DENVER FRONT RANGE STUDY OF DIOXINS IN SURFACE SOIL

SUMMARY REPORT

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working in cooperation with:

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and
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LIST OF ACRONYMS AND ABBREVIATIONS

Ah	aryl hydrocarbon
ATSDR	Agency for Toxic Substances and Disease Registry
CAS	Columbia Analytical Services
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act (also known as Superfund)
D/F	dioxin/furan
HRGC/MS	High Resolution Gas Chromatography/Mass Spectrometry
LCS	Laboratory Control Sample
MDL	Method Detection Limit
MQL	Method Quantitation Limit
MRI	Midwest Research Institute
PARCC	Precision, Accuracy, Representativeness, Comparability, and Completeness
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzodioxin
PCDF	polychlorinated dibenzofuran
PE	Performance Evaluation
ppt	parts per trillion (1 nanogram per kilogram, or 1 picogram per gram)
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
QATS	Quality Assurance Technical Support
RPD	Relative Percent Difference
SOP	Standard Operating Procedure
TEF	Toxicity Equivalency Factor
TEQ	*2,3,7,8*-tetrachlorodibenzo-*p*-dioxin equivalents
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

LIST OF CHEMICAL ABBREVIATIONS

Dioxins/Furans

HpCDD	heptachlorodibenzodioxin
HpCDF	heptachlorodibenzofuran
HxCDD	hexachlorodibenzodioxin
HxCDF	hexachlorodibenzofuran
OCDD	octachlorodibenzodioxin
OCDF	octachlorodibenzofuran
PeCDD	pentachlorodibenzodioxin
PeCDF	pentachlorodibenzofuran
TCDD	*2,3,7,8*-tetrachlorodibenzo-*p*-dioxin
TCDF	*2,3,7,8*-tetrachlorodibenzofuran

PCBs

HpCB	heptachlorobiphenyl
HxCB	hexachlorobiphenyl
PeCB	pentachlorobiphenyl
TCB	tetrachlorobiphenyl

EXECUTIVE SUMMARY
DENVER FRONT RANGE DIOXIN SOIL STUDY

INTRODUCTION

Chemistry and Toxicity of Dioxins

Dioxins are a class of compounds that are of potential human health concern because they may pose an increased risk of cancer and non-cancer adverse health effects at extremely low levels of exposure. The most toxic member of the class is *2,3,7,8*-tetrachlorodibenzo-*para*-dioxin (TCDD). Several other polychlorinated dibenzodioxins (PCDDs) as well as some polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) also display TCDD-like toxicity due to their structural similarity to TCDD (see **Figure ES-1**). For the purposes of this report, the term "dioxins" is used to refer to the sub-set of 29 TCDD-like congeners (out of a total of 419 different polychlorinated dioxins, furans and biphenyls) that are listed in **Table ES-1**.

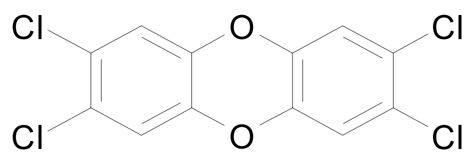
However, not all of these 29 congeners are equally toxic. The relative potency of a congener compared to TCDD is expressed in terms of the Toxicity Equivalency Factor (TEF). **Table ES-1** lists consensus TEF values for mammals (including humans), birds, and fish. These TEF values were developed by a panel of experts assembled by the World Health Organization (Van den Berg et al. 1998). Note that TEFs are often based on limited data, and so they are only approximations of the relative toxicity of each congener, rounded up to the highest half order of magnitude in order to be conservative.

Overview of the Denver Front Range Dioxin Soil Study

Because of the potential health concerns associated with exposure to dioxins, and because dioxins tend to be pervasive (at trace levels) and persistent in the environment, EPA often investigates the occurrence of dioxins in environmental media (mainly soils) at hazardous waste sites. One such site is the Rocky Mountain Arsenal (RMA), located near Denver, Colorado. In order to investigate whether dioxins were of potential concern at the RMA, USEPA Region 8, working in cooperation with the State of Colorado and the Rocky Mountain Arsenal Remediation Venture Office, undertook a series of related studies to characterize the occurrence and levels of dioxins at the site. The first study (BAS 2001) focused on measurement

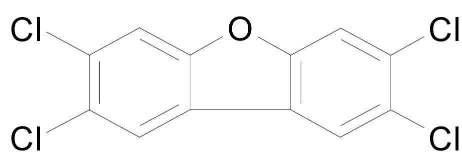
Figure ES-1. Structure of Dioxins, Furans and PCBs

Dioxins
75 congeners, 7 of which have significant TCDD-like activity
Most potent is



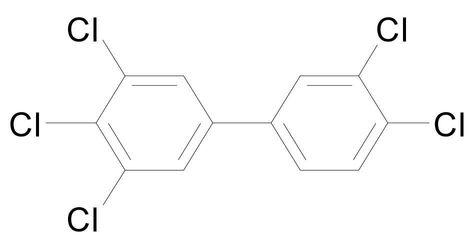
2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) (TEF = 1.0)

Furans
135 congeners, 10 of which have significant TCDD-like activity
Example structure:



2,3,7,8-tetrachlorodibenzofuran (TEF = 0.1)

PCBs
209 congeners, 12 of which have significant TCDD-like activity
Example structure:



3,3',4,4',5-Pentachlorobiphenyl (PCB-126) (TEF = 0.1)

Toxic congeners are flat with lateral chlorines, and bind to the Ah-receptor

Table ES-1. List of Dioxin-Like Analytes and TEFs

Class	Target Analyte	TEF		
		Mammals	Birds	Fish
Dibenzo-p-dioxins (PCDDs)	2,3,7,8-TCDD	1	1	1
	1,2,3,7,8-PeCDD	1	1	1
	1,2,3,4,7,8-HxCDD	0.1	0.05	0.5
	1,2,3,6,7,8-HxCDD	0.1	0.01	0.01
	1,2,3,7,8,9-HxCDD	0.1	0.1	0.01
	1,2,3,4,6,7,8-HpCDD	0.01	< 0.001	0.001
	OCDD	0.0001	0.0001	<0.0001
Dibenzofurans (PCDFs)	2,3,7,8-TCDF	0.1	1	0.05
	1,2,3,7,8-PeCDF	0.05	0.1	0.05
	2,3,4,7,8-PeCDF	0.5	1	0.5
	1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
	2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
	1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
	OCDF	0.0001	0.0001	<0.0001
Co-planar PCBs	3,3',4,4'-TCB (77)	0.0001	0.05	0.0001
	3,4,4',5-TCB (81)	0.0001	0.1	0.0005
	3,3',4,4'-5-PeCB (126)	0.1	0.1	0.005
	3,3',4,4',5,5'-HxCB (169)	0.01	0.001	0.00005
Mono-ortho PBCs	2,3,3',4,4'-PeCB (105)	0.0001	0.0001	< 0.000005
	2,3,4,4',5-PeCB (114)	0.0005	0.0001	< 0.000005
	2,3',4,4',5-PeCB (118)	0.0001	0.00001	< 0.000005
	2',3,4,4',5-PeCB (123)	0.0001	0.00001	< 0.000005
	2,3,3',4,4',5-HxCB (156)	0.0005	0.0001	< 0.000005
	2,3,3',4,4',5'-HxCB (157)	0.0005	0.0001	< 0.000005
	2,3',4,4',5,5'-HxCB (167)	0.00001	0.00001	< 0.000005
	2,3,3',4,4',5,5'-HpCB (189)	0.0001	0.00001	< 0.000005

TEF = Toxicity Equivalency Factor
TEF values are consensus estimates recommended by the World Health Organization (Van den Berg et al. 1998) for use in estimating relative toxicity in biological tissues.

of dioxin levels in the tissues of birds (kestrel eggs and owl livers) and fish (carp eggs) collected from several areas on the RMA compared to those for receptors collected at comparable off-site reference areas. Based on the results from this study, a series of four follow-on studies were designed to focus on direct measurement of dioxins in surface soils at numerous on-post locations (USEPA 2001 b, c, d) as well as at multiple off-post reference locations (USEPA 2001a). These four soil studies were planned and performed together in order to maximize the scientific utility of the data and help minimize time and cost. Collectively, these four studies are referred to as the Denver Front Range Dioxin Soil Study. The results of these studies have been presented previously in a series of separate reports (USEPA 2001 a, b, c, d) that can all be found in the Region 8 Records Center, and may also be available on-line at the Region 8 web site (http://www.epa.gov/Region8/superfund/sites/rmdioxrpt.html).

Purpose of This Document

This current document consolidates the data and findings from each of the four studies that comprise the Denver Front Range Dioxin Soil Study in order to provide a comprehensive presentation of the soil data and to facilitate evaluations that can only be based on the consolidated data.

METHODS

Soil Sampling Design

Table ES-2 presents an overview of the field surface soil samples which were collected during this project. Further details on each component of the soil sampling effort are presented below.

Off-Post Sampling Locations

The area selected for investigation of dioxin levels in soil samples at "off-post" reference areas (i.e., outside the boundaries of the RMA) was a square approximately 30 miles on a side, centered approximately on Denver, Colorado. All soil sampling locations in this study were on public lands, including properties controlled by Federal, State, County, City, or other Denver-area agencies. In order to achieve spatial representativeness, the study area was divided into four quadrants, and efforts were made to distribute sampling locations evenly between and within the quadrants. Five different types of land use categories were considered, including Agricultural, Open Space, Residential, Commercial, and Industrial. Approximately 25-35 samples of each

Table ES-2. Summary of Surface Soil Samples Collected

Location	**Sub-Location**	**Number of Samples**	**Sample Type**
Off-Post (Samples from 1,000 square mile area of Denver Front Range)	Agricultural	27	Grab
	Commercial	31	Grab
	Industrial	30	Grab
	Open Space	38	Grab
	Residential	39	Grab
	TOTAL	**165**	**Grab**
On-Post (Sampling locations on RMA)	Random	28	Grab
	Western Tier Parcel	10	Composite
	South Plants	12	Composite
	Historic Use Areas	10	Composite
	TOTAL	**60**	**Mixed**

land use category were collected, for a total of 165 off-post samples. **Figure ES-2** is a map which shows the sampling locations and the land use at each off-post soil-sampling location.

On-Post Sampling Locations

Soil sampling at on-post locations (i.e., within the boundaries of the RMA) included the following data sets

