COMPARISON OF SOIL CONCENTRATIONS OF DIOXINS AND FURANS WITH PREDICTIONS BASED ON AERIAL DEPOSITION MODELING

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Introduction

Ketchikan Pulp Company (KPC) operated its bleached pulp mill on Ward Cove north of Ketchikan, Alaska from its construction in 1954 until shutdown in 1997. To supply power for mill operations, saltwater-soaked wood waste, dewatered wastewater treatment plant sludge, and fuel oil were burned in two power boilers. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) in sludge ranged from 6 to 17 pg/g (expressed as toxic equivalent concentrations [TEQs] of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin), whereas flyash concentrations ranged from 2,800 to 6,000 pg (TEQ)/g. (TEQs are calculated assuming one-half the detection limit for non-detected congeners.) Aerial deposition modeling was used to delineate the offsite areas of maximum historical deposition of particles emitted from the power boilers. The purpose of the modeling was to identify areas for collecting soil samples to determine if PCCDs/Fs from aerial deposition posed a risk to human health or the environment. The soil sampling program was designed to evaluate these risks and was not specifically designed to validate the model predictions. However, by using a reasonable range of assumptions, the soil concentration results provided a means to check the general accuracy of the historical PCDD/F loading predicted by the model. The soil sampling results agreed surprisingly well with concentrations predicted by modeling historic deposition.

Materials and Methods

Aerial Deposition Modeling. The model, ISCST3 [1], is a Gaussian-plume based model that is most applicable in areas where a straight-line trajectory exists between the source and receptor. The input values and assumptions are discussed in detail elsewhere [2] and are summarized briefly here.

Emission rates. We estimated rates for five different periods defined by increasingly efficient air pollution controls. PCDD/F mass emission estimates for the first four periods (1954–1991) were based on a compilation of all relevant stack test data on particulate emission rates. The PCDD/F loading was then estimated by assuming that all particles had a concentration equivalent to the average value reported for electrostatic precipitator (ESP) flyash (3 ng (TEQ)/g). Stack tests for PCDDs/Fs were available for the fifth period (1991–1997), so those data were used in calculating emission rates for that period. To ensure that PCDD/F deposition rates were not underestimated, we assumed all PCDDs/Fs were in the particulate phase by increasing the emission factor by 40 percent to account for possible loss of gaseous phase PCDDs/Fs.

Following installation of ESPs in 1991, the estimated emission rate of PCCDs/Fs was approximately 73 ng TEQ/s (6.3 mg/day). Estimates of historical emission rates range from 217 to 499 ng TEQ/s, depending on the emission control system that was in place. After sludge burning was discontinued in 1997 and the only chlorine source was saltwater-soaked hog fuel, the emission rate dropped to 27 ng (TEQ)/s (post-shutdown emission data were not used in modeling).

Particle size distribution. We assumed that PCDDs/Fs were distributed on the available surface area of all particles emitted by the boilers. The particle size distributions for the different periods were estimated from literature sources [refer to 2] for bark boilers, centrifugal collectors, and, for the last period, high-efficiency ESPs.

Meteorological Data. Meteorological data collected onsite (wind speed and direction, and temperature) and at nearby National Weather Service stations from 1990 to 1995 were used to represent conditions for the 1954–1996 modeling period. During precipitation events, winds are more frequently from southerly directions, which significantly impacted model results because wet deposition was a major influence in the total deposition patterns.

Modeling Results. Estimated peak total deposition followed the wet deposition pattern. This finding is expected in the Ketchikan setting, given the high precipitation rates (average 383 cm/year). Highest offsite deposition occurred to the north of the mill on a densely forested hillside known as "Slide Ridge." Peak offsite deposition in these locations was estimated to be in the range of 1–5 μg (TEQ)/m^2.

