Dioxin2015

A FIELD EXAMPLE OF DIOXIN-LIKE COMPOUND TRANSPORT IN CONSOLIDATED GLACIAL TILL

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Introduction

Measurements of 17 dioxin and furan congener concentrations were made as successive layers of clay soil were excavated at a former municipal and industrial dump site. The measurements demonstrate separation of 1,2,3,4,6,7,8-HpCDD, 2,3,7,8-TCDD, and OCDD with depth. Application of the advective-dispersive one-dimensional transport equation for a reactive solute resulted in a reasonably good fit to subsurface measurements. To calculate 1,2,3,4,6,7,8-HpCDD, 2,3,7,8-TCDD, and OCDD concentration distributions, all variables were treated as constants except the retardation factor, R_d and initial concentration, C_o, which depended on the congener being modeled. A good fit between the measured and calculated concentration distribution with depth occurred when the ratio of R_d's was 6:1:3.5 for 1,2,3,4,6,7,8-HpCDD, 2,3,7,8-TCDD and OCDD respectively. These results indicate greater subsurface transport rates for both OCDD and 1,2,3,4,6,7,8 HpCDD relative to that of 2,3,7,8-TCDD than would be expected if R_d varied in similar proportion to octanol-water partitioning coefficients (K_{ow}). Dioxin-like compounds other than 1,2,3,4,6,7,8-HpCDD, 2,3,7,8-TCDD, and OCDD were not detected in the subsurface at reportable concentrations.

The dioxin-like compounds evaluated at this site are those compounds with nonzero toxicity equivalency factors as identified in Estimating Exposure to Dioxin-Like Compounds , EPA/600/6-88/005B[1].

Materials and methods

Dioxin and furan measurements were made in 1996 and during recent remediation of the Krejci Dump Site[2,3,4,5]. The roughly 200,000 m^2 site is a former municipal and industrial dump and salvage located within the Cuyahoga Valley National Park in Summit County, Ohio, USA. During the years of operation, from approximately 1950 to 1980, large volumes of solid and liquid waste materials were brought to the dump, where significant quantities of hazardous substances were released to the environment as a result of open dumping, spills, leaking containers, and burning. The United States purchased the land in 1980 for management by the Department of the Interior National Park Service (NPS). In 1987, it was determined that the Site may constitute a threat to human health and the environment. In response to this determination, the U.S. Environmental Protection Agency (EPA) initiated an emergency removal in June 1987. In November 1988, NPS completed the removal of wastes staged during the initial EPA activity, as well as the removal of some unconsolidated wastes and contaminated soil. Large quantities of debris and contaminated soil remained. Extensive investigations were performed during 1995 and 1996. Debris and soils containing unacceptable levels of contaminants were excavated and removed from the site between October 2005 and December 2011.

Sampling and Measurement Processes

The 1996 site characterization determined that dioxin-like congener concentrations in surface soil were discernable from background within and adjacent to a 10 m to 20 m deep debris-filled ravine where a fire had purportedly burned during most of the facilities 30 years of operation. Seventeen discrete locations were investigated during this event. The dioxin and furan contaminated area was determined to be approximately 44,000 m^2. Many other chemical contaminants were also found to be present[5].

It was determined that soil having a calculated 2,3,7,8 TCDD toxicity equivalency factor (TEQ)[1] greater than 3 pg/g was to be excavated and removed from the site[6]. Initially, debris, visibly contaminated or altered soil, and minimally 15 cm of native soil were removed. This removal was followed by collection of 40-part composite soil samples representing each of 11 approximately 4000 m^2 areas. The 11 areas are outlined on Figure 1.

Equal volume increments of surface soil were collected at 10 m spacings and combined to create the composite samples. The concentrations of 17 dioxin and furan congeners were determined. Only 2 of the 11 areas achieved the TEQ goal of 3 pg/g following this initial removal effort.

A second effort was made to remove the soil contaminated with dioxin-like compounds. The 11 areas described in the previous paragraph were each divided into four approximately 1000 m^2 subareas shown on Figure 1. Within each of the 11 areas, minimally 15 cm of soil was removed from the entire surface of one or more of these subareas. Subsequently, 40-part composite samples representing each of 11 approximately 4000 m^2 areas were collected and analyzed for dioxin-like compounds. At the end of this second effort, 5 of the 11 areas had achieved the 3 pg/g TEQ goal.