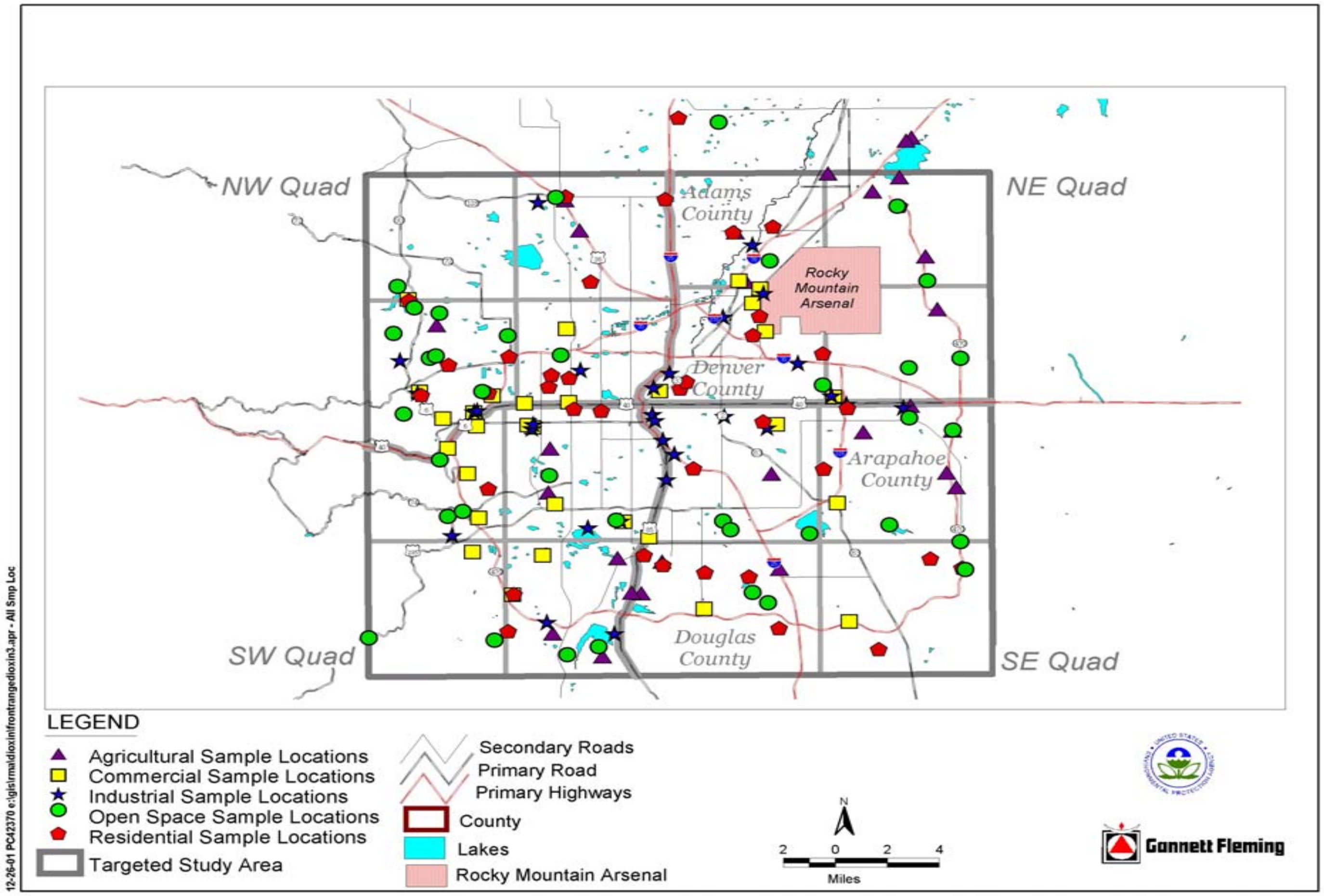
- 28 grab samples collected from stratified random locations across the RMA.
- 10 composite samples collected for an area of approximately 960 acres located along the western boundary of the RMA. This area is referred to as the Western Tier Parcel (WTP).
- 12 composite samples collected from the central (South Plants) area of RMA, along with 10 composite samples from areas known or suspected of having received waste materials from the manufacturing operations.

These on-post sampling locations are shown by the crosses in **Figure ES-3**.

Sample Collection and Preparation

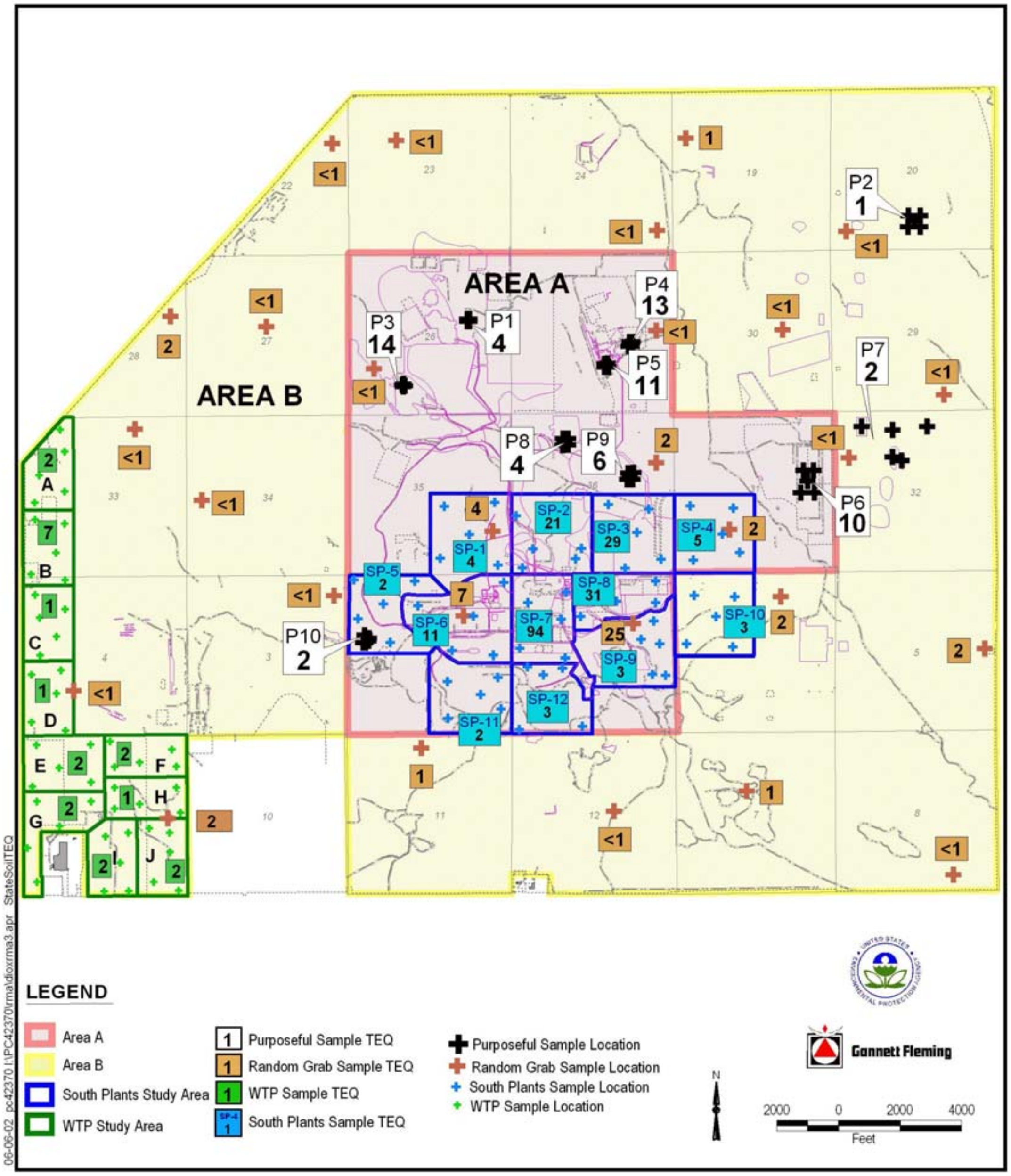
All soil samples were collected from a depth of 0-2 inches. Each unprocessed ("raw") sample was air-dried at about 37°C and weighed, followed by coarse-sieving through a 10-mesh (2 millimeter) stainless steel screen. The soil fraction passing the coarse screen was referred to as the “bulk” fraction. In most cases, the bulk fraction was further sieved through a 60-mesh (250 micrometer) stainless steel screen in order to isolate soil particles less than 250 micrometers in diameter. The soil passing through this screen was referred to as the "fine" fraction. The fine fraction was prepared for analysis because fine soil particles are more likely be ingested by humans (hand to mouth contact) and ecological receptors (preening feathers, grooming fur) than coarse particles, and hence constitute the most relevant media for use in evaluating health risk. In some cases, both the coarse and fine fraction were analyzed to determine if there was a significant difference between the two.

Figure ES-2. Off-Post Soil Sampling Locations



A total of 165 surface soil samples were collected from the off-post study area. Samples were stratified into five different land use categories and four quadrants to help assure the data would be representative.

Figure ES-3. Map of Full TEQ(D/F) for Fine-Sieved Samples at On-Post Sampling Locations



Sample Analysis

Following sample preparation as described above, samples were submitted to Midwest Research Institute (MRI) for trace-level congener-specific analysis of the 7 PCDDs, 10 PCDFs, and 12 PCBs listed in **Table ES-1**. The analytical method used in this study (see Appendix E for details) is a high resolution GC-MS method based on EPA Methods 1613B, 1668, and 8290, with several modifications (increased sample mass, calibration curve extended to lower levels, more stringent performance criteria) designed to improve performance at the trace levels (low parts per trillion) (ppt) of dioxins expected in ambient surface soils.

Congener concentration values were used for Principal Components Analysis (PCA) to define a "fingerprint" for each sample, and for calculation of TCDD-equivalent concentration values, as described below.

Calculation of TCDD-Equivalents (TEQ) in Soil

For purposes of characterizing the overall dioxin content of surface soil, the toxicity-weighted sum of each of the 29 dioxin-like congeners (17 dioxins and furans, plus 12 PCBs) was calculated as follows:

$$\text{TEQ (total)} = \sum_{i=1}^{29} (C_i \cdot TEF_i)$$

In cases where interest focused on the soil content of PCDDs and PCDFs only (i.e., PCBs not included), the value was calculated as:

$$\text{TEQ (D / F)} = \sum_{i=1}^{17} (C_i \cdot TEF_i)$$

It is very important to recognize that TEFs are based on the relative magnitude of biological responses to different congeners for exposures at the cellular or molecular level, and do not account for potential differences in absorption, distribution, metabolism, and excretion of different congeners that may occur when dioxins are ingested in soil. Thus, the use of TEFs and TEQs as a means for characterizing the toxicity of dioxin levels in soil should be considered as a screening-level approach only.

Two different approaches were used for evaluating congeners that were present at concentrations below the method detection limit (MDL) or the method quantitation limit (MQL):

1) a semi-quantitative set of results in which congeners that yielded signals below the MDL were generally evaluated by assuming a concentration value equal to ½ the detection limit for that congener. This is referred to in this report as the "**Full**" data set, since all congeners are included in the value.

2) a quantitative set of results in which congeners below the MDL were assigned a value of zero, and congeners below the MQL but above the MDL were assigned a value ½ the MQL. This is referred to in this report as the "**Quant**" data set, since only values above the detection limit are included.

Thus, there are a total of four different measures of TEQ considered in this report:

Designation	Congeners Included		Treatment of Low Values	
	PCDDs/PCDFs	PCBs	Value < MDL	Value > MDL but < MQL
Full TEQ(D/F)	17	0	Use ½ MDL	Use value
Full TEQ(total)	17	12	Use ½ MDL	Use value
Quant TEQ(D/F)	17	0	Don't use	Use ½ MQL
Quant TEQ(total)	17	12	Don't use	Use ½ MQL

In general, the Full TEQ(D/F) results (indicated by the shaded row above) were considered to be the most relevant for screening potential health risks from dioxins, since EPA risk assessment guidance generally recommend assuming a value of ½ the detection limit for analytes below the detection limit.

RESULTS

Data Quality Assessment

A number of different types of analyses were performed to evaluate the quality (accuracy, precision) of the data generated during this study. These analyses are summarized below.

Method Blanks

Full TEQ(D/F) and Full TEQ(Total) values for 22 method blanks (matrix = white sand) both averaged 0.4 ppt (range = 0.1-1.7 ppt). These data indicate that there was no significant source of PCDD, PCDF, or PCB contamination during sample processing or analysis within the analytical laboratory.

Field Blanks

Multiple samples (N=27) of a fine-sieved "clean soil" sample yielded low results for both Full TEQ(D/F) (1.7 ± 0.5 ppt) and Full TEQ(Total) (1.9 ± 0.5 ppt), indicating that there was no significant source of contamination with PCDDs, PCDFs, or PCBs during the sample processing or the sample analysis steps.

Splits and Duplicates

The results for field split and field duplicate soil sample pairs were generally in good agreement. For most samples with a Full TEQ(D/F) concentration less than 5-times the MQL (i.e., less that 25 ppt TEQ), the absolute difference between sample pairs averaged about 1.5 ppt TEQ (splits) to 1.7 ppt TEQ (duplicates), well within the acceptability criterion of plus or minus one MQL (about 5 ppt TEQ) that was established by the Quality Assurance Project Plan (QAPP) (USEPA 1999) for samples with concentration values less than 5-times the MQL. For samples with Full TEQ(D/F) values greater than 5-times the MQL (i.e., greater than 25 ppt TEQ), the average Relative Percent Difference (RPD) ranged from 6% (splits) to 21% (duplicates), also well within the acceptance criterion of 30% established by the QAPP (USEPA 1999). These results indicate that good reproducibility was achieved for trace levels of dioxins in soil samples.

Performance Evaluation Samples

Full TEQ(D/F) results for a series of Performance Evaluation (PE) samples were generally close to expected values (average = 100%-110%), and nearly all PE samples were within specified acceptance criteria. Precision between multiple analyses of the PE samples was good, with coefficient of variation values generally less than 20%. These results indicate that the field data have good accuracy and precision.

