DECISION UNIT SELECTION IN INCREMENTAL SOIL INVESTIGATION OF MULTIPLE POTENTIAL SOURCES AND STATISTICAL TREATMENT OF DIOXIN AND FURAN RESULTS

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Abstract

To evaluate contamination from 3 potential sources with diferent conceptual depositional pathways, CH2M performed a Soil Investigation using Incremental Sampling Methodology (ITRM, 2012). Areas where drums and waste were stored above ground on permeable surfaces were identified as potential sources via spills or leakage, and 4 Decision Units (DU) of restricted area (<5,000 m^2) and high sampling density (approx. 4m/pt.). A former waste incinerator was identified as potential source of dioxins and furans via atmospheric deposition, defining a 5th DU. Within this area, a third potential source was identified as a storage for Ascarel-containing transformers, and a smaller DU with higher sampling density was subset into the Dioxin sampling area to ascertain the presence of PCB´s via a spillage/leakage scenario.

Results of parameters with concentration-based regulatory standards where treated statistically by calculating the 95% Upper Confidence Level mean value of 3 replicate ISM samples using Chebyshev´s Inequality, and the Toxic Equivalencies (TEQ) of Dioxin and Furan congeners were calculated using World Health Organization toxicity factors to obtain total TEQ for each replicate sample before similar statistical treatment.

Results between replicate samples were consistent to within one order of magnitude, and statistical estimations of the mean value of respective analytes allowed for a evaluation of the area in manner conservative, defensible, and protective of human health.

Palavras-chave: Amostragem Multi-Incremento, Dioxinas, Furanos

1 - INTRODUÇÃO

CH2M HILL was contracted by a confidential client to conduct a soil investigation using Incremental Sampling Methodology (ISM) at an industrial site involved with the production of defensive agricultural products. In addition to performing sampling and evaluating analytical results, CH2M HILL employed *a priori* knowledge of the site´s history, including a Conceptual Site Model developed in a prior CH2M HILL project, in order to develop specific areas of interest for sampling and decision-making called Decision Units (DUs) that are *specific to each area* considering its past use, potential contamination sources, and possible human exposure pathways.

2 – OBJETIVOS

The objective of the study was to evaluate the exposed soil in areas identified as former drum/waste storage areas, a former incinerator, and a transformer disposal area.

3 – METODOLOGIA

ISM is a structured composite sampling and processing method designed to produce analytical results representative of defined volumes of soil specified in the investigation. ISM is designed to reduce the variability between measurements that occurs with discrete soil sampling approaches due to the heterogeneous spatial distribution of contaminants and the particulate nature of soil. In order to limit this variability, ISM uses controls in both the field sample collection and the processing and preparation of the sample for laboratory analysis.

ISM produces a single analytical aliquot with constituent concentrations present in the same proportion as in a defined volume of soil, known as a Decision Unit (DU).

Decision Unit Selection:

Historical aerial image analysis of the site identified several areas where drums, waste products, and scrap were stored in several unpaved and paved areas since at least 1977. These areas were then evaluated based on: a) the potential contaminants presented by the source, b) the deposition/contamination scenario likely from the source, and c) the human exposure pathways presented. These criteria allowed CH2M HILL to determine the size, sampling density (# of increments collected/area), analytical parameters, and depth interval of collection of soil.

Depth Intervals:

Soil increments comprising the ISM sample for dioxins and furans in the area of the former waste incinerator were collected from 0-5 cm bgs. This interval was selected as the potential source of these compounds was identified in the Conceptual Site Model as former incinerator, whose ashes and particulate matter may have been deposited superficially. Furthermore, the low solubility of dioxins and furans means these compounds are highly resistant to leaching and vertical transport and thus relatively immobile in the soil profile.

Toxic Equivalency Factors (TEF) and total Toxic Equivalency (TEQ)

The total Toxic Equivalency (TEQ) for all 17 Dioxin and Furan congeners analyzed was calculated using the 2005 World Health Organizations Toxic Equivalency Factors (TEF) assigned to each Dioxin and Furan congener. These TEF´s essentially act as coefficients to convert detected concentrations of congeners of lesser known-toxicity to be a comparable (in terms of toxicity and health risk) concentration of the most known-toxic dioxin congeners, 2,3,7,8,-TetraCDD and 1,2,3,7,8-PentaCDD.