Subsequent excavation, sampling and testing episodes focused on the remaining subareas having calculated TEQ greater than 3 pg/g. The excavation, sampling and analysis sequence was iterated in each subarea until the calculated TEQ of the subarea composite sample was less than 3 pg/g. Each subarea sample was a representative 40-part composite of surface soil created using equal volume soil increments collected from node points of an approximately 5 m grid. Each failure to achieve the desired TEQ resulted in minimally 15 cm of soil being removed from the entire subarea. Excavation as deep as 1.7 m was required to achieve the TEQ goal in the remaining 24 subareas. Three of the subareas required no additional excavation.

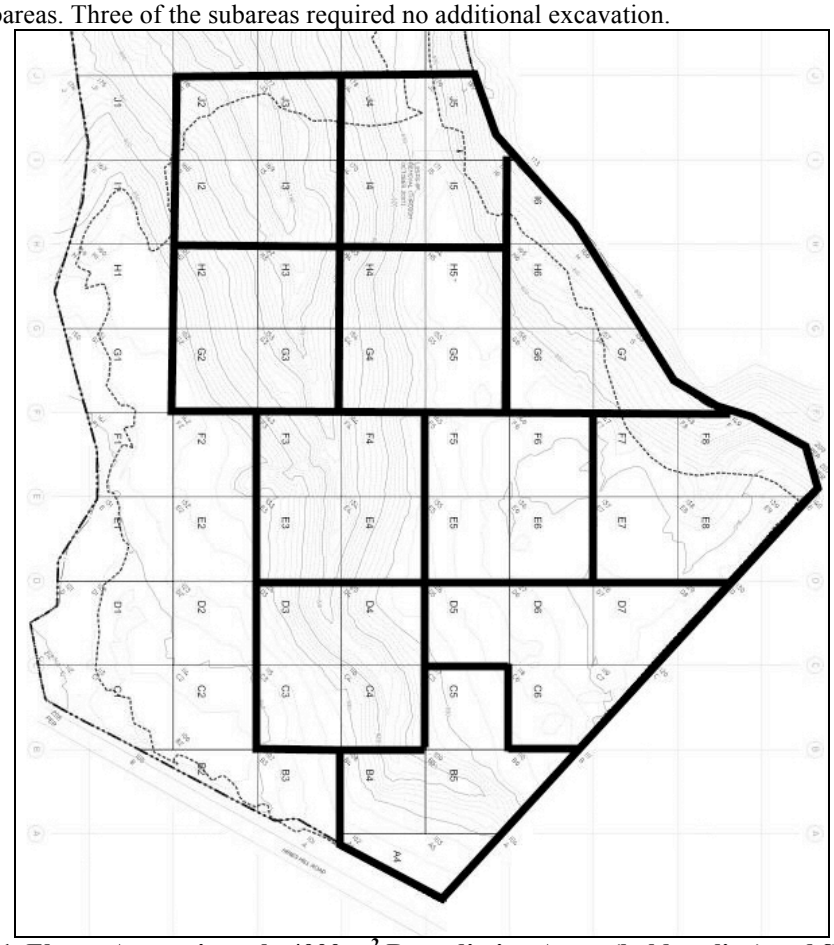

Figure 1. Eleven Approximately 4000 m^2 Remediation Areas (bold outline) and Subareas

Stratigraphy

The site is located on a narrow ridge of glacial, glaciofluvial, and lacustrine sediments within the buried pre-glacial valley of the Cuyahoga River (41°16'18.11"N, 81°32'40.64"W). These sediments are at least 200 feet thick beneath the site and consist of four basic glacial till units[5]. Only the upper two of these units are pertinent to this discussion.

The uppermost unit consists of approximately 10 m of weathered, dense, homogenous, relatively stiff, yellow-brown clay till with a few scattered pebbles and cobbles. Naturally occurring near surface soil is typically lean clay with about 10 percent fine sand and about 90 percent medium-plasticity fines (fines are particles less than 0.075 mm in size.). In-situ dry unit mass is about 1680 kg/m^3 and the particle average specific gravity is about 2.7. Near surface clay minerals are composed of about 5 to 25 percent vermiculite, 5 to 25 percent illite/mica, and 5 to 20 percent kaolinite, and contain minor traces of mixed-layer minerals. The stratum is continuously saturated. Laboratory measurement of hydraulic conductivities ranged from 2.8 x 10^{-8} cm/s to 8.6 x 10^{-8} cm/s. However, significant high angle to vertical fractures occur throughout the strata. Six approximately 46-cm diameter surface infiltration tests and one of the laboratory tests measured hydraulic conductivities ranging from 7 x 10^{-6} cm/s and 6 x 10^{-5} cm/s [5].