Laboratory Spikes

Average recovery of individual PCDD/PCDF congeners ranged from 75% to 109%, with an average of 93% across all samples and all PCDD/PCDF congeners. Recovery of individual PCBs averaged across all samples ranged from 105% to 127%, with an average of 110% across all samples and all PCB congeners. When expressed as Full TEQ, recovery across different samples ranged from 91% to 103% (mean = 98%) for TEQ(D/F), and from 92% to 104% (mean = 98%) for TEQ(Total). This indicates that matrix interference is not likely to be of concern, and that accuracy of the method is good.

Inter-laboratory Comparison

Forty samples of soil were sent to an independent laboratory for analysis using the same method as was used by MRI. This included 32 representative field soil samples from the off-post, South Plants, and WTP sample sets as well as 8 quality assurance samples. Full TEQ(D/F) values were generally consistent between the two laboratories, with an average between-laboratory difference for field samples of 1.9 ppt TEQ (range= 0.02 to 11.2 ppt). This close agreement between different laboratories indicates that the results are reproducible and accurate.

TEQ Values in Off-Post Field Samples

Of the 165 off-post field samples collected during this study, sufficient sample mass was available to sieve and analyze the fine fraction for 162 samples. Two data points in the off-post data set (the maximum value for the commercial and the residential land use data groups) were judged to be un-representative of their respective land uses (outside the 99th percentile of the other data points), and they were excluded from further analysis. Summary statistics for the remaining 160 samples are shown in **Table ES-3**. As seen, there is a fairly wide range of TEQ(D/F) values observed in this set of samples, from a minimum of less than 0.1 ppt TEQ up to a maximum of 103 ppt TEQ. Mean values for TEQ (both Full and Quant) are lowest for open space and agricultural sampling locations, with somewhat higher values observed in industrial, commercial and residential areas. The distributions of Full TEQ(D/F) for each land use all tend to be right-skewed and may be reasonably approximated by lognormal probability density functions.

Samples collected on lands that were ranked as agricultural or open space tend to have values somewhat lower than those from commercial or industrial areas, and these differences are statistically significant. The distribution for residential samples is generally similar to that for

Table ES-3. Summary Statistics for Off-Post Fine-Sieved Soil Samples

Land Use	N	Stat	Full TEQ (ppt)			Quant TEQ (ppt)		
			D/F	**PCB**	**Total**	**D/F**	**PCB**	**Total**
Agricultural	27	Mean	**1.5**	**0.3**	**1.8**	**1.0**	**0.3**	**1.3**
		StdDev	1.9	0.4	2.1	1.4	0.4	1.6
		Min	0.0	0.0	0.0	0.0	0.0	0.0
		Max	7.6	1.6	7.8	4.7	1.6	5.6
Commercial	30	Mean	**6.4**	**2.1**	**8.5**	**5.3**	**2.0**	**7.3**
		StdDev	11.3	7.2	17.9	9.8	7.2	16.5
		Min	0.3	0.0	0.4	0.1	0.0	0.1
		Max	57.7	39.8	97.5	50.2	39.8	90.0
Industrial	29	Mean	**9.9**	**5.5**	**15.4**	**7.9**	**3.6**	**11.6**
		StdDev	14.3	16.4	22.8	11.1	8.7	14.6
		Min	0.0	0.0	0.0	0.0	0.0	0.0
		Max	54.6	88.1	103.2	42.6	44.2	58.2
Open Space	37	Mean	**1.5**	**1.2**	**2.7**	**1.3**	**0.8**	**2.1**
		StdDev	2.2	4.0	5.3	2.1	2.1	3.8
		Min	0.0	0.0	0.0	0.0	0.0	0.0
		Max	9.0	23.6	28.0	8.3	11.9	16.0
Residential	37	Mean	**7.2**	**1.6**	**8.8**	**5.9**	**1.3**	**7.2**
		StdDev	10.2	2.5	11.7	8.2	2.0	9.3
		Min	0.1	0.0	0.1	0.0	0.0	0.0
		Max	43.0	8.7	51.7	32.3	7.8	36.6
Total	160	Mean	**5.2**	**2.1**	**7.3**	**4.3**	**1.6**	**5.8**
		StdDev	9.8	8.1	14.5	8.0	5.1	11.1
		Min	0.0	0.0	0.0	0.0	0.0	0.0
		Max	57.7	88.1	103.2	50.2	44.2	90.0
Rural (Open Space + Agricultural)	64	Mean	**1.5**	**0.8**	**2.3**	**1.2**	**0.6**	**1.8**
		StdDev	2.1	3.0	4.2	1.8	1.7	3.1
		Min	0.0	0.0	0.0	0.0	0.0	0.0
		Max	9.0	23.6	28.0	8.3	11.9	16.0
Heavy Use (Commercial + Industrial)	59	Mean	**8.1**	**3.8**	**11.9**	**6.6**	**2.8**	**9.4**
		StdDev	12.9	12.6	20.5	10.4	7.9	15.6
		Min	0.0	0.0	0.0	0.0	0.0	0.0
		Max	57.7	88.1	103.2	50.2	44.2	90.0

commercial properties. In interpreting this finding, it is important to note that none of the "residential" sampling locations are actually on private residential properties, but rather all are on public lands properties located in or near residential neighborhoods, and that the land use history may have included some influences from nearby light commercial or industrial activities.

TEQ Values in On-Post Field Samples

Of the 60 field samples collected for analysis from various areas of the RMA, sufficient mass was available for all samples to sieve and analyze the fine fraction. The results for Full TEQ(D/F) for these 60 samples are shown in **Table ES-4**, stratified by location, and are also indicated in **Figure ES-3**. As seen in the table and figure, dioxin levels tend to be low (1-3 ppt) for most locations at the RMA. However, TEQ levels are slightly elevated in soil samples from the South Plants area, with values ranging from 2-94 ppt Full TEQ(D/F). The spatial pattern of these elevations is consistent with the hypothesis that low levels of dioxins were released to soils near the former chemical manufacturing operations near the center of the RMA. However, the areal extent of the contamination is relatively small in scope, decreasing rapidly as a function of distance from the central South Plants area. In addition, a few of the historic waste disposal areas have slightly elevated (max = 14 ppt) Full TEQ(D/F) levels.

Another sample that is slightly anomalous is from Zone B of the WTP. The Full TEQ(D/F) value for this sample (7 ppt) is higher than for all of the other samples at WTP (1.2-2.3 ppt), and for most of the other random samples from non-use areas of RMA. The source of the somewhat increased concentrations of PCDDs/PCDFs and PCBs in WTP sub-parcel B is not known; however, an earlier study of organo-chlorine pesticide levels in the WTP also detected slight elevations in aldrin and dieldrin concentrations in this same area.

DATA ANALYSIS AND DISCUSSION

Comparison of TEQ Levels at On-Post and Off-Post Locations

In order to perform a comparison of on-post and off-post TEQ levels, the on-post samples were divided into two groups, as shown in **Figure ES-3**:

Area A (indicated by the pink area) includes most of the samples in the vicinity of South Plants and the near-by historic waste disposal areas (an area of about seven square miles). This area contains 26 total sampling locations, including 11 composite samples from the

Table ES-4. TEQ Summary Statistics for RMA On-Post Fine-Sieved Soil Samples

Sample Category	N	Stat	Full TEQ (ppt)			Quant TEQ (ppt)		
			D/F	**PCB**	**Total**	**D/F**	**PCB**	**Total**
South Plants	12	Mean	**17.4**	**2.0**	**19.3**	**15.0**	**1.7**	**16.7**
		StdDev	26.3	2.0	28.2	23.7	1.8	25.4
		Min	1.9	0.4	2.8	1.2	0.2	1.9
		Max	93.8	7.2	101.0	83.9	6.5	90.4
Purposeful	10	Mean	**6.5**	**5.5**	**12.0**	**5.8**	**3.5**	**9.3**
		StdDev	4.8	11.3	13.9	4.8	5.5	8.6
		Min	1.4	0.2	1.6	0.9	0.2	1.1
		Max	13.5	37.5	48.7	12.3	18.8	29.3
RMA Random	28	Mean	**2.0**	**0.4**	**2.5**	**1.8**	**0.3**	**2.2**
		StdDev	4.8	0.4	4.9	4.7	0.3	4.8
		Min	0.0	0.0	0.1	0.0	0.0	0.0
		Max	25.4	1.5	26.1	24.7	1.1	25.2
Western Tier Parcel	10	Mean	**2.2**	**1.1**	**3.3**	**1.3**	**1.1**	**2.3**
		StdDev	1.9	0.7	2.5	2.1	0.7	2.7
		Min	1.2	0.6	1.8	0.4	0.6	1.0
		Max	7.4	2.9	10.3	7.2	2.8	10.0

South Plants area, 8 composite samples from historic use areas, and 7 random grab samples.

Area B includes all other on-post samples (N = 34), including 10 composite samples from the WTP, 21 random grab samples, 2 composites from historic use areas, and one composite sample from the eastern end of the South Plants area.

Table ES-5 (Panel A) provides summary statistics for Full TEQ(D/F) in these two groups of on-post samples. The lower panel of **Table ES-5** presents summary statistics for the off-post samples, and compares the data with the two on-post areas. As seen:

- Random grab samples from on-post Area B are not significantly different than any of the rural-type off-post land use samples (open space, agricultural), either alone or together.

- Random grab samples from on-post Area B are significantly lower than off-post residential land use samples.

- Samples from on-post Area A are a mixture of grabs and composites and are mainly from biased sampling locations, so rigorous statistical comparisons with random grab samples from off-post commercial/industrial land uses cannot be performed. However, simple inspection of the data suggest that on-post Area A is similar to but perhaps slightly greater than off-post commercial/industrial areas.

Comparison of Current Data with Literature Values

Limited data are available in the literature on the concentrations of PCDDs and PCDFs in "background" soil. Despite a number of limitations and uncertainties in the published data (see Section 4.2), it is evident that there is general agreement between the findings from the Front Range Dioxin Soil Study and the available literature values:

Data Source	Average Full TEQ(D/F) (ppt)	
	Rural	Urban
Front Range Dioxin Soil Study	1-2 (a)	6-10 (b)
Published Literature Values	1-6	2-21

(a) Range is for mean values in Open Space and Agricultural areas
(b) Range is for mean values in Commercial, Industrial, and Residential areas

Table ES-5. Comparison of Full TEQ(D/F) Values in Fine-Sieved Soil at Off-Post and On-Post Locations

Panel A: On-Post Summary Statistics

RMA On-Post Area	Sample Type	Summary Statistic			
		N	Mean (ppt)	Min (ppt)	Max (ppt)
Area A	**All**	26	11.8	0.1	93.8
	Grabs	7	5.8	0.1	25.4
	Composites	19	14.1	1.9	93.8
Area B	**All**	34	1.3	0.0	7.4
	Grabs	21	0.8	0.0	1.6
	Composites	13	2.1	1.2	7.4

Panel B: Comparison of On-Post and Off-Post Values

Off-Post Land Use	Off-Post Summary Statistics			Comparison with On-Post Areas		
	N	Mean (ppt)	Max (ppt)	Area A N = 26 total (a)	Area B N = 21 Grabs	p Value (b)
Open Space	37	1.5	9.0	na	nsd	0.482
Agricultural	27	1.5	7.6	na	nsd	0.383
Rural (c)	***64***	***1.5***	***9.0***	***na***	***nsd***	***0.412***
Residential	37	7.2	43.0	na	Area B is lower	<0.001
Commercial	30	6.4	57.7	Area A slightly greater than off-post	na	na
Industrial	29	9.9	54.6		na	na
Heavy Use (d)	***59***	***8.1***	***57.7***		***na***	***na***

na = not applicable because land uses are different
nsd = no significant difference (Mann Whitney Rank Sum Test)

(a) Area A samples are a mixture of grabs and composited and are mainly biased, and can't be statistically compared
(b) Grab samples only
(c) Rural = open space and agricultural combined
(d) Heavy use = Commercial and industrial combined

This general agreement suggests that even though regional differences are likely to exist in ambient dioxin levels in soils, these differences appear to be relatively small in scale (probably less than a factor of 5-fold in most cases), and that reliable data collected from one area may be used as a reasonable approximation for results from other similar but unstudied areas. In this regard, because of the improved analytical methodology and high emphasis on representativeness and quality control, the data sets collected during the Front Range Dioxin Study constitute the most robust, reliable and representative data for comparative purposes with other sites.

