Threshold Levels for PCDD/PCDF Uptake in Plants from Soil in the Canadian Arctic

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1. Introduction

The recent review of PCDDs/PCDFs by the US EPA supports the view that the wide-scale input of dioxin-like compounds to terrestrial ecosystems occurs primarily via atmospheric deposition[1]. Combustion and incineration sources contribute to PCDD/PCDF redistribution via atmospheric transport. The polar regions, including the Canadian Arctic, are known sinks for the deposition of atmospherically-transported, environmentally-persistent organochlorines including PCDDs/PCDFs, polychlorinated biphenyls, cyclodiene-type pesticides and other chlorinated pesticides[2]. The proposed mechanism for partitioning of organochlorines into cold, polar regions is summarized by Wania and Mackay[3]. The subsequent biomagnification of several organochlorines in arctic food webs, and into animals which are consumed by residents of the Arctic, is a cause for concern among the Canadian regulatory and scientific community[4].

Inputs of contaminants via long-range atmospheric transport are not necessarily indicative of impact. Deposition onto plant surfaces and levels in arctic plants, however, provide a direct indication of the potential for entry of PCDDs/PCDFs and other organochlorines into terrestrial food webs.

Soil and plant samples were collected from the eastern Baffin Island Region of the Arctic and the Yukon Territories in the western Arctic as part of a 1994-95 study to assess the fate of local PCDD/PCDF sources. Source characterization of arctic soils contaminated by local and distant PCDD/PCDF sources is described by Grundy *et al.* (these proceedings). The objectives of this study include (i) the determination of PCDD/PCDF levels attributable to long-range transport in soil and plant samples from areas removed from local input, and (ii) description of the relationship between PCDD/PCDF levels and signatures in soils and vascular plants (willow, *Salix* spp.) associated with local and distant contaminant sources. In particular, we present data that suggests a threshold for the redistribution of PCDDs/PCDFs from soils to plants.

2. Methods

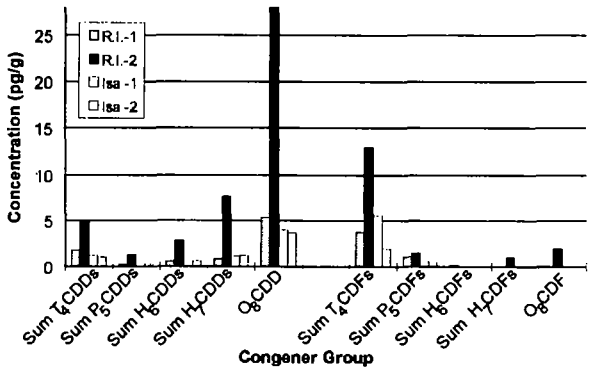
Soil and plant samples were collected as part of a larger environmental study of waste disposal sites near Iqaluit, Baffin Island, Northwest Territiories as well as studies of active and abandoned military sites throughout the Canadian Arctic. For the purpose of the discussion, samples are categorized as being collected from remote locations - i.e., in pristine tundra at least 20 km from any major site of human activity affected only by long-range transport - or from stained soils, where contaminants have been introduced directly either through spillage or aqueous transport from an adjacent contaminated area. The plant samples consisted of the above-ground portion of willows, *Salix* spp., including annually-produced leafs as well as woody portions.

The samples were analyzed for 2,3,7,8-substituted PCDDs/PCDFs by high-resolution GC/high-resolution MS. In addition, several samples were analyzed for mono-, di-, and trichlorinated PCDDs/PCDFs, non-2,3,7,8-substituted congeners and dioxin-like PCBs (IUPAC no. 77, 126, 169). Only a subset of the data is discussed below. All results are expressed on a dry-weight basis for soils and a wet-weight basis for plant tissue.