The lower second unit is 20 m to 30 m of predominantly unweathered, dense, gray lean clay, approximately 95 percent fines, containing a few pebbles and cobbles and infrequent 0.7 m to 3 m thick zones of thinly laminated slits and clays of lacustrine origin. This unit also contains occasional lenses of silt or sand which are generally 0.3 m to 1 m thick. These lenses are expected to be isolated, discontinuous, and may not be oriented horizontally. This soil is highly erosive. Fracturing is infrequent in this layer. Laboratory testing measured hydraulic conductivity of the gray clay ranging from 1.5 x 10^{-8} cm/s to 8.7 x 10^{-8} cm/s.

The approximately 10 m to 20 m deep ravine in which the subject dioxin and furan contamination was found completely incises the yellow clay unit and extends about 10 m deep into the gray clay unit. Fourteen measurements of cation exchange capacity representing both deep and shallow clays at the site ranged between 6.9 meq/100g and 15.1 meq/100g. Twenty-one site-wide measurements of total organic carbon content, representing near surface soil, ranged between 4.7 and 0.28 percent with an arithmetic mean of 1 percent.

Expected Dioxin-Like Compound Vertical Concentration Distribution

Surface dioxin-like compound measurements were made at 17 locations during the 1996 site characterization. There were no subsurface measurements made prior to initiating excavation in 2005. Dioxin-like compounds moved vertically downward through the soil by mechanisms of advective transport and diffusion. It is likely that other organic contaminants, such as solvents, may have facilitated dioxin-like compound movement. Information was insufficient to formulate a useful transport model. Nevertheless, it was expected that 2,3,7,8 TCDD would move a greater distance into the ground than most other measured dioxin and furan congeners. This expectation was derived from the observation that the K_{ow} for 2,3,7,8 TCDD is generally estimated to be substantially lower than that of the other congeners present at the site at notable concentrations. Compounds having higher K_{ow} are more likely to sorb to organic matter within the soil thereby impeding transport.

Results and discussion:

The dioxin-like compound investigation programs and results are presented and discussed in several project reports [2,3,4,5]. Of the 17 dioxin and furan congeners investigated, only three had reportable concentrations in subsurface soil following the second excavation effort. These were 1,2,3,4,6,7,8 HpCDD, 2,3,7,8 TCDD and OCDD. Concentrations were observed to decrease with depth for all three of these compounds. The ratios of measured concentrations to the measured surface concentration following the second excavation effort were calculated and are presented on Figures 1, 2 and 3. Individual subareas are identified in the legends of these figures using alphanumeric notation. The depth of the initial soil excavation was not measured but observations suggest it varied between 0.5 m and 2 m. A depth of 1 m is used to represent the initial excavation on Figures 1, 2, and 3 and the graphs are shaded in this depth range to remind the reader that this depth is uncertain. It is also noteworthy that varied physical characteristics of the soil removed by initial excavation were observed.

The well-known solution to the advective-dispersive equation for one-dimensional flow through soil of reactive solutes subject to reversible sorption reactions was fit to each of the distributions. The calculated results are shown on Figures 1, 2 and 3. All variables in the equations were held constant for all calculations except that different R_d and C_o were selected to represent each congener. A good fit between the measured and calculated concentration distribution with depth occurred when the ratio of R_d's was 6:1:3.5 for 1,2,3,4,6,7,8-HpCDD, 2,3,7,8-TCDD and OCDD respectively.

These results would suggests greater subsurface transport rates for both OCDD and 1,2,3,4,6,7,8 HpCDD relative to that of 2,3,7,8-TCDD than expected if R_d were to vary in approximate proportion with octanol-water partitioning coefficients (K_{ow}). Transport facilitated by dissolved solvents is suspected.