Contribution of PCBs to Total TEQ

At off-post locations, PCBs in agricultural and open space soils contribute about 0.3 to 1.2 ppt TEQ to the Full TEQ(Total), but may contribute about 1.6 to 5.5 ppt TEQ in commercial, industrial or residential samples. On average across all off-post samples, PCBs contribute about 29% of the total TEQ. Results are generally similar at on-post locations, with PCBs contributing between 0.4 to 1.1 ppt Full TEQ (18-33% of total) in non-impacted areas of the site, with slightly higher values (2.0 to 5.5 ppt Full TEQ) in the South Plants and historic use areas of the site. Increased PCB levels tend to be associated with elevated PCDD/PCDF levels, although the correlation between the two groups is not strong: the coefficient of determination (R^2) between Full TEQ(D/F) and Full TEQ(PCB) is 0.10 in all off-post samples and 0.06 in all on-post samples.

Contribution of Congeners Below the Method Quantitation Limit

The average contribution of congeners below the MQL is about 1.0 ppt for Full TEQ(D/F) and about 1.5 ppt for Full TEQ(Total). These contributions correspond to an average of about 18% to 20% of the total. This finding supports the conclusion that in this study, Full TEQ results are not unduly influenced by congeners below the MQL or the MDL, even at these relatively low soil levels. At higher soil levels, the relative contribution of congeners below the MQL would be even lower.

Congener Pattern Analysis

The congener composition of a soil sample may provide useful information about the source of the dioxin contamination, and helps to reveal which specific congeners are contributing the majority of the risk. The results of several alternative approaches to congener pattern analysis are presented below.

Graphical Summary

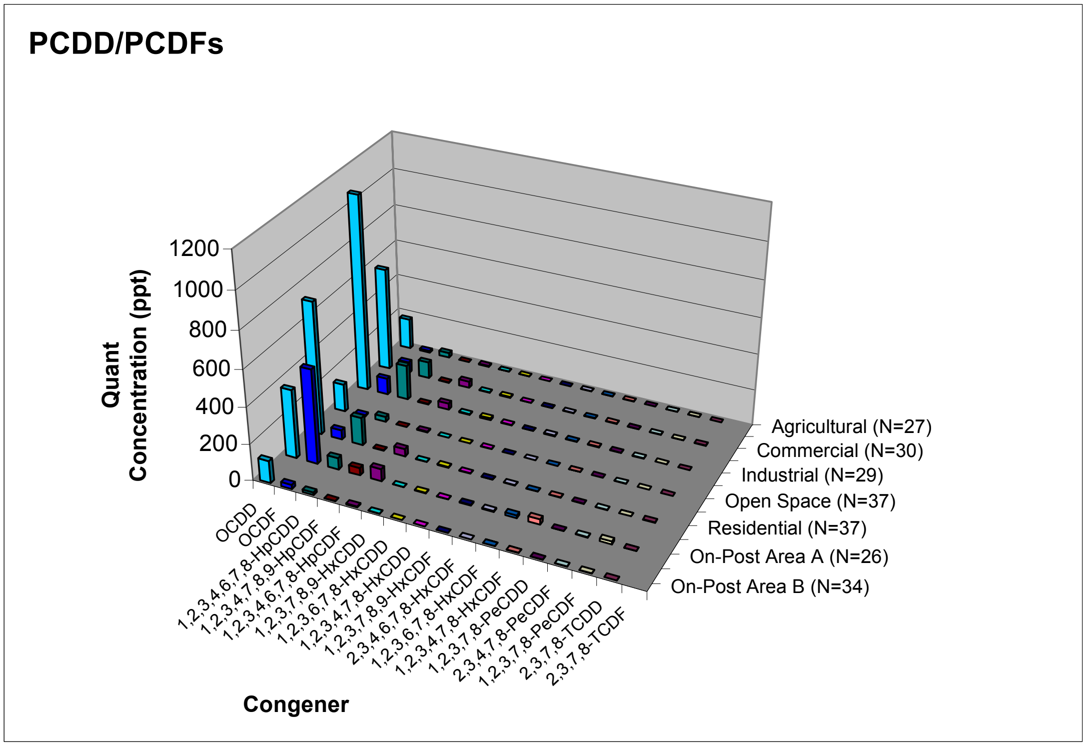
Figure ES-4 summarizes the average quantitative congener concentration pattern in study soils. The upper panel shows congeners in the PCDD/PCDF class, while the lower panel shows congeners in the PCB class. The congener in the dioxin/furan class occurring at the highest concentration level is usually OCDD, along with varying amounts of OCDF, *1,2,3,4,6,7,*8-HpCDD, and *1,2,3,4,6,7,8*-HpCDF. As seen in the lower panel, several PCBs are usually present, primarily 105, 118, and 156, with lower levels of 157 and 167. These data indicate there is a relative increase in OCDF and several other PCDFs in Area A compared to Area B and off-post areas.

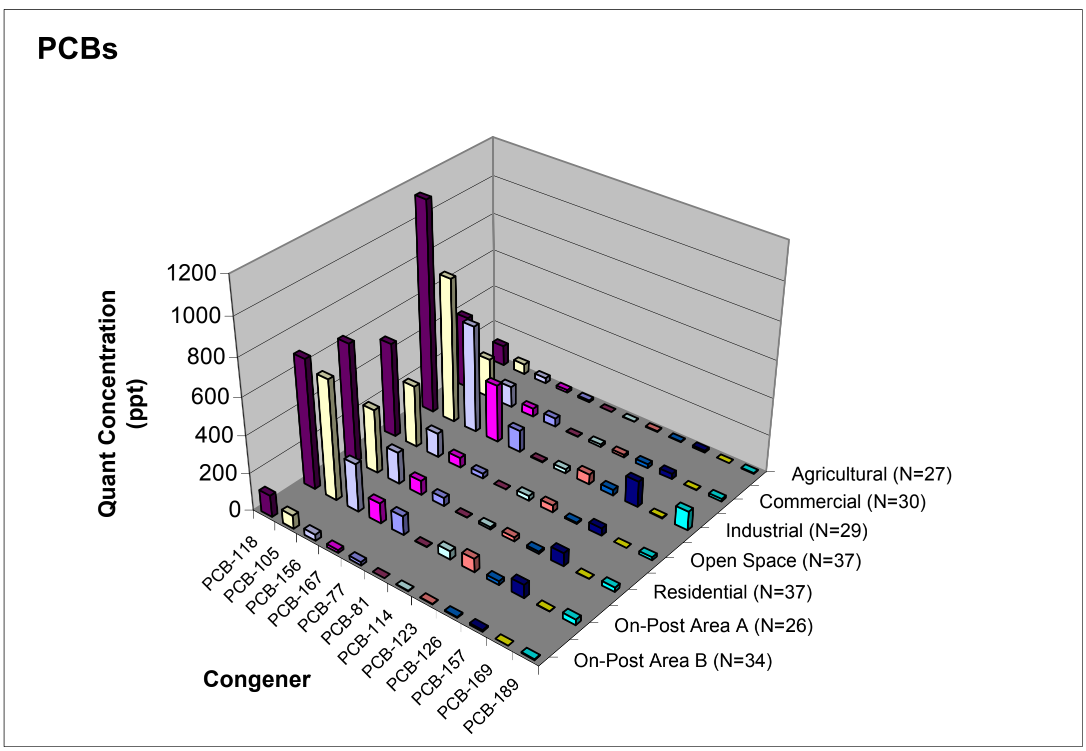
Principal Components Analysis (PCA)

Multivariate statistical analysis using Principal Components Analysis (PCA) was conducted to investigate the congener pattern for PCDDs and PCDFs in both the on-post and off-post surface soil samples collected during this study. Based on this analysis, it appears that samples from on-post Area A (the central manufacturing area and historic use areas of RMA) are characterized by the presence of a signature PCDD/F profile containing higher chlorinated PCDF congeners. That is, samples from the off-post reference areas are more influenced by the presence of higher chlorinated PCDD congeners, as would be expected for samples influenced by a range of general human activities such as traffic and light industrial applications. The presence of a PCDF signature for Area A of RMA samples does not necessarily indicate a major source of these contaminants on-site. Indeed, the relatively diffuse nature of the sample clusters would argue strongly against the presence of a single large source. Instead the predominance of the PCDF congeners on-post is probably indicative of the mixed industrial activities that took place in Area A of the site and that PCDD congeners that predominate off-site were not able to be generated or transported onto the site in corresponding amounts. Most of the samples collected from the peripheral areas on the RMA have PCDD/PCDF congener profiles that are indistinguishable from the off-post reference area.

A multivariate statistical analysis was also conducted to evaluate the congener pattern of PCBs in on-post and off-post soil samples. The analysis found that the concentrations of all the 12 PCBs congeners were highly correlated in the data set as a whole as well as when examined by land-use category and location, with essentially all the samples having the same PCB congener profile. This indicates that the source of PCBs in Denver-area soils (both on-post and off-post) is more likely to be a diffuse area source than a series of different point sources.

Figure ES-4. Average Congener Concentration Profile for Fine-Sieved Soils





Regression Analysis

In an effort to gain additional information on potential similarities and differences in congener patterns in various categories of on-post and off-post surface soil samples that conventional PCA might not be sensitive enough to detect, an exploratory analysis of the data for the WTP and Open Space land uses was performed using a new approach involving multiple pair-wise regression analysis of congener mass ratios. This analysis revealed no major differences between Open Space and WTP, although differences in the identity of some of the correlated pairs was interpreted as suggestive evidence of subtle differences, and several atypical samples were identified in each data set.

Evaluation of Potential Confounders

Soil TOC

A priori, binding of dioxins to soil might be expected to depend on the total organic carbon (TOC) content of the soil. Correlation analysis of the samples collected during this study indicated that there is a relationship between TOC and Quant TEQ(D/F) for both off-post and on-post samples ($p < 0.05$), but the coefficients of determination are quite low ($R^2 = 0.088$ and 0.085, respectively). Similar results were obtained for Full TEQ(D/F). This suggests that the TEQ value in a soil sample may depend in part on the TOC of the soil, but that this is not the main determinant of the TEQ value.

Particle Size Distribution

Binding of dioxins to soil particles is a physical process that might be expected to depend mainly on the surface area of the soil particles. Thus, smaller particles, having a higher surface area to mass ratio than larger particles, might tend to have higher concentrations of dioxins per unit mass than larger particles. However, samples collected during this study did not show a statistically significant relationship between Quant TEQ(D/F) and the fraction of the sample composed of fines, and there was no significant tendency for TEQ values to be higher for fine soil particles than for bulk samples. Similar results were obtained for Full TEQ(D/F). These findings suggest that soil particle size distribution is not an important determinant of TEQ in these samples.

Temporal Variability

Even though dioxins tend to be relatively stable in the environment, it is possible that levels in soil vary as a function of time due to seasonal differences in emission rates and/or environmental transport rates. Most samples from on-post locations were collected in December, 1999, and a majority of off-post samples were collected in January and February, 2000. However, no clear temporal pattern in TEQ values is apparent in this study, with high values occurring in samples collected in each month. Thus, seasonality is not considered to be an important issue in this study.

Comparison of Soil Data to Data from Biological Tissues

As noted above, the initial investigation into dioxin levels at the RMA focused on biological tissue levels of dioxins rather than soil levels (BAS 2001). This was because ecological receptors tend to integrate exposures of bioaccumulative compounds over a wide area, and because tissue data can be used to evaluate the likelihood of adverse ecological responses in the exposed receptors. The indicator species selected for study included the American kestrel, the great horned owl, and the common carp. Samples of kestrel eggs, owl liver, and carp eggs were obtained from animals collected at both on-post and off-post (reference) locations. In brief, this study found equivocal evidence of a small increase in liver dioxin levels for owls that resided in the vicinity of the South Plants area of RMA, but no evidence of an increase in exposure for receptors at areas outside the South Plants area. These results based on the RMA biological sampling program are fully consistent with the results of the on-post soil sampling studies, which also found apparent small elevations in dioxin levels in soil samples from the South Plants area and a few nearby waste disposal areas, but no substantial elevations in the peripheral areas of RMA.

