MEASUREMENT OF 29 DIOXIN* CONGENERS IN 165 AMBIENT SOIL SAMPLES ACROSS 1000 SQ. MILES OF DENVER'S FRONT RANGE

(*POLYCHLORINATED AROMATIC HYDROCARBONS)

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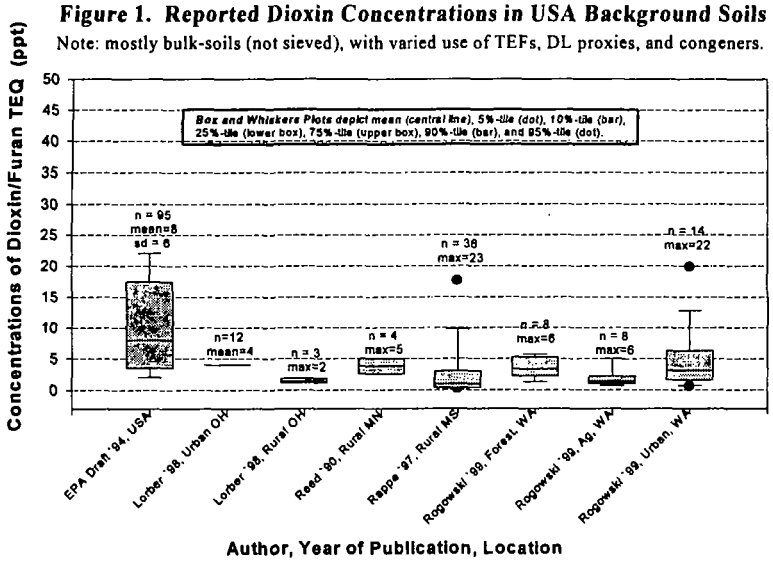
Introduction

Accurate information on the quantities and types of dioxins (chemicals with 2,3,7,8-TCDD-like Ah-agonistic activity) in ambient soils is needed for several important reasons in risk assessments that are conducted by the US Environmental Protection Agency (EPA). As with any potent toxicant that poses potential risks at trace-level concentrations in the environment, the understanding of background levels found from non-point sources becomes essential. Reference concentrations should be collected from representative exposure media, geographical areas and relevant times so that they can best be used in risk assessment and risk management for several purposes[1,2]: 1) to distinguish site-related sources of contamination from natural or anthropogenic levels, leading to a) demarcation of boundaries of where the gradient of point-source contamination falls off to non-point source levels, and b) knowledge about how far to clean to, when potential for excess risks exist down to background levels; 2) to understand the potential for incremental risks from exposure to point sources of contamination vs. risks presented by exposure to ubiquitous background levels; and 3) for comparing local background levels with media-concentrations cited in promulgated standards or laws, such as ARARs (applicable or relevant and appropriate requirements).

It is well known that dioxins have been produced and released to the environment from a wide range of anthropogenic and natural sources or activites[3]. A review of recent literature on ambient levels of dioxins in USA soils shows data to be limited and quite uncertain for quantitative uses in risk assessment[4,5,6,7,8]. Figure 1 shows historical literature values for dioxins that range from about <1 to >20 ppt, but these concentrations of TEQs (toxic equivalents of 2,3,7,8,-TCDD) are calculated from substantially varying conditions. The studies differed in or did not specify: a) soil sampling depths, locales, and processing; b) sources of TEFs used to calculate TEQs; c) the definitions of analytical detection and quantitation limits, and the extent of quality control; d) the use of proxy values for non-detects; e) the numbers and types of dioxin-like congeners analyzed; and f) the periods of time when soil samples may have been contaminated by varying source emissions of dioxins. These confounders could conceivably produce uncertainty in soil background concentrations of dioxin TEQs by as much as 10 to 100 fold, which greatly hinders the ability to confidently extrapolate these data for quantitative use in risk assessments at other sites across the nation.

Figure 1. Reported Dioxin Concentrations in USA Background Soils
Note: mostly bulk-soils (not sieved), with varied use of TEFs, DL proxies, and congeners.



Based on this assessment and conversations with national experts, EPA Region VIII decided that the historical data were too uncertain to use, and therefore conducted a study that better estimates concentrations of dioxins in reference soils from the Denver, CO, Front Range. These results can then be used with more certainty, in terms of applicability and quantitativeness, for EPA R8 risk assessments in the local area and perhaps elsewhere. Attempts were made in the sampling design to overcome many limitations of past background studies, potentially making the new data more useful for quantitative risk assessment and risk management of hazardous waste sites where contamination of soils by dioxins may be a human health related or an ecological concern.

Methods and Materials

The main objective of this study design was defined as to "characterize the existing dioxin concentrations in surface soils from multiple locations and multiple land use categories in the Denver Front Range area." The data collected during this study will be used by EPA risk assessors and risk managers to help determine whether concentrations of dioxins in surface soils at CERCLA, RCRA, or other sites are higher than those which occur in similar lands that are not known to be impacted by any specific point sources of dioxin releases, and whether or not dioxins need to be evaluated as a chemical of potential concern to either humans or ecological receptors.

