CONGENER-SPECIFIC DEPOSITION OF DIOXINS FROM AN INCINERATOR IN MIDLAND, MICHIGAN

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Introduction

During 2002-2004, the University of Michigan Dioxin Exposure Study (UMDES) conducted a soil sampling program in Midland, MI to quantify the level of dioxin contamination in the area. The source of contamination in Midland soil is presumably from the Dow Chemical Company's incinerators, which for decades have been operated to burn hazardous wastes from various production processes. The 51 UMDES soil samples were then analyzed for 17 dioxin and furan congeners and 12 PCB congeners. Dioxin congeners often are expressed in term of toxic equivalent (TEQ), which is a toxicity-weighted sum of concentrations that accounts for the congeners' differences in their level of toxicities. The dioxin TEQ however might not be helpful in explaining the fate and transport behavior of dioxin in the environment as each congener displays different behaviors based on chemical physical properties, transformation and transportation. In order to characterize the deposition pattern of dioxin congeners we applied AERMOD, a newly EPA promulgated air dispersion model, to a number of dioxin compounds using the Dow incinerator stack emission rates of 1992[1]. Five dioxin congeners (TCDD, 23478-PeCDF, 123678-HxCDD, 1234789-HpCDF and OCDD), ranging from low to high number of chlorine substitutes and varying in emission loads, particle bound fractions and partitioning properties, were selected.

Materials and Methods

Air dispersion modeling: The modeling area is a 261x261 grid (spacing = 50m) centered on the incinerator but excluding the plant property. Each grid node is considered as a receptor in the AERMOD model. Five year (2001-2005) meteorological data used as input files to AERMOD were provided by the Michigan Department of Environmental Quality (MDEQ) for the weather station at Midland-Bay-Saginaw (MBS). Emission rates of the 5 dioxin congeners are identified with the real emission measured in 1992 (EPA)[1] for the 830 incinerator stack and adjusted based on the new WHO-$TEF_{D/F}$ 2005 scheme. As deposition of dioxins is associated with particles, particle size distribution, particle fraction and particle diameters are important parameter inputs in the deposition algorithm (AERMOD). In addition, dioxin congeners are unevenly distributed among vapor and particulate phases; therefore vapor/particle partitioning is another essential input parameter. The dioxin-bound particulate percentage, particle size characterization and real emission rates of the selected dioxin congeners are reported in table 1. AERMOD runs were conducted using the particle deposition option and the same 1 gram/second emission rate for each congener. Model outputs (air concentration, total deposition, wet and dry deposition fluxes) were then modified for each congener to reflect the real emission rates and the proportion of dioxin partitioned into vapor and particulate phases[1,4].

Geostatistical modeling[2]: The relationship between the output of the air dispersion model (dry and wet depositions) and field data (normal score transformed values of congener concentration) is modeled using linear regression. The regression function is later applied to the entire 261x261 grid, generating a spatial trend that is incorporated in Sequential Gaussian simulation (sGs). One hundred grids of simulated congener concentrations were generated by sGs using the semivariogram of regression residuals and the 51 UMDES soil data. The concentration at each receptor point is predicted as the average of 100 simulated values. Data visualization is conducted using STIS software (Space-Time Intelligence System™, TerraSheer®.)

Results and Discussions

Figure 1 shows the spatial patterns of dry and wet deposition modeled using AERMOD for five congeners. Differences between maps reflect differences in congener distribution between vapor and particulates, and in particle size categories. Particle size distribution has an important effect on the amount and spatial deposition of dioxin

congeners. Indeed if the same emission rates are applied to all congeners in AERMOD, compounds associated with finer particles (e.g. less halogenated compounds) are deposited closer to the source than compounds bound to the larger particles. For example, dry and wet deposition fluxes for TCDD and 123678-HxCDD are about the same within the boundary of the modeling area, although TCDD emissions are one order of magnitude smaller than those of 123678-HxCDD. Only 20% of TCDD partitions to the particulate phase while that of 123678-HxCDD is 64% (table 1). This result is explained by the TCDD model using 90% mass fraction in a particle size of 0.32 µm, whereas 123678-HxCDD is modeled using two particle size categories of 0.13 µm and 0.75 µm with an equal amount of 42% each[3]. The shift to a greater particle size category delays the deposition of 123678-HxCDD further away from the incinerator. Dry deposition fluxes vary strongly among dioxin homologues: higher fluxes are found close to the source, e.g. for TCDD and 23478PeCDF. Higher chlorinated compounds (hexa-, hepta- to octa-chlorinated compounds) tend to be diluted with air masses further away along the NE plume direction corresponding to prevailing winds, leading to smaller dry fluxes across the area. Wet deposition seems to be confined to the immediate vicinity of the incinerator and occurs mainly South-West of the plant. Similar wet deposition patterns are observed across dioxin homologues.