Comparison to Human-Health Based Guidelines

Although the primary purpose of the Denver Front Range Dioxin Study was to characterize the distribution of ambient dioxin levels in surface soil samples from the Front Range area and the RMA (and not to perform a health risk evaluation), it may be of some use to provide a health-based frame of reference by which the measured concentrations of dioxins in soils may be placed in context.

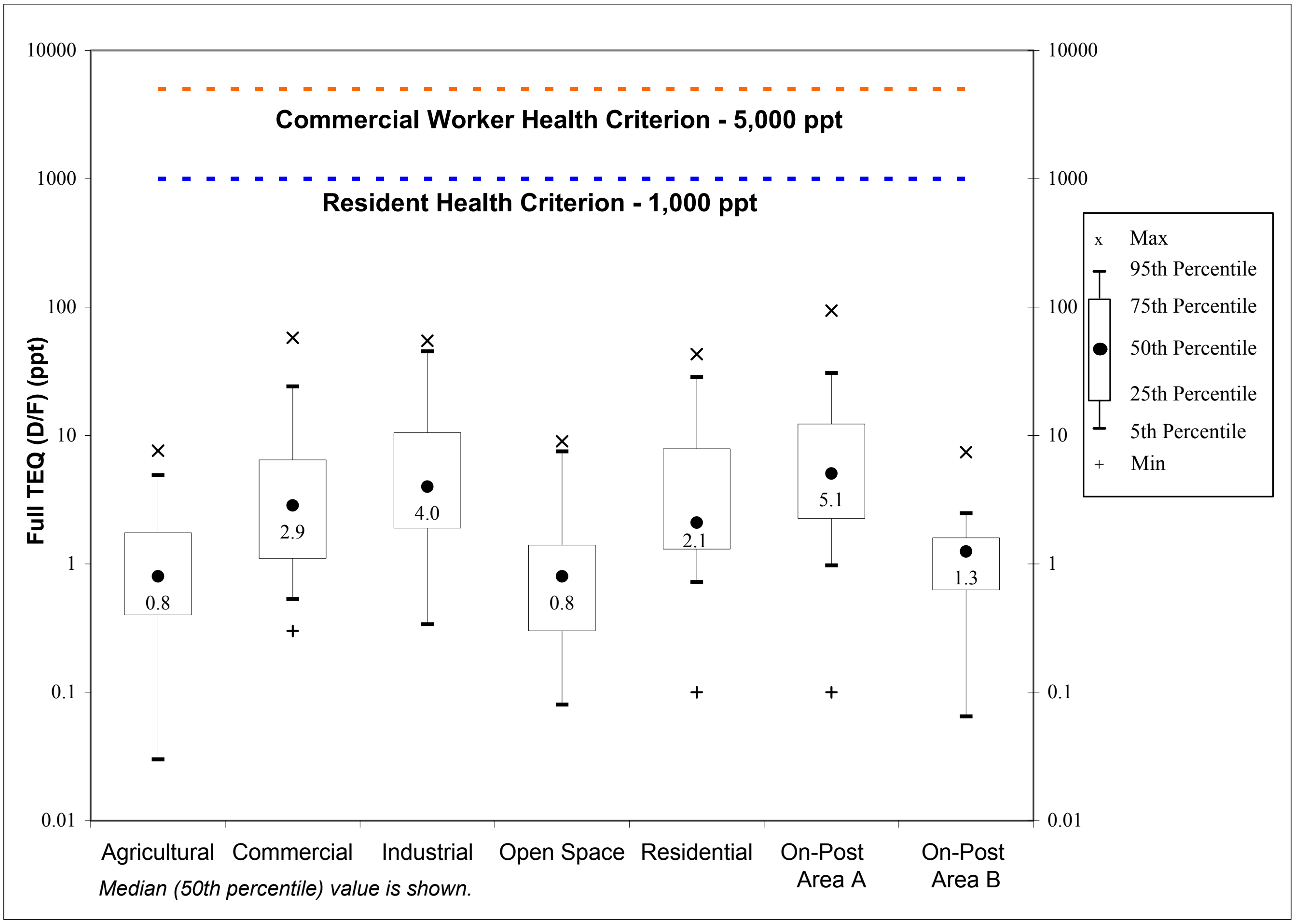
The USEPA Superfund Program has currently established a default screening concentration value of 1,000 ppt (1 ppb) TEQ in surface soil as a concentration that is not of cancer or non-cancer concern for lifetime exposure of residents (USEPA 1998a). For commercial and industrial land uses, USEPA guidelines identify 5,000 to 20,000 ppt (5-20 ppb) TEQ as the screening concentration of concern in surface soil. These soil screening concentrations are based only upon the 17 TCDD-like PCDDs and PCDFs. ATSDR currently identifies a concentration of 50 ppt TEQ in soil as a "screening level," below which no further investigation or characterization will usually be required in residential areas. ATSDR identifies a concentration of 1,000 ppt TEQ as an "action level," indicating that public health actions such as surveillance, research, health studies, community education, or exposure investigations should be considered. Concentrations between 50 ppt and 1000 ppt TEQ are identified as "evaluation levels," indicating that further investigation of site-specific factors regarding the extent and possible public health implications of the exposure may be warranted.

As illustrated graphically in **Figure ES-5**, none of the samples collected during the Denver Front Range Study approach or exceed the USEPA level of concern for either residents (1,000 ppt TEQ) or commercial workers (5,000 ppt TEQ). Of the 38 off-post soil samples where land use was classified as residential, only one has a TEQ value that exceeds the ATSDR "screening level" of 50 ppt TEQ, and none approached the ATSDR "action level" or EPA's screening level of 1,000 ppt TEQ. As discussed previously, this one residential value (155 ppt Full TEQ(D/F)) appears to be an outlier (greater than the 99th percentile of the other samples in the residential land use group), even though no apparent local point source was identified for this sample. In addition, like all the samples in the "residential" land use category, the sample is not from an actual private residence where exposure is estimated to occur for 24 hours per day, 7 days per week. In consideration of these factors, USEPA Region 8 has determined that dioxin levels in Denver Front Range "background" samples are not of significant human health concern for any land use category.

SUMMARY AND CONCLUSIONS

The results of the Front Range Dioxin Soil Study provide an accurate, sensitive and complete data set on the average and range of PCDD, PCDF and PCB concentrations and TEQ levels which occur in a variety of soil sampling locations in the Denver Front Range area and at the Rocky Mountain Arsenal. The mean value for Full TEQ for dioxins and furans across all off-post samples was about 5 ppt, with individual values ranging from less than 1 ppt TEQ up to a maximum of 58 ppt TEQ. Values from open space and agricultural areas tended to be the lowest (mean Full TEQ(D/F) = 2 ppt), while values from industrial, commercial, and residential areas included some higher values (mean Full TEQ(D/F) = 8 ppt). Full TEQ(D/F) values in soil from the central area of RMA (Area A in **Figure ES-3**) are slightly elevated (mean = 12 ppt,

Figure ES-5. Full TEQ (D/F) Levels in Fine-Sieved Soils Compared to Health Criteria



If minimum TEQ value is not shown, the value is off-scale low.

maximum = 94 ppt; see **Table ES-5**), a finding that is consistent with the findings of potential slight elevations of dioxin levels in livers of owls residing in this area. However, dioxin levels in the central area of RMA appear to be generally similar to off-post industrial or commercial areas around Denver. Soil samples from the peripheral areas of RMA (Area B in **Figure ES-3**) are generally low (mean = 1 ppt, maximum = 7 ppt) and are not significantly different from off-post open space or agricultural areas. None of the samples collected either on-post or off-post approached or exceeded the level of health concern for either residents or workers.

In conclusion, this study provides a large and comprehensive data set for concentrations of 29 TCDD-like PCDD, PCDF, and PCB congeners in soil. Advanced analytical techniques achieved lower detection and quantitation limits than most other studies, and extensive quality control data establish that the data are reliable and accurate. Confounders were evaluated and found to be minimal. These strong methods and robust study design provide greater assurance that the data have high quality and usability at trace levels. This study and its design and methods are an excellent template for future studies that may be needed to provide high quality data with adequate quantitative usability for risk assessments.

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1.0 INTRODUCTION

1.1 Chemistry and Toxicity of Dioxins

Dioxins are a class of compounds that are of potential human health concern because they may pose an increased risk of cancer and adverse non-cancer health effects at extremely low levels of exposure (USEPA 2000a). The most toxic member of the class is *2,3,7,8*-tetrachlorodibenzo-*para*-dioxin (TCDD). The toxicity of TCDD is believed to be initiated by binding of the TCDD molecule to a cellular protein referred to as the aryl hydrocarbon (Ah) receptor. However, there are many different halogenated chemicals besides TCDD that can bind to this receptor and trigger some or all of the toxic responses that are associated with TCDD exposure. This includes other members (congeners) of the polychlorinated dibenzodioxin (PCDD) class, as well as some polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), other types of halogenated (e.g., brominated) dioxins and furans, as well as various other chlorinated hydrocarbons (e.g., some chlorinated naphthalenes and di-phenyl ethers). For the purposes of this report, the term "dioxins" is used to refer to the set of 29 TCDD-like congeners in the polychlorinated dioxin/furan/biphenyl group listed in **Table 1**.

All of the congeners listed in **Table 1** are relatively planar (flat), and have lateral chlorine substituents at locations similar to that for TCDD. The structural similarity among this group of compounds is illustrated in **Figure 1**. Because of this structural similarity, all of these congeners bind to the aryl hydrocarbon (Ah) receptor and possess TCDD-like toxicity. However, not all of the congeners are equally toxic, due to differences both in toxicokinetics (the rates of absorption, distribution, metabolism, and excretion of the congeners, all of which affect the concentration of congener in the target tissue) and in toxicodynamics (binding of the congener to the Ah receptor and the nature the magnitude of response that follows). The relative potency of a congener compared to TCDD is expressed in terms of the Toxicity Equivalency Factor (TEF). **Table 1** lists current consensus TEF values for mammals (including humans), birds, and fish. These TEF values were developed by a panel of experts assembled by the World Health Organization (Van den Berg et al. 1998). Note that TEFs are often based on limited data, and so they are only approximations of the relative toxicity of each congener, rounded up (in order to be conservative) to the nearest half order of magnitude. Also note that most TEFs are based on relative binding affinity of the congener for the Ah receptor, and so do not account for potential differences between congeners with regard to absorption and distribution to target tissues.

Table 1. List of Dioxin-Like Analytes and TEFs

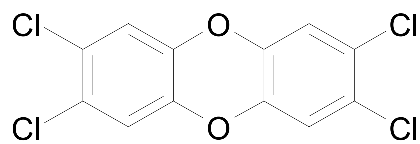
Class	Target Analyte	TEF		
		Mammals	Birds	Fish
Dibenzo-p-dioxins (PCDDs)	2,3,7,8-TCDD	1	1	1
	1,2,3,7,8-PeCDD	1	1	1
	1,2,3,4,7,8-HxCDD	0.1	0.05	0.5
	1,2,3,6,7,8-HxCDD	0.1	0.01	0.01
	1,2,3,7,8,9-HxCDD	0.1	0.1	0.01
	1,2,3,4,6,7,8-HpCDD	0.01	< 0.001	0.001
	OCDD	0.0001	0.0001	<0.0001
Dibenzofurans (PCDFs)	2,3,7,8-TCDF	0.1	1	0.05
	1,2,3,7,8-PeCDF	0.05	0.1	0.05
	2,3,4,7,8-PeCDF	0.5	1	0.5
	1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
	2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
	1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
	OCDF	0.0001	0.0001	<0.0001
Co-planar PCBs	3,3',4,4'-TCB (77)	0.0001	0.05	0.0001
	3,4,4',5-TCB (81)	0.0001	0.1	0.0005
	3,3',4,4'-5-PeCB (126)	0.1	0.1	0.005
	3,3',4,4',5,5'-HxCB (169)	0.01	0.001	0.00005
Mono-ortho PBCs	2,3,3',4,4'-PeCB (105)	0.0001	0.0001	< 0.000005
	2,3,4,4',5-PeCB (114)	0.0005	0.0001	< 0.000005
	2,3',4,4',5-PeCB (118)	0.0001	0.00001	< 0.000005
	2',3,4,4',5-PeCB (123)	0.0001	0.00001	< 0.000005
	2,3,3',4,4',5-HxCB (156)	0.0005	0.0001	< 0.000005
	2,3,3',4,4',5'-HxCB (157)	0.0005	0.0001	< 0.000005
	2,3',4,4',5,5'-HxCB (167)	0.00001	0.00001	< 0.000005
	2,3,3',4,4',5,5'-HpCB (189)	0.0001	0.00001	< 0.000005

TEF = Toxicity Equivalency Factor

TEF values are consensus estimates recommended by the World Health Organization (Van den Berg et al. 1998) for use in estimating relative toxicity in biological tissues.

