stack gas dispersion models, for the areas surrounding the proposed 3000 ton-per-day municipal incinerator in Brooklyn, New York¹ and the 990 ton-per-day facility in North Hempstead New York². These are compared to the measured and calculated vapor pressures of the pure solid isomers at 25°C.

TABLE 1

ESTIMATED MAXIMUM AMBIENT YEARLY AVERAGE PCDD AND PCDF GROUND LEVEL
CONCENTRATIONS (ug/M³) FROM INCINERATOR STACK EMISSION COMPARED
TO OBSERVED AND ESTIMATED VAPOR PRESSURES AT 25°C

<u>ISOMER</u>	<u>BROOKLYN NAVY YARD*</u>	<u>NORTH HEMPSTEAD</u>	<u>VAPOR PRESSURE**</u>
2,3,7,8-TCDD	2.16X10 ⁻⁹	1.23X10 ⁻⁹	2.6X10 ⁻²
1,2,3,7,8-PeCDD	3.87X10 ⁻⁹	3.61X10 ⁻⁹	8.2X10 ⁻³
2,3,7,8-TCDF	1.25X10 ⁻⁸	1.09X10 ⁻⁸	2.5X10 ⁻¹
1,2,3,7,8- + 2,3,4,7,8-PeCDF	9.64X10 ⁻⁹	3.27X10 ⁻⁸	7.9X10 ⁻²

* The concentrations of the 2,3,7,8- chlorinated species listed in this Table for the Brooklyn Navy Yard facility, other than the 2,3,7,8-TCDD, were calculated from the data given in Ref. 1 by taking 1/14, 1/38 and 1/14, respectively, of the total congener group concentrations of the PeCDD, TCDF and PeCDF isomers.

**The vapor pressure of 2,3,7,8-TCDD is based on actual measurement, whereas the others are calculated estimates. (See Ref. 2).

As can be seen from the Table, the vapor pressures of all of the major contributors to the total toxic equivalents are between six and seven orders of magnitude greater than the ambient concentration estimates. Although adsorption on particulate surfaces could significantly reduce the volatility of these compounds compared to the pure solid, there is no a priori reason to assume that this effect will be so great as to justify rejecting the likelihood that vaporization from PCDD and PCDF contaminated dust deposits might make a significant - perhaps dominant - contribution to ambient concentrations close to ground level. Studies of actual measured ambient PCDD and PCDF levels^{4,5} have produced concentrations in urban areas that are roughly an order of magnitude higher than those predicted by the Brooklyn Navy Yard and North Hempstead assessments, but the air samplers

were positioned at rooftop elevations and are thus not directly relevant to testing our hypothesis. We propose that air samplers sited at ground level on dark surfaces such as asphalt, where solar heating is likely to have maximum impact, would be the appropriate field test to determine whether volatilization from particulate matter laden with PCDDs and PCDFs is a major contributing factor to local air concentrations of these toxins. The effect is likely to be most pronounced in enclosed areas such as narrow city streets and alleys where exposure to children who frequently play in such locales might be a significant health risk issue.

Evidence of a temperature dependent variation in vapor to particulate PCDD and PCDF ratios is reported by Eitzer and Hites* in their ambient air baseline study. At 26°C they found that practically all of the TCDDs and TCDFs were in the vapor phase, whereas at lower temperatures an appreciable fraction of these most volatile isomers were associated with airborne particulate matter. This clearly suggests that volatilization and condensation of particle bound dioxins and furans is occurring. The selective transport of lower chlorinated PCDDs and PCDFs from the filter to the PUF plug section of an air sampler in a 26°C air stream has also been reported*. This migration is reported to occur during either ambient air sampling or when spiked synthetic fly ash is added to the sampler filter, but not when fly ash extracted from an incinerator's electrostatic precipitator is added*. The most obvious interpretation of these results is that the most readily vaporized surface PCDDs and PCDFs have been stripped off the fly ash surface by the relatively hot flue gas stream, leaving only the much more tightly bound molecules in the interstices of the particles.

CONCLUSIONS

We conclude that suggestive evidence exists to support the proposition that the volatilization of PCDDs and PCDFs incorporated in particulate matter emitted by waste incinerators and other combustion sources that deposits on surfaces that are exposed to sunlight may be important contributors to ground level ambient concentrations of these toxins that are presently ignored in health risk assessments.

To test this hypothesis we are in the process of planning and seeking funding for a series of studies. Included will be experiments designed to determine the steady-state concentrations of selected PCDDs and PCDFs in air that has been circulated over previously cleaned fly ash maintained at temperatures ranging from 0 to 50°C, which has been spiked with the isomers in question.

We suspect that particulates contain a variety of surface and interior binding sites for PCDDs and PCDFs. If this is true, repeated vaporization and condensation should result in decreasing volatility as the molecules become selectively bound to less accessible, but more energetically favorable sites. Testing this proposition is important in order to determine the potential volatilization from "old" as opposed to newly deposited material.

The goal of our planned studies is to provide data that can be used in attempting to include the potential effect of PCDD and PCDF volatilization in future health risk assessment models. Conducting direct field tests, using ground level high volume air samplers positioned in carefully chosen sites near combustion sources known to emit significant amounts of dioxin and furan laden particulates, would, of course, also be an obvious research activity suggested by our proposal. We are presently exploring the feasibility of conducting such studies.

REFERENCES

1. Final Environmental Impact Statement - Proposed Resource Recovery Facility at the Brooklyn Navy Yard, Appendix D-11, Table 4-2, prepared by Camp Dresser and McKee for the City of New York Department of Sanitation, (June 1985).
2. Draft Site and Technology Specific Impact Addendum to the Generic Environmental Impact Statement For the North Hempstead Solid Waste Management Facility Project, Volume 2, Table 4, prepared by Malcolm Pirnie, Inc., for the Solid Waste Management Authority, Town of North Hempstead, New York (February 1987).
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5. T.O. Tiernan, D.J. Wagel, G.F. VanNess, J.H. Garrett, J.G. Solch and L.A. Harden, *Chemosphere*, 19, 573 (1989).
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