Soil Sampling and Analysis. Twelve composite soil samples were collected from forested areas that may have been affected by aerial deposition [2]. The soils on Slide Ridge are acidic and poorly drained and consist of a thin horizon of organic soil (muskeg) that varies from less than 6 to more than 30 cm in thickness and overlies bedrock. The sampling depth (average 20 cm) was determined by the thickness of this muskeg layer for two reasons: 1) the PCDDs/Fs have been likely attenuated in this organic soil layer and 2) the only potentially significant pathway of PCDDs/Fs to ecological receptors would be through soil invertebrates to small mammals to predators; soil invertebrates, if present, would inhabit the muskeg layer, not the underlying mineral or rock material. The soil samples (as well as the ESP flyash samples) were analyzed for PCDDs/Fs by high-resolution gas chromatography/high-resolution mass spectroscopy following U.S. EPA Method 1613A.

Results and Discussion

Soil Concentrations. The TEQs in the forest soil samples showed a general decreasing trend with distance from the mill. The concentrations ranged from 80 pg/g at the station closest to the power boiler stacks to 5 pg/g at the farthest point. As a point of reference, the average forest soil background concentrations in the Ketchikan area was about 5 pg (TEQ)/g.

Conversion of Aerial Deposition Estimates to Soil Concentrations. To convert mass TEQ per unit area (ng/m^2) to mass TEQ per soil mass (pg/g), the unit area was first converted to soil volume and then the volume was converted to soil mass. The area was converted to volume by

multiplying the area by the depth of PCDDs/Fs in the soil profile. The soil volume was then converted to mass by multiplying the volume by the bulk density (g/cm^3) of the soil.

A soil depth of 20 cm was assumed for the vertical distribution of PCDDs/Fs in the forest soils. This depth is the average thickness of the muskeg horizon where, it is assumed, the PCDDs/Fs have accumulated. This vertical distribution assumes that: 1) the PCDDs/Fs have not leached downward into the soil profile and conversely, 2) the PCDDs/Fs have not accumulated in the upper few centimeters but have been distributed downward by the annual process of litter accumulation and decomposition. In estimating the depth of PCDDs/Fs in the forest soils, a conceptual model of deposition and accumulation in soils was defined: 1) Fine particles with PCDDs/Fs adsorbed to their surfaces were deposited on the foliage of the dense conifer canopy. 2) The particles were either adsorbed to the waxy cuticle of the conifer needles or washed off into the underlying forest soil. The PCDDs/Fs in the washed off particles adsorbed strongly to the decomposed litter in the underlying forest soil. The particles adsorbed to the foliage eventually were deposited to the forest floor as the needles were shed. 3) PCDD/F molecules are retained by the organic material and are not lost through leaching or surface erosion. 4) The litter is slowly decomposed, primarily by fungi in these cold, wet, acidic, organic soils. 5) Annual accumulation of leaves, twigs, cones, and branches is subsequently decomposed and buries previously deposited layers. 6) The decomposed organic material forms a "muskeg" soil over the underlying bedrock.

An unusual drought in the 1940s resulted in a hot forest fire on Slide Ridge that likely burned much of the forest floor and shallow muskeg horizons. Thus, most of the muskeg accumulated since that time has been receiving aerial deposition from the mill. Based on this conceptual model and the fire history of Slide Ridge, it can be reasonably assumed that there has been historical deposition of PCDDs/Fs in the muskeg layer, which averages 20 cm thick. Thus, the unit area of one m^2 can be converted to a typical volume of 0.2 m^3 ($2X10^5$ cm^3).

The aerial deposition model estimated that historical loading of PCDDs/Fs in the maximum offsite deposition zone ranged from 1 μg (TEQ)/m^2 to 5 μg (TEQ)/m^2. Assuming 0.2 m^3 has a mass of 50 kg (based on a bulk density of 0.25 g/cm^3 [3]), the estimated soil concentrations predicted by the model would be about 20 pg/g to 100 pg/g.