Statistical Treatment of Laboratory Results:

Due to the inherent heterogeneity in soils and potential spatial variance in concentration levels of soil-borne contaminants, neither the individual concentrations reported in the analytical results for a given set of replicate samples nor the mean of these values can be considered the true mean concentration of any potential contaminant in a DU. The use of a statistical estimate of a DU´s true mean concentration is a conservative approach that is protective of human health, and typically provides mean concentrations higher than those derived using a simple arithmetic average. In order to estimate the true mean value for decision-making purposes, a statistical approximation of the true mean called the 95% Upper Confidence Limit (UCL) was calculated using the *Chebyshev* method. The *Chebyshev* method does not require the use of any *a priori* data to constrain the upper limits of the calculated mean value and is designed to achieve or exceed the desired coverage to include the true mean of data populations regardless of the non-normality or skewness of distribution. As such, the *Chebyshev* method tends to estimate higher mean concentrations in a given DU than other methods, such as the *Student´s t-test,* and is considered a conservative approach in estimating the true mean concentration of a constituent in a DU.

The *Chybyshev* 95% UCL is calculated as follows:

$UCL = \bar{X} + \left(\sqrt{1/\propto - 1}\right) \times \frac{S_{\bar{X}}}{\sqrt{r}}$ Where:

$\bar{X}$ = arithmetic mean, $S_{\bar{X}}$ = standard deviation of all ISM samples, r=number of ISM samples, α = alpha level, or the probability of rejecting a true null hypothesis. Alpha is equal to 1 minus the desired confidence level. Thus, for a 95% confidence level, alpha = 0.05

For all cases in which at least one replicate sample (A, B, or C) resulted in a non-detection and another replicate sample returned an analytical detection, the value of the non-detect was assumed to be equal to the limit of quantification for the purpose of statistical estimation of the true mean concentration in DUs.

4- RESULTADOS

The results of the investigation showed that, while trace concentrations of various dioxin and furan congeners were detected, neither the most known-toxic congeners (2,3,7,8,-TetraCDD and 1,2,3,7,8-PentaCDD) were present in the study area, nor did the 95% UCL estimate of the true mean value of the Decision exceed USEPA Regional Screeening Levels, as shown below.

Total Toxic Equivalency (TEQ) of Dioxin and Furan congeners - (ng/kg)	**Laboratory Results**		
	Sample A	**Sample B**	**Sample C**
WHO-PCDD/F-TEQ 2005 excluding LOQs[a]	**0.280**	**0.532**	**0.831**
WHO-PCDD/F-TEQ 2005 including LOQs[b]	**3.37**	**3.47**	**3.77**
Simple Mean	**Arithmatic Mean of Replicate Samples (A,B,C)**		
WHO-PCDD/F-TEQ 2005 excluding LOQs[a]	**0.55**		
WHO-PCDD/F-TEQ 2005 including LOQs[b]	**3.53**		
Chebyshev´s Calculation of Mean	**95% UCL Mean of Replicate Samples (A, B, C)**		
WHO-PCDD/F-TEQ 2005 excluding LOQs[a]	**1.24**		
WHO-PCDD/F-TEQ 2005 including LOQs[b]	**4.06**		
Regional Screening Level - USEPA (2014)	***22.00***		

5- CONCLUSÕES

This study suggests that ISM can be provide a cost-effective solution for investigations where a variety of different compounds, including dioxin and “dioxin-like” compounds such as furans and PCBs, from multiple sources can be evaluated considering both the Conceptual Site Model and potential human exposure pathways, and provides a basis for intelligent decision-making through a structured, conservative, and scientifically defensible methodology.

6- REFERÊNCIAS BILIOGRÁFICAS

Interstate Technology Regulatory Council (ITRC). 2012. Incremental Sampling Methodology Manual. http://www.itrcweb.org/ISM-1/. Accessed on 11/3/2014.