The application of the 1992 Dow incinerator emission profile and vapor/particle partitioning ratios (percentage of dioxin associated with particles, table 1) to the output of AERMOD causes the equivalent particle emission to increase from TCDD to OCDD within two orders of magnitude. The output dry and wet deposition fluxes increase from low to high chlorinated compounds, except for TCDD whose finer particles are favored by dry deposition. In contrast, larger particles are scavenged by rain in wet deposition. The ratio of dry over wet deposition suggests the increasing role of wet deposition in removing larger particles of the higher chlorinated compounds (right column of figure 1.) Although wet and dry depositions are overall both important processes in removing the dioxin particles from ambient air, dry deposition remains the most important mechanism.

Figure 2 shows the geostatistical prediction[2] of congener concentrations in soil. The model is based on 51 UMDES soil samples. High OCDD concentrations are predicted as the result of its high emission load from incinerator and high ground measurements. Concentration of TCDD spreads more evenly than that of 23478-PeCDF whereas concentration of 1234789-HpCDF is not surprisingly low. Figure 2 (right column) presents the contribution of these congeners in term of toxic equivalent, TEQ. Only TCDD and 23478-PeCDF are compounds of concern since they contribute the most to total soil TEQ, from tens to hundreds part per trillion TEQ.

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Table 1. Input parameters (Emission rates, particulate percentage and particle size distribution) to AERMOD[1,3,4]

Compound	Emission				Particle Size Distribution				
	Emission Rate (g/s)	Particulate (%)	Vapor Emission Rate (g/s)	Particulate Emission Rate (g/s)	Compound (mass fraction, %)	Representative Particle Diameter (µm)			
						0.13	0.75	4.24	31.62
TCDD	2.99E-11	19	2.42E-11	5.69E-12	TCDD	0.9			0.1
23478-PeCDF	2.77E-11	29.75	1.94E-11	8.24E-12	23478-PeCDF	0.36	0.39	0.19	0.06
123678-HxCDD	2.21E-11	64	7.96E-12	1.42E-11	123678-HxCDD	0.42	0.43	0.12	0.03
1234789-HpCDF	2.03E-11	89.5	2.14E-12	1.82E-11	1234789-HpCDF	0.45	0.4	0.08	0.03
OCDD	8.96E-10	99	8.96E-12	8.87E-10	OCDD	0.23	0.58	0.16	0.02