Comparison of Predicted Soil Concentrations with Measured Soil Concentrations. The predicted soil concentration contours from the aerial deposition modeling are shown together with the actual soil sampling results on Figure 1. Given the uncertainties associated with the modeling, the estimated PCDD/F concentrations of 20–100 pg (TEQ)/g in the maximum offsite deposition zone agree surprisingly well with the measured concentrations of approximately 10–80 pg (TEQ)/g.

The strong agreement between the measured and predicted concentrations is unusual given the typical degree of uncertainty in aerial deposition modeling as well as assumptions regarding transport and fate of PCDDs/Fs from combustion sources. The strong agreement is likely due to: 1) site-specific meteorological data; 2) predominant deposition close to the mill due to meteorological and topographic conditions; 3) uniformity of soil properties in the maximum deposition zone; 4) minimal degradation (i.e., insufficient light for photo-oxidation); and 5) strong retention within the soil. The model would not likely be as accurate at other sites where the input

data to the model are not as complete or where the PCDDs/Fs may be subject to environmental degradation and transport in the receptor areas.

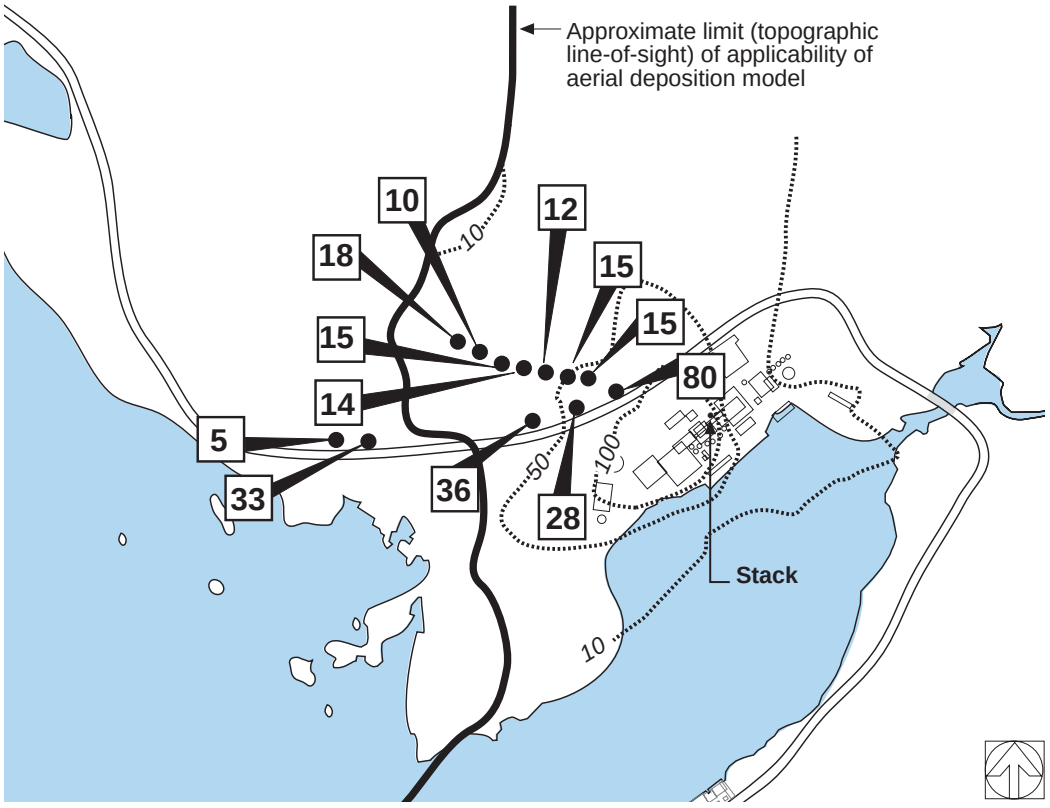

Figure 1.
Model estimates of soil concentration contours and actual soil sampling results.

References

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