The study design for the sampling and analyses of surface soils included the following aspects:

- identify public lands to collect samples from over a >1000 sq. mi. area along the Front Range
- select spatially representative locations over the study area according to 5 major land-uses
- through voluntary public participation, access properties and collect soil samples per SOPs:
  - sample least disturbed surface soil from the top 2 inches, removing vegetation and gravel
  - use disposable clean supplies, chain of custody procedures, random blind sample labeling
  - record the field descriptions, photographs, GPS (global positioning system) coordinates

  - verify soil's land-use as residential, commercial, industrial, agricultural, or open space; and collect about 30 representative samples for each land-use over a short time period
  - insert random, blind, field blanks and duplicates at 5% rate to processing lab – C.A.S.
- sieve the soil samples to <250 um for analyses, as well as analyzing about 5% of bulk soils
- submit samples to analytical lab with 5% QC: splits, spiked standards at 35 and 59 ppt TEQ
- merge and refine analytical methods[9] 8290, 1613, and 1668 to achieve more accuracy with the isotope dilution, high resolution, gas chromatography/mass spectrometry method at the MDL
- analysis of all 29 congeners with 2,3,7,8-TCDD-like activity: 7 dioxins, 10 furans, 12 PCBs
- define detection limits (DL) and quantitation limits, validate the data[10], use WHO TEFs[11]

Results and Discussion

Soil samples were collected from December 1999 until March 2000, as weather and public access permitted. Good spatial representation and adequate sample sizes per each land-use were achieved (see Figure 2). All soil samples have been processed with sieving and for archiving, and analyses are expected to be completed by summer 2000. Laboratory performance using the merged methodology was excellent, as demonstrated by QC results that are very close to target ranges. The refined method has been producing MDLs (defined as 2.5 times the signal to noise ratio) of about 1ppt TEQ from the 2,3,7,8-substituted PCDD/Fs, with MQLs at about 4 ppt. This level of quantitation provides good confidence in the reference soil concentrations and is sufficiently low for use in distinguishing background or ambient soil concentrations from elevated site contamination. This MQL was attained with the use of extra sample mass and insertion of an extra low calibration standard, so the previously reported results with soil concentrations below these levels (i.e., <1 to 5 ppt) are suspect in terms of their certainties for reported quantities of TEQ.

Current results from analyses of Denver Front Range soils show that the mean concentrations of TEQs, based on the 2,3,7,8-polychlorinated dioxin and furans, are less than the 8 ppt estimated in the draft 1994 EPA Dioxin Reassessment Report[4]. Figure 3 shows that out of 34 soil samples analyzed by June 2000, an average TEQ of 1 ppt was found in sieved surface soil from a mix of all land-uses in the Denver Front Range. In addition, peripheral soil at the Rocky Mountain Arsenal in Denver, which was the first site evaluation for soil dioxins, also had low mean levels of TEQ.

Figure 2. 165 Soil Sample Locations

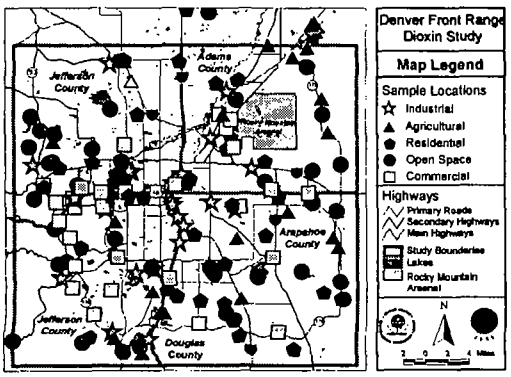
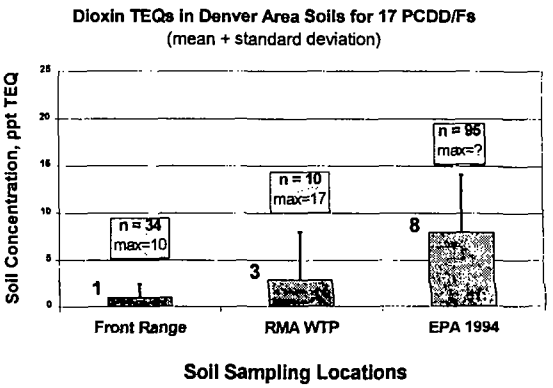


Figure 3. Results of Soil Study



In conclusion, this study is the largest and most comprehensive scientific investigation that has

ever been conducted on the quantitative concentrations of dioxin TEQs in reference soils. Even though sieving of soils showed some relative increases (a near doubling) in dioxin concentration associated with smaller particle sizes, the background concentrations of dioxins in the urbanized Front Range soils around Denver may be nearly 10-fold lower than anticipated from the previous reports in the literature. If the proposed levels of safe exposure to environmental dioxins decrease, then these methods and results will become more important in site evaluations of dioxins in soils.

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