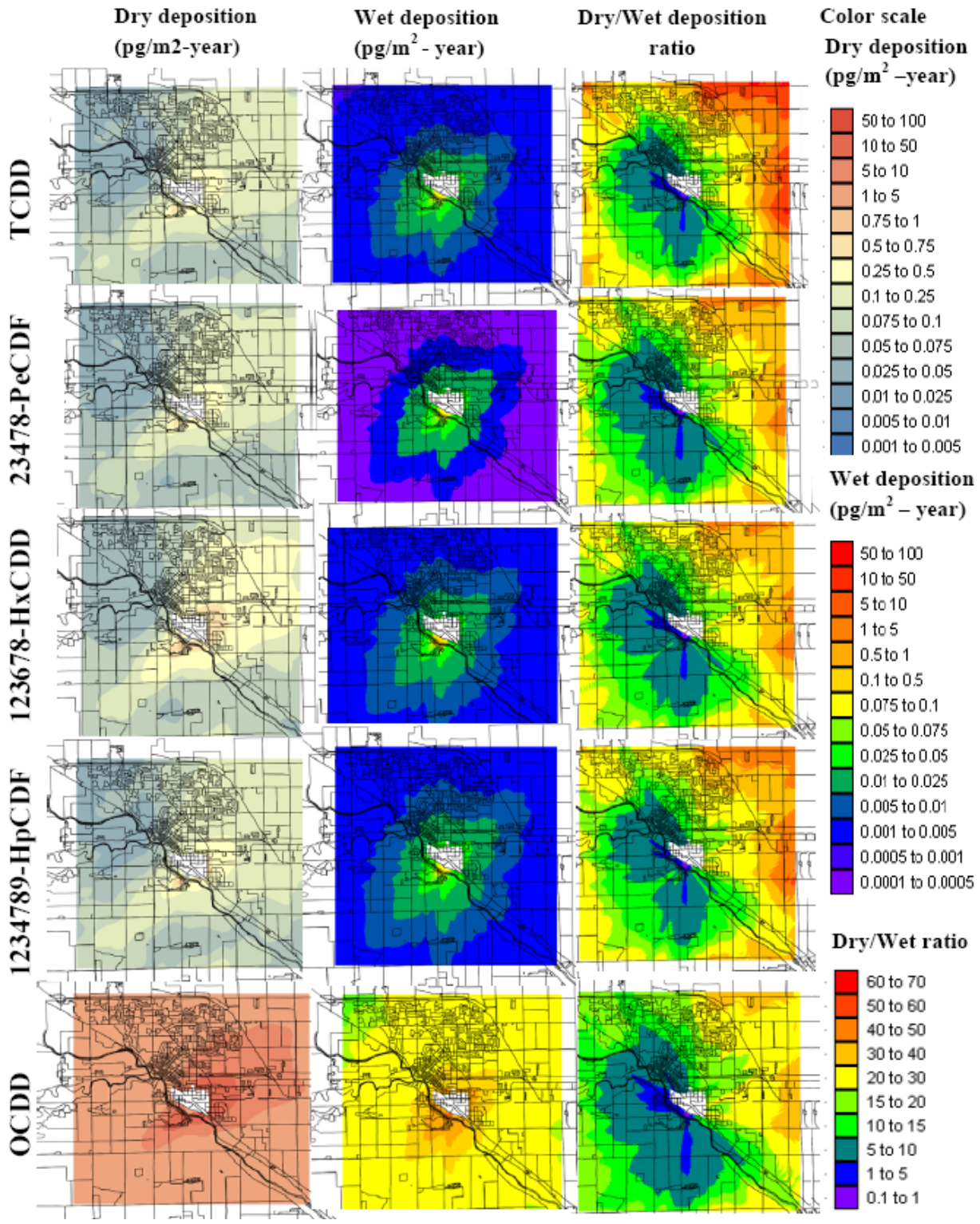

Figure 1. Dry and wet deposition fluxes (pg/m^2 –year) of dioxin congener specifics (left and middle columns) and ratio of dry/wet deposition (right column)

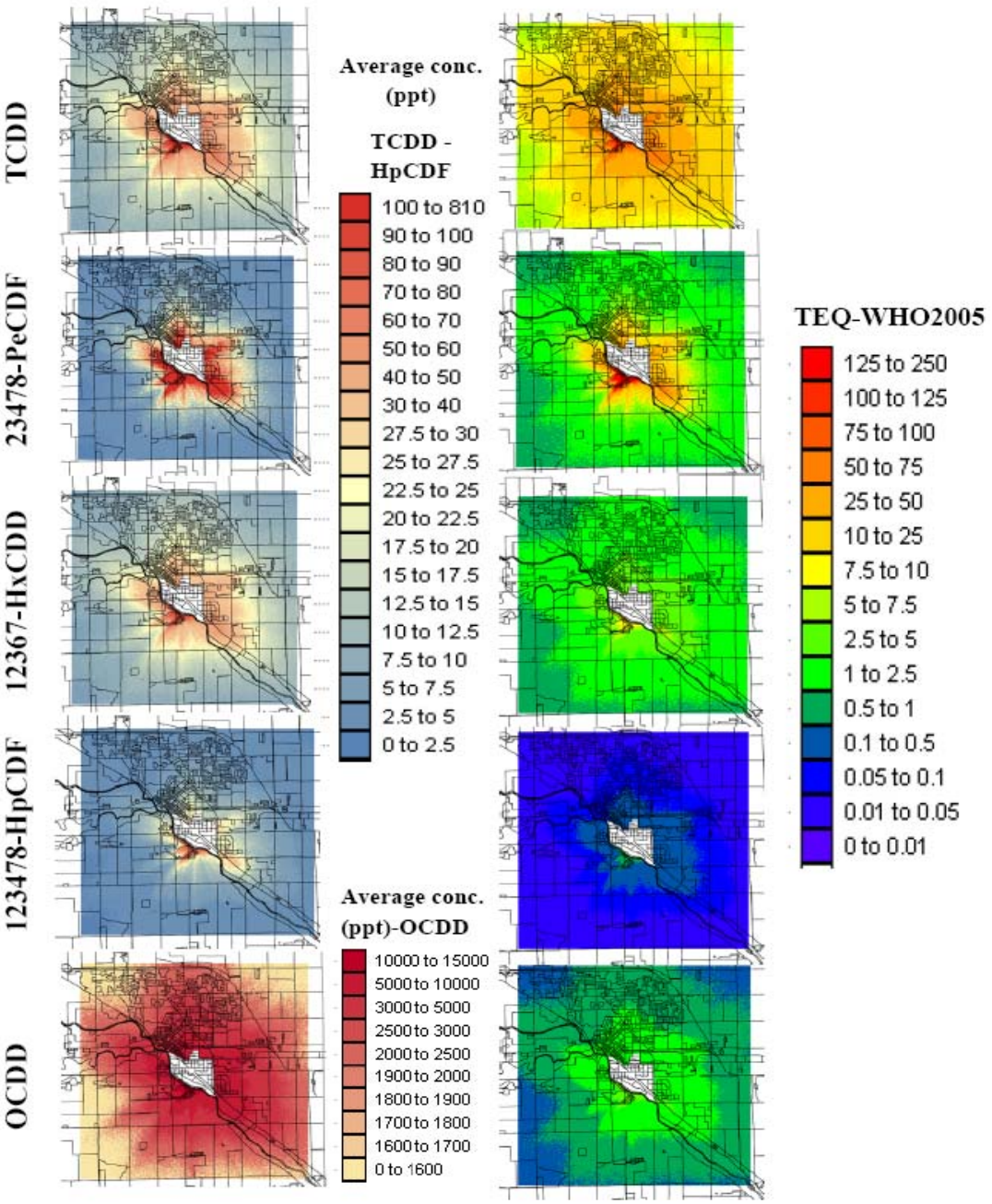

Figure2. Spatial distribution of dioxin concentration (part per trillion, ppt) in soil (left column) and the conversion of soil concentration into toxic equivalent (ppt.) according to WHO-TEF2005 scheme

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