3. Results and Discussion

PCDDs in Remote Arctic Soils and Plants: The levels of PCDDs/PCDFs, expressed as the sum of congener groups for the tetra- to octachlorinated congeners in four remote soil samples are shown in Figure 1. Samples R.I. -1, and -2 were collected on Resolution Island, at a latitiude of approximately 61° 30' N., and samples Isa -1, and -2 were collected from an island in Isabella Bay at a latitude of approximately 69° 38' N. The levels of PCDDs/PCDFs in sample R.I. -2 was markedly higher than in the other remote samples; however, the dominance by hepta- and octachlorinated dibenzo-*p*-dioxins and tetrachlorinated dibenzo-*p*-furans is similar for all remote samples. The total concentration in soils of specific congener groups was generally less than 6 pg/g to 15 pg/g.

Figure 1: Levels and Signature of PCDD/PCDF Congener Group Totals in Four Remote Soil Samples



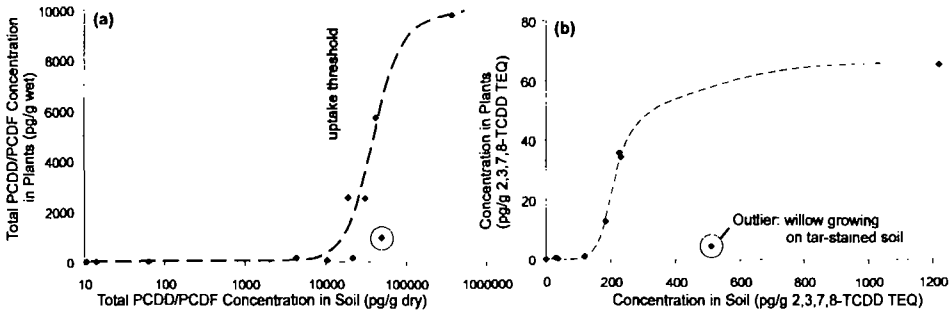
In three plant samples (*Salix* spp.) from the remote locations, individual 2,3,7,8-substituted congeners were not found at levels in excess of the detection limits (<0.1 to <0.4 pg/g), and the only congener groups detected included T_4CDD (0.3 to 0.5 pg/g), O_8CDD (<0.5 to 0.7 pg/g) and T_4CDF (0.2 to 1.2 pg/g). PCDD/PCDF levels in plants were, thus, lower in plant tissue than in the corresponding remote soil sample. This would still be true if plant concentrations were expressed on a dry-weight basis. The instantaneous partitioning of PCDDs/PCDFs onto plant surfaces from an atmospheric source should be greater in magnitude than deposition to soils, given the higher lipid-, and organic carbon-content of the leaf surface; however, the willow analytical samples included the woody, perennial portions of the plant with a low surface area to mass ratio relative to leaves. Annual shedding of leaves would also result in the long-term accumulation of contaminants into underlying soils, as opposed to woody plant structures. Samples representative of the entire above-ground portion of arctic plants were collected and analyzed since the entire plant is often consumed by herbivores such as caribou, musk-ox, or arctic hare.

PCDDs/PCDFs at a Locally-Contaminated Site: The range of concentrations of dioxins and furans, expressed as the sum of all tetra- to octachlorinated dibenzodioxins and furans, in the locally-contaminated soil near Iqaluit was 2,700 pg/g (or parts-per-trillion, ppt) to

370,000 pg/g (n = 12). Similarly, the range in plant samples of total concentration of tetra- to octachlorinated dibenzodioxins and furans from the same area was 73 to 9,800 pg/g (wet weight basis) (n = 6). The range of dioxin/furan levels in Iqaluit soils when expressed as a 2,3,7,8-TCDD TEQ was 73 to 9,800 pg/g. Similarly, the range of corresponding plant concentrations was 0.5 to 66 pg/g 2,3,7,8-TCDD TEQ. It is apparent that the concentrations of dioxins/furans in plants is generally much lower than the underlying soil at both locally-contaminated sites, and in areas subject to deposition in association with long-range atmospheric transport. Data are available from an additional 3 soil and 2 plant samples from Resolution Island in areas contaminated with PCB- and dioxin-containing dielectric fluid.