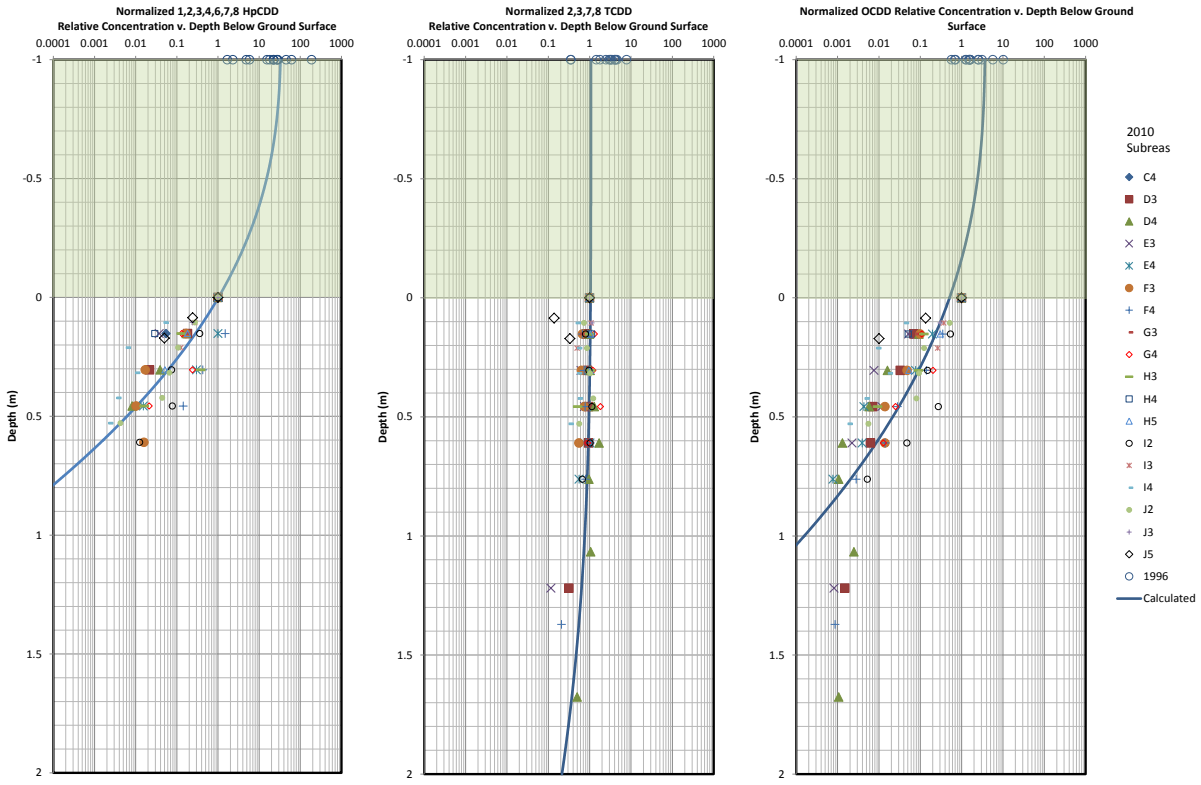

Figure 2. Relative Concentration Measurements v. Depth

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References:

1. Blancato, J., D. Cleverly, R. Fares, G. Huse, M. Lorber, J. Schaum, G. Schweer, AND P. White. Estimating Exposure to Dioxin-Like Compounds. U.S. Environmental Protection Agency, Washington, D.C., EPA/600/6-88/005B (NTIS PB95148193.
2. U.S. Bureau of Reclamation, Technical Memorandum No.11, Krejci Dump Site Supplemental Soil Sampling Plan, Dioxin/Furan Investigations, Memorandum to Mr. Richard Smith, Ohio Environmental Protection Agency, Northeast District Office, 2110 Aurora Road, Twinsburg OH, Sept. 27, 1996. http://www.mcggeotechnical.com/ (see Documents tab)
3. U.S. Bureau of Reclamation Technical Memorandum, Krejci Dump Data Transmittal, Dioxin Sampling, Memorandum to Mr. Richard Smith, Ohio Environmental Protection Agency, Northeast District Office, 2110 Aurora Road, Twinsburg OH, December 12, 1996. http://www.mcggeotechnical.com/
4. U.S. National Park Service, Data Usability Report 3, Cleanup Verification Sampling Data, Krejci Dump Site, Cuyahoga Valley National Park, Summit County, Ohio, Prepared by: MCG Geotechnical Engineering, Inc. 4817 South Zang Way, May 2012. http://www.mcggeotechnical.com/
5. U.S. Bureau of Reclamation, Final Remedial Investigation Report, Krejci Dump Site, Cuyahoga Valley National Recreation Area, prepared for the National Park Service by the Bureau of Reclamation, Lakewood CO. June 2000
6. U.S. Bureau of Reclamation. 2002. Record of Decision, Krejci Dump Site, Cuyahoga Valley National Park, September 2001.