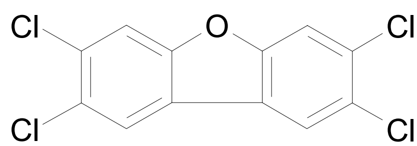
Figure 1. Structure of Dioxins, Furans and PCBs

Dioxins
75 congeners, 7 of which have significant TCDD-like activity
Most potent is



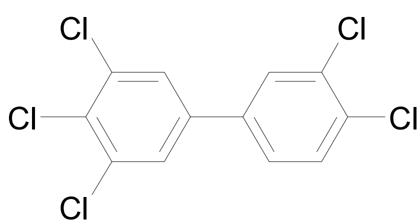
2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) (TEF = 1.0)

Furans
135 congeners, 10 of which have significant TCDD-like activity
Example structure:



2,3,7,8-tetrachlorodibenzofuran (TEF = 0.1)

PCBs
209 congeners, 12 of which have significant TCDD-like activity
Example structure:



3,3',4,4',5-Pentachlorobiphenyl (PCB-126) (TEF = 0.1)

Toxic congeners are flat with lateral chlorines, and bind to the Ah-receptor

1.2 Overview of the Denver Front Range Dioxin Soil Study

Because of the potential health concerns associated with exposure to TCDD-like dioxins, and because dioxins tend to be very persistent in the environment, EPA often investigates the occurrence of dioxins in environmental media (mainly soils) at CERCLA (Superfund) sites and other sites of regulatory concern. One such site is the Rocky Mountain Arsenal (RMA). The RMA is a parcel of land that is approximately 27 square miles in area, located northeast of Denver, Colorado, in USEPA Region 8. The RMA was used by the US Army for the manufacture and testing of munitions, and was also leased by Shell Oil Company for the manufacture of pesticides. Because of extensive chemical contamination in the central portion of the site, in 1982 the USEPA (Region 8) became involved in studies to address the clean up of RMA, and the site was placed on the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) National Priorities List (NPL) in 1987. The chemicals of principal health concern at RMA vary from location to location, and include pesticides, metals, solvents, chemical process intermediates, and chemical warfare agents. In particular, several organochlorine pesticides (OCPs), mainly aldrin and dieldrin, are the primary contaminants of concern (COCs), as well as a number of their intermediates and degradation products (USEPA 1999).

In order to investigate whether dioxins were of potential concern at the RMA, USEPA Region 8, working in cooperation with the State of Colorado's Department of Public Health and Environment and the Rocky Mountain Arsenal Remediation Venture Office, undertook a series of related studies to characterize the occurrence and levels of dioxins at the site. The first study (BAS 2001) focused on measurement of dioxin levels in tissues of ecological receptors. This approach was used because ecological receptors tend to bioaccumulate dioxins and integrate exposures over a wide area, and hence may be a more sensitive measure of dioxin contamination than soil analysis. Ecological receptors investigated in the study included birds (kestrel eggs, owl livers) and fish (carp eggs). Samples were collected from several areas on the RMA, and these were compared to samples from receptors collected at off-site reference areas. The results (discussed in greater detail in Section 4.7) did not indicate any evidence of dioxin contamination except possibly in birds from the central (South Plants) area of RMA where chemical manufacturing formerly occurred at the site.

Based on the results from the BAS (2001) study, a series of four follow-on studies were designed to focus on direct measurement of dioxins in on-post surface soils (i.e., soils from within the boundaries of RMA), as well as an extensive set of off-post reference soils (USEPA 1999). These four soil studies (three on-post soil investigations and one off-post soil investigation) were planned and performed together in order to maximize the scientific utility of the data and help minimize time and costs. These four studies are briefly outlined below.

Study 1 (USEPA 2001a) was a study of dioxin levels in off-post surface soils collected from an area of over 1,000 square miles along the front range of the Rocky Mountains in the greater metropolitan Denver area. These samples were collected to characterize "ambient" concentration levels of dioxins in soil, stratified according to land use (open space, agricultural, industrial, commercial, residential). This study was needed because 1) there are multiple sources of dioxin release to the environment, including incineration of medical and municipal organic wastes which have high contents of chlorine (USEPA 1994) as well as combustion products released from power plants, wood burning furnaces, forest fires, etc. (USEPA 1998b), and 2) because data on ambient levels of dioxins in the literature are subject to a number of limitations and uncertainties (see Section 4.2). The goal of this study was to provide a reliable data set on dioxin levels in ambient surface soils for use in interpreting data on dioxin levels in soil from the RMA as well as at other hazardous waste or dioxin-contaminated sites in USEPA Region 8 or elsewhere, as appropriate.

Study 2 (USEPA 2001b) focused on characterization of dioxin concentration levels in stratified random on-post soil samples collected from the RMA. The primary goal was to determine if dioxin soil concentrations in soil on the RMA site are significantly elevated above existing concentrations in the surrounding Denver area.

Study 3 (USEPA 2001c) focused on the Western Tier Parcel (WTP) of the RMA. This is an area of about 960 acres located on the western edge of RMA. Previous investigations performed in the WTP indicated the area is not substantially impacted by pesticide wastes, and the Rocky Mountain Arsenal National Wildlife Refuge Act of 1992 directed that the WTP be sold as surplus Federal property for potential future commercial development. The primary goal of this study was to determine if dioxin levels in the WTP would be of potential health concern if the parcel were developed for commercial use (including a child day-care center).

Study 4 (USEPA 2001d) focused on soil samples from the central (South Plants) area of RMA, along with several other "historic use" areas that may have been used for disposal of chemical wastes. The primary objective was to determine if dioxin levels in soil were elevated in any of these sub-locations, and to evaluate potential health risks to on-site workers who might come into contact with the soil in these areas during cleanup activities.

Collectively, these four studies are referred to as the Denver Front Range Dioxin Soil Study. The results of these studies have been presented previously in a series of separate reports (USEPA 2001a, b, c, d). These documents can all be found in the Region 8 Records Center, and may also be available on-line at the Region 8 web site (www.epa.gov/Region8/superfund/sites).

1.3 Purpose of This Document

This current document is the final report regarding the Denver Front Range Study of Dioxins in Surface Soil. It consolidates the data and findings from each of the four soil studies that comprise the Denver Front Range Dioxin Soil Study in order to provide a comprehensive presentation of the soil data and to facilitate evaluations that can only be based on the consolidated data. This includes an analysis of the data using Principal Components Analysis (PCA) as a means for "fingerprinting" the dioxins that are present at on-site and off-site locations. In addition, this document interprets the soil data in light of related data on dioxin levels in biological tissues from on-post and off-post ecological receptors (BAS 2001).

2.0 METHODS

A detailed description of the rationale, methods, and Standard Operating Procedures (SOPs) used in this study is provided in the Quality Assurance Project Plan (QAPP) for the study (USEPA 1999). A summary of key elements of the study design and of the methods employed is presented below.

2.1 Soil Sampling Design

Table 2 presents an overview of the soil samples which were collected during this project. Because dioxins are very poorly water soluble and they tend to bind tightly to organic material in soil, it is expected that any dioxin contamination in soil that has occurred as a result of atmospheric deposition and/or disposal of dioxin-contaminated wastes will be most concentrated in surface soil. Therefore, all soil samples collected for this study were collected at 0-2 inches in depth. Further details on each component of the soil sampling effort are presented below.

2.1.1 Off-Post Sampling Locations (Study 1)

The area selected for investigation of dioxin levels in soil samples at "off-post" reference areas (i.e., outside the boundaries of the RMA) was a square approximately 30 miles on a side, centered approximately on Denver, Colorado. This area encompasses approximately 1,000 square miles, and includes a wide variety of different land uses.

Property Ownership

All soil sampling locations in this study were on governmental (public) lands, including properties controlled by Federal, State, County, City, or other Denver-area agencies.

Spatial and Land-Use Representativeness

In order to be generally useful, the data set of ambient soil concentration values in Denver Front Range area soils must be representative of the range of conditions which exist within the entire study area. In order to achieve spatial representativeness, the study area was divided into four quadrants, and efforts were made to distribute sampling locations evenly between and within the quadrants. Because it was considered likely that dioxin levels might also

Table 2. Summary of Fine-Sieved Surface Soil Samples Collected, Analyzed and Evaluated

Location	Sub-Location	Number of Samples			Sample Type	Map	Details (Coordinates, descriptions)
		Collected	Analyzed	Evaluated			
Off-Post (Samples from 1,000 square mile area of Denver Front Range)	Agricultural	27	27	27	Grab	Figure 2	Appendix C1
	Commercial	31	31	30 (b)	Grab		
	Industrial	30	29 (a)	29	Grab		
	Open Space	38	37 (a)	37	Grab		
	Residential	39	38 (a)	37 (b)	Grab		
	TOTAL	**165**	**162**	**160**	**Grab**		
On-Post (Sampling locations on RMA)	Random	28	28	28	Grab	Figure 3	Appendix C2
	WTP	10	10	10	Composite	Figure 4	
	South Plants	12	12	12	Composite	Figure 5	
	Historic Use Areas	10	10	10	Composite	Figure 6	
	TOTAL	**60**	**60**	**60**	**Mixed**	Figure 12	

(a) Three off-post samples had insufficient mass to analyze the fine-sieved fraction

(b) Two off-post samples were judged to be outliers and were excluded from subsequent evaluations vary as a function of land use, efforts were also made to distribute samples approximately evenly across five different types of land use categories, as defined below:

A. Rural Land Use Group

> Agricultural - Land that is now, or has been within the past 40-50 years, tilled and used for crop production. Such lands may have had agricultural products (pesticides, fertilizers) applied, and may have been tilled.
>
> Open space - Land that is greater than 20 acres in area that has not been developed or improved and is essentially in its natural state with the exception of minor changes such as hiking trails or dirt access roads. This category may include lands used for grazing of livestock. Such lands are not expected to have received significant treatment with pesticides or fertilizers, and are not expected to have been tilled.

B. "Light" Land Use Group

> Residential - For the purposes of this study, "residential" land was defined as public property that is within 200 feet and adjacent to private residential development, but which is not within private yards. This may include public parks, neighborhood greenbelts and trails, and street medians. Schools and playgrounds are not included in this category for this study. Lands in this category are often grass-covered and may be irrigated, mowed, fertilized and/or treated with lawn-care products.
>
> Commercial - Land that is developed and used for commercial purposes, such as shopping centers, restaurants, office buildings, post offices, etc. Lands in this category may have been disturbed during development and may have current surface soil conditions ranging from lawns to weeds.

C. Industrial/Occupational Land Use Group

> Industrial - Land that is used for manufacturing, refining, warehousing, or transportation purposes (e.g., garages, railroads, etc.). Such lands may include facilities that employ chemicals in manufacturing processes, and may include facilities that have on-site power-generation and/or waste disposal facilities.

Each sampling station that was selected for inclusion in the study was assigned to one of these five land use categories based on knowledge of current site conditions and any available information on site history. While it was not uncommon to encounter sampling locations with a mixed land use history (e.g., previously agricultural or open space, currently commercial or residential), the predominant land use was employed to assign the land use category. As discussed in the QAPP (USEPA 1999), the goal was to collect approximately 30 samples from each of these five different land uses, for a total of 150 samples. As shown in **Table 2**, the actual number of off-post samples collected was 165, with a range of 27 to 39 samples in each of the different types.