Soil-Plant Relationships: PCDD/PCDF levels in plants were related to soil levels in a non-linear fashion, as illustrated in Fig. 2. The sigmoidal curves were hand-fitted using a limited amount of data (n = 11), and are therefore somewhat speculative; the data do suggest, however, that there is a threshold concentration of dioxins/furans in arctic soils below which there is little uptake in plants. One plant sample had a much lower concentration of dioxins/furans than the other plants relative to the level in the underlying soil. This sample is identified as an outlier in Fig. 2a, since the soil here was atypical for the site, and was composed of a tar-like substance. The presence of tar in soil undoubtedly limits soil porosity and affects other soil properties which control the affinity of soil particles for organochlorine contaminants.

Figure 2: Uptake of PCDDs/PCDFs from Soil by Willows at Locally-Contaminated Sites on Baffin Island, Northwest Territories.



The relationship between dioxins/furans in soils and plants may also be asymptotic at higher concentrations; that is, plant levels may reach a maximum after which increasing levels in soils are not reflected in further plant uptake. This latter possibility must be viewed cautiously, given the limited amount of data; however, an upper limit to uptake might be attributed to a limited above-ground surface area for adsorption from the air. Many plants, including many willow species, have fine hair-like projections or other structural features which increase surface area.

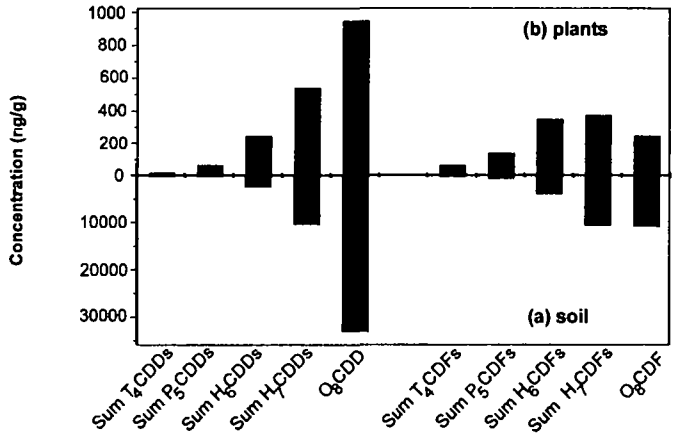
The apparent uptake threshold for plants collected from the locally-contaminated sites merits critical evaluation, since uptake into plants directly controls bioavailability to the Arctic terrestrial foodweb. The published literature suggests that uptake of dioxins and furans by above-ground portions of plants occurs via the air; i.e., through adsorption from either the vapour phase or deposition of air-borne particulates. Root crops, on the other hand, may adsorb dioxins directly from soil, at least in external tissues. Uptake onto above-ground

portions of willow (*Salix* spp.) at Iqaluit or Resolution Island should be controlled by the net effect of upward loss from soil and deposition onto leaves and woody structures. Other influences on plant uptake of air-borne contaminants should include factors such as the mass of contaminants in surrounding soils which is available for aerial transport, and climatic conditions such as the strength and prevailing direction of the wind, or the amount of precipitation.

One plausible mechanism for a threshold level in soil below which uptake of dioxins/furans in plants is limited relates to the number of reversible binding sites in surface soils. For example, soils might exhibit a retention threshold where there is a high affinity between dioxins/furans and a limited pool of organic carbon. Beyond this threshold, retention of dioxins and furans adsorbed to soil particles would rely on weaker interactions. This mechanism requires that uptake from soils by above-ground portions of plants be controlled primarily by transport in the vapour-phase in local air masses.

The composition of congener groups in plants versus soils is, in fact, consistent with plant uptake from the vapour phase. The dioxin/furan congener composition of soils and plants from the Iqaluit site or Resolution Island are shown in Fig. 3.

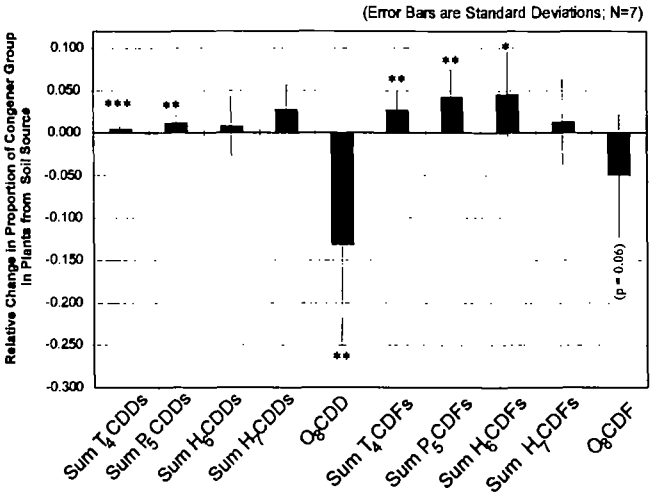
Figure 3: PCDD/PCDF Congener Signatures of Soil and Plant Samples from the Iqaluit Strategic Air Command Base and Resolution Island.



The averaged congener signatures of soil and plant samples is similar. If the relative proportion of individual congener groups in soils, however, is subtracted from that of the corresponding plant samples, then the difference between plants and soils is more easily distinguished (Fig. 4).

The dioxin/furan congener composition in plants was significantly enhanced relative to the source in soils for the tetra- and pentachlorinated dibenzodioxins and furans, and significantly diminished for congeners with a lower volatility, i.e., octachlorodibenzodioxin and furan. The change in congener composition is best explained by differences in the average vapour pressure of the congener groups. This, in turn suggests, that dioxin/furan uptake in plants at the Iqaluit site occurs primarily from the vapour phase rather than through the deposition of contaminated particles on plant surfaces.

Figure 4: Bias in the Congener Uptake of Dioxins/Furans by Plants from Arctic Soils
Proportion in Plant vs Soil:(paired sample t-test); * p < 0.05; ** p < 0.01; *** p < 0.001



4. Conclusions

The deposition of dioxins and furans onto the above-ground portion of plants from atmospheric sources is a major source to terrestrial food webs on a global scale. The redistribution of PCDDs/PCDFs and other organochlorines from sources in industrialized, urbanized regions to remote areas including polar regions has been extensively documented; however, we are only beginning to understand the factors that control bioavailability to lower-trophic order organisms and subsequent biomagnification in animals at higher trophic levels. There is still some uncertainty regarding the possibility of a concentration threshold for molecular/biochemical responses to 2,3,7,8-TCDD in target organisms, via activation of the Ah receptor[5,6]. Our data suggest that threshold levels are also plausible on a geochemical/ecological scale.

5. References

1) Anon (1995). Dioxin Risk: EPA's Dioxin Reassessment. Environ. Sci. Technol. 29(1), 26A-28A.
2) Barrie, L.A., D. Gregor, B. Hargrave, R. Lake, R. Shearer, B. Tracey and T. Bidleman (1992), Arctic Contaminants: Sources, Occurrence and Pathways. Sci Tot. Environ. 122, 1-74.
3) Wania, F. and D. Mackay (1993). Global Fractionation and Cold Condensation of Low Volatility Organochlorine Compounds in Polar Regions. Ambio, 22(1), 10-18.
4) Muir, D.C.G., R. Wagemann, B.T. Hargrave, D.J. Thomas, D.B. peakall and R.J. Norstrom (1992). Arctic Marine Ecosystem Contamination. Sci. Tot. Environ. 122: 75-134.
5) Clapp, R., P. deFur, E. Silbergeld and P. Washburn (1995). Dioxin Risk: EPA on the Right Track. Environ. Sci. Technol. 29(1), 29A-30A.
6) Environ Dioxin Risk Characterization Expert Panel (1995). Dioxin Risk: EPA Assessment Not Justified. Environ. Sci. Technol. 29(1), 31A-32A.