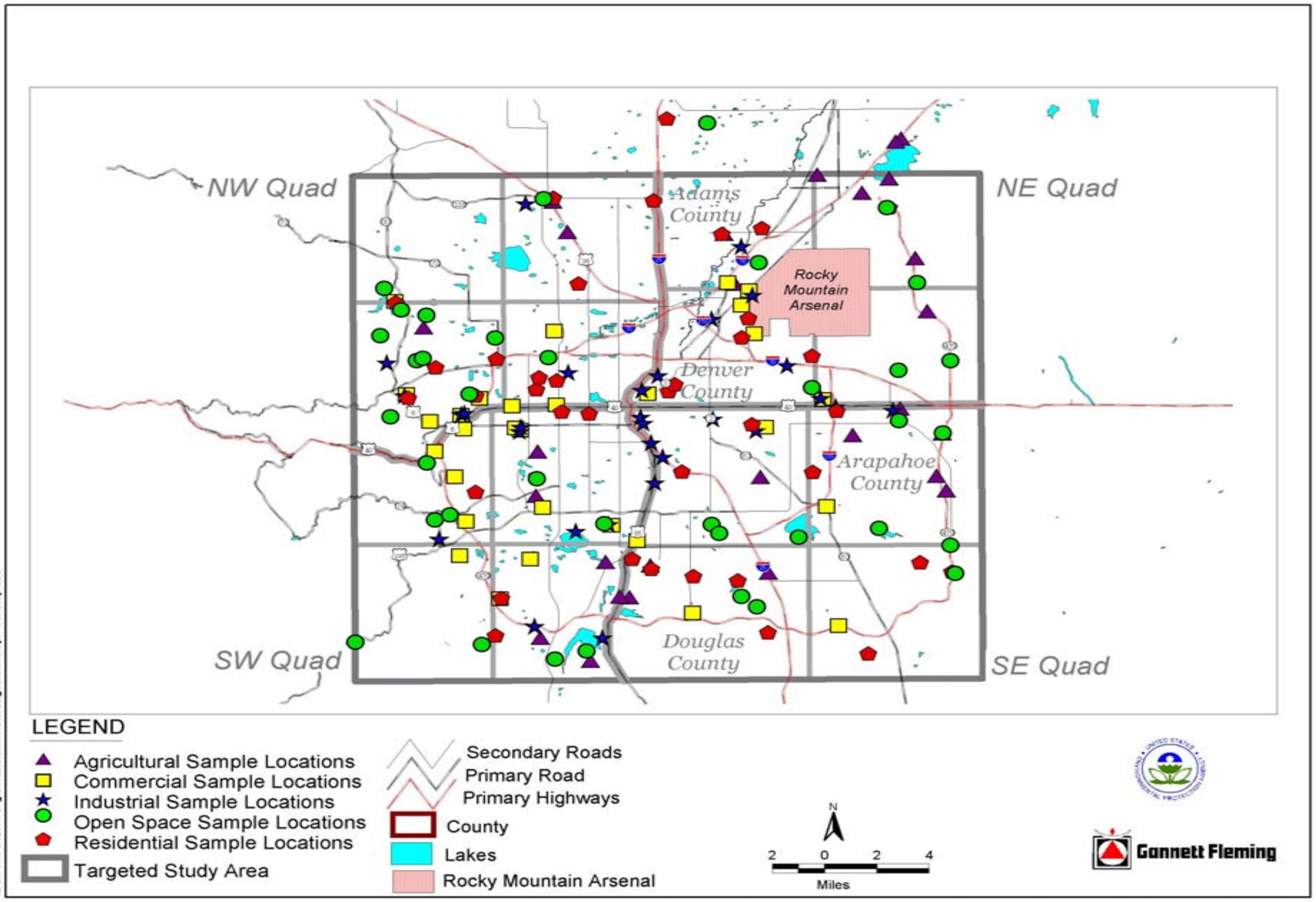
Figure 2 is a map which shows the sampling locations and the land use at each off-post soil sampling location. As seen, the samples are well-distributed across the study area, helping to ensure that the data are spatially representative. More detailed maps of the sampling locations, stratified by quadrant, are presented in Appendix C1, along with sample Global Positioning System (GPS) coordinates.

Soil samples were collected at each designated sample location without regard to the geochemical soil type at that station. However, because dioxin levels potentially could tend to vary as a function of soil type, field observations on the nature of each sample (color, texture, cover, etc.) were recorded, and the total organic carbon level and the soil particle size distribution (percent smaller than 250 um) of each sample were measured. Soil samples were not collected from locations that were known to have been covered with fill or used for borrow material within the last 10 years, since the dioxin content of such relatively recently disturbed areas might tend to underestimate dioxin levels in soils that had remained undisturbed for a long interval.

2.1.2 On-Post Sampling Locations

Three studies (Studies 2, 3, and 4, as described above) were performed to characterize dioxin levels in "on-post" soils (i.e., within the boundaries of RMA). In each study, sampling locations were selected that had soil which appeared to be undisturbed and were judged to be characteristic of the general area. Photographs were taken and descriptions of each sub-sample site were recorded, and sampling locations were surveyed to an accuracy of 0.1 foot in accord with standard practice for all sampling activities at RMA. A brief description of each phase is presented below, and details on exact sampling locations are given in Appendix C2.

Figure 2. Off-Post Soil Sampling Locations



A total of 165 surface soil samples were collected from the off-post study area. Samples were stratified into five different land use categories and four quadrants to help assure the data would be representative.

Study 2. The RMA is comprised of land that lies within 28 different platted Sections (each Section is about 1 square mile). In this study, one surface soil grab sample was collected from a random location within each of the 28 sections, as shown by the brown “x's” in **Figure 3**.

Study 3. In this study, soil sampling was focused on the Western Tier Parcel (WTP). In order to achieve spatial representativeness, the WTP was subdivided into 10 sub-parcels of approximately 80-90 acres each. Within each sub-parcel, a set of five surface soil (0 to 2 inches) samples were collected using a stratified random sampling scheme. These 10 sub-parcels and the locations of the five surface soil samples within each sub-parcel are shown in **Figure 4**. The set of 5 sub-samples from each sub-parcel were then composited to produce a single representative sample for the sub-parcel, as described in Section 2.2, below.

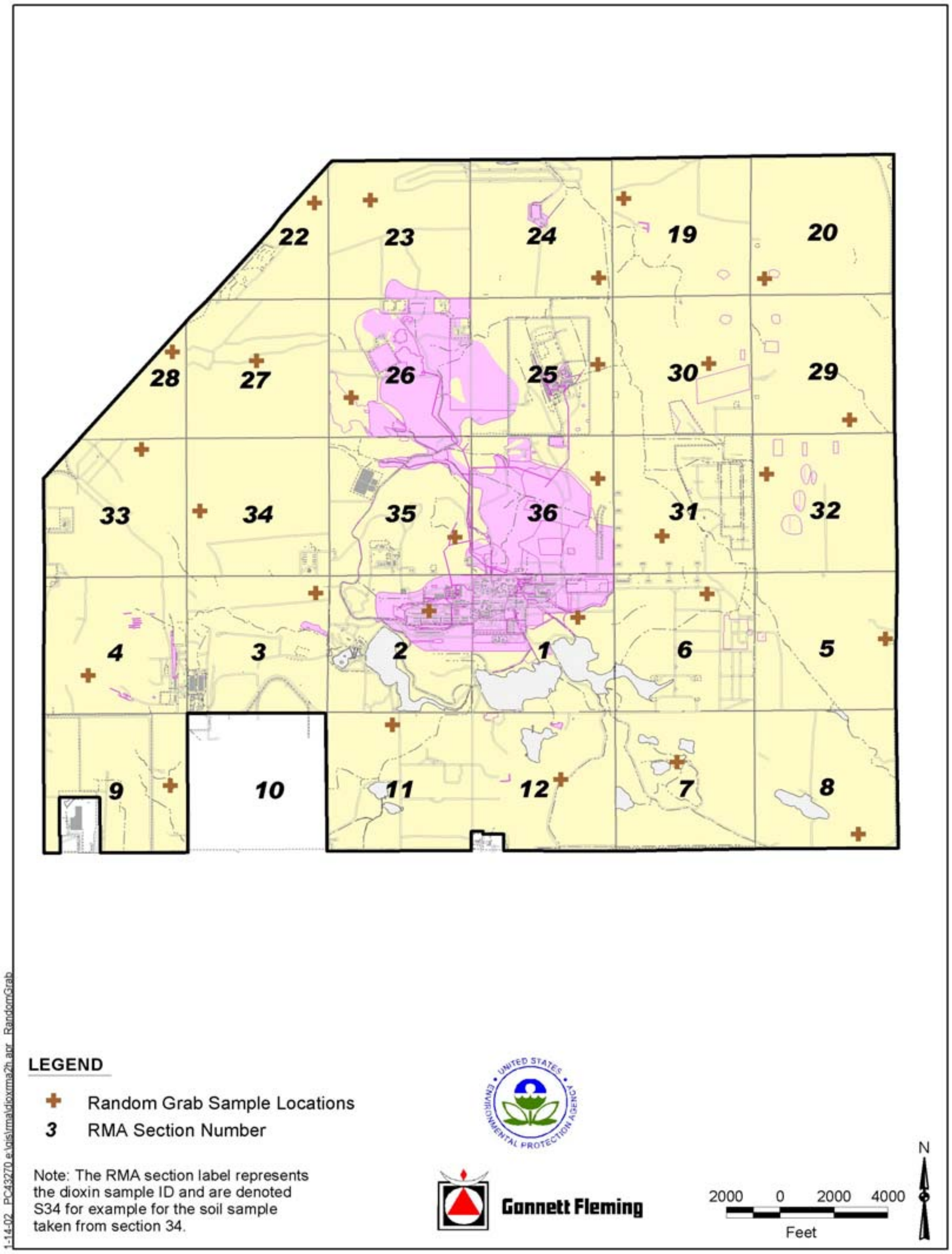
Study 4. In this study, biased soil samples were collected from several locations within the RMA that were associated with the former manufacturing operations (Study 4a), or from areas known or suspected of having received waste materials from the manufacturing operations (Study 4b). The area of chief potential concern was the South Plants area, located in the south-center (care area) of the site. In the past, this area was the chief location of pesticide and chemical manufacturing activities, and this was the area that the BAS study suggested might be causing elevated exposures in owls (BAS 2001). In order to guide the collection of samples from the South Plants area, a 12-section grid that had been established by the BAS committee was used, as shown by the blue lines in **Figure 5**. Within each grid, a set of five sub-samples was collected from stratified-random sampling locations, as shown by the blue crosses. These five sub-samples were combined into a single composite sample (one for each grid, comprising about 1/4 square mile), as described in Section 2.2, below.

In addition to the South Plants area, there are a number of other areas of varying size at RMA where historic industrial land uses or waste disposal activities might have resulted in increased levels of dioxins in soil. These areas of potential concern are described in **Table 3**. One composite sample (prepared from five stratified-random sub-samples) was collected from each of these 10 “purposeful” sampling locations, as shown by the black crosses in **Figure 6**.

2.1.3 Sampling Methods

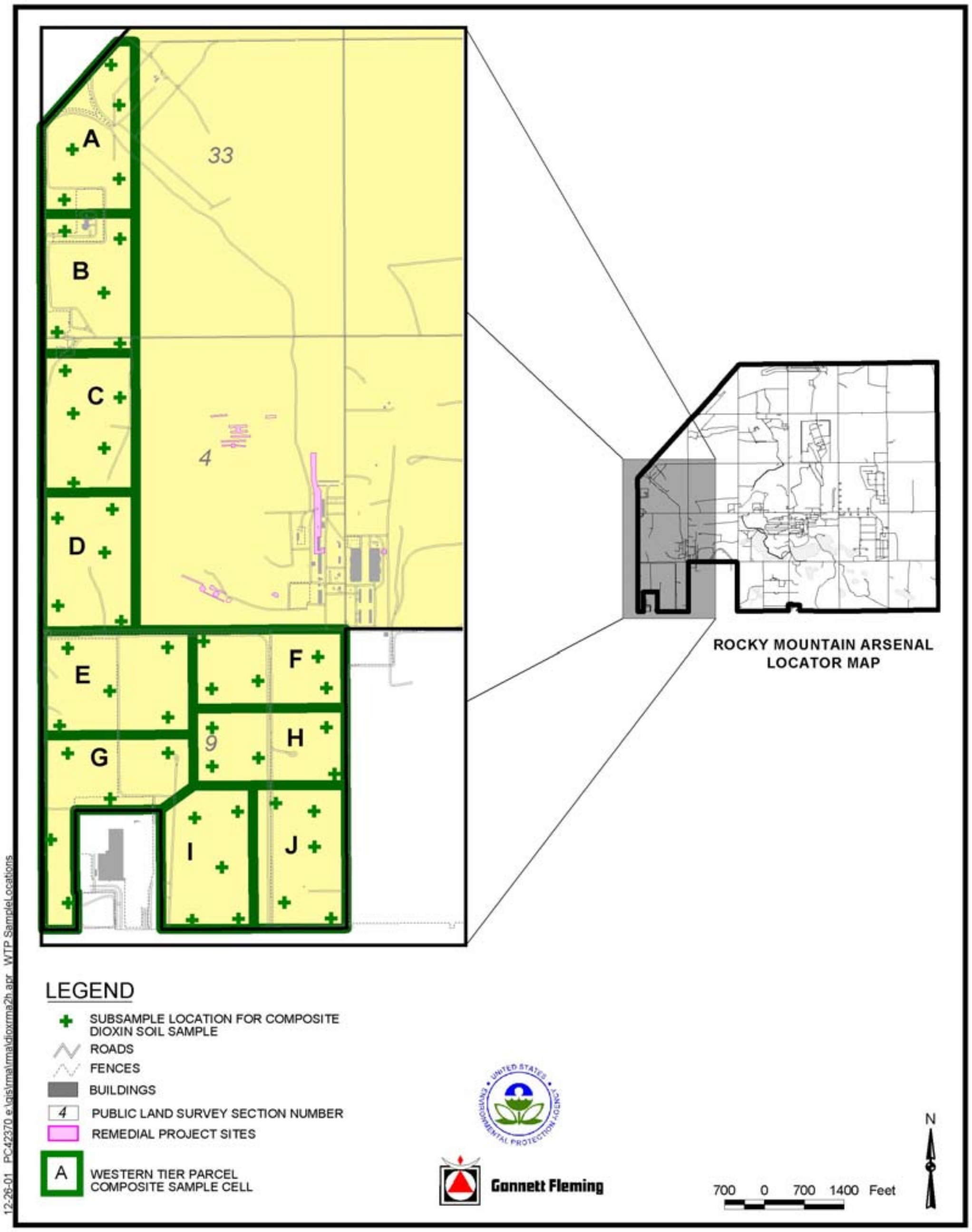
Sampling occurred between December 1999 and March 2000. All samples were collected using clean techniques that included use of disposable stainless steel trowels (one per sampling location) and plastic gloves. A ruler was used to ensure that the actual depth to which

Figure 3. RMA On-Post Stratified Random Soil Sampling Locations



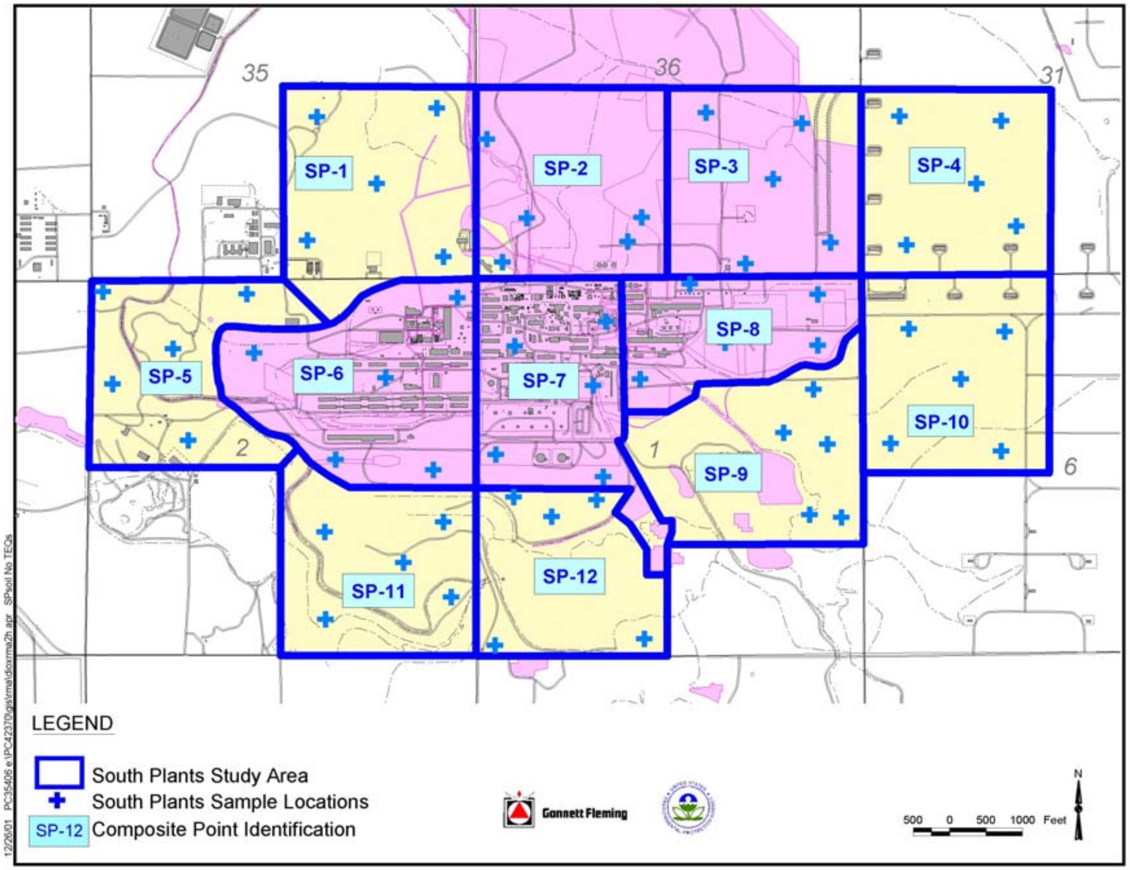
One surface soil sample was collected from each of the 28 Sections within RMA. These soil sampling locations are indicated by the red crosses. Bold numbers are the Section numbers. The pink area represents locations currently undergoing remediation for organochlorine pesticide contamination.

Figure 4. RMA Western Tier Parcel Soil Sampling Locations



The WTP was divided into 10 grids (A-J) and five surface soils were collected from each grid. These sampling locations are indicated by the green crosses. These samples were then combined to yield one composite soil sample per grid area.

Figure 5. RMA South Plants Soil Sampling Locations

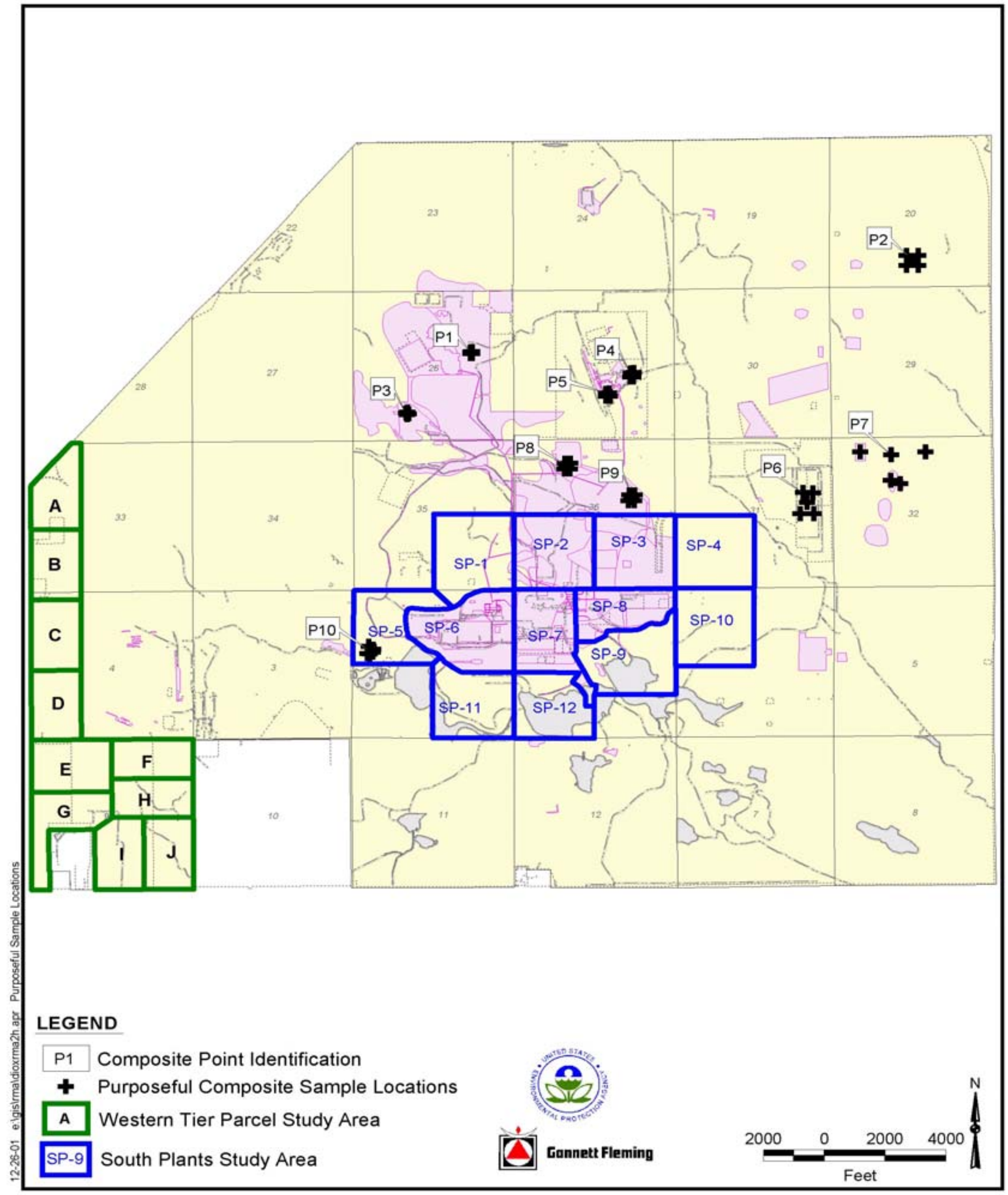


The South Plants area of RMA was divided into 12 grids (SP-1 to SP-12), and 5 surface soil samples were collected from within each grid. These sampling locations are indicated by the blue crosses. These samples were then combined to yield one composite surface soil sample from each South Plants grid area.

Table 3. RMA Purposeful Soil Sample Locations and Descriptions

Sample	Location/Description
P1	Sample P1 is located just east of the southeast corner of former Basin F in the Basin F Exterior Soils. This sample represents soils that have been impacted by the windblown distribution of Basin F liquids from the spray evaporation system.
P2	Sample P2 is located in the south central portion of Section 20 in the ash disposal area. This sample represents soils/ash where incinerator and electrostatic precipitator ash from Mustard demilitarization operations were disposed.
P3	Sample P3 is located in secondary Basin D in Section 26. This sample represents soils impacted by the disposal of liquid wastes from RMA production areas.
P4	Sample P4 is located just east of the North Plants production facility. This sample represents soils potentially impacted by the incineration operations in North Plants.
P5	Sample P5 is located within the North Plants production facility. This sample represents soils potentially impacted by GB operations within North Plants as well as the incineration operations in North Plants.
P6	Sample P6 is located in the Toxic Storage Yard (TSY) in Section 31. This sample represents soils potentially impacted by spills of various materials stored in the TSY.
P7	Sample P7 is located in former burn pits and burial trenches located in Section 32. This sample represents soils impacted by the pits and trenches.
P8	Sample P8 is located just southwest of the trash incinerator in Section 36. This sample represents soils potentially impacted by emissions from the trash incinerator.
P9	Sample P9 is located east of the Complex/Army Trenches in Section 36. This sample represents soils potentially impacted by windblown dispersion of waste and emissions from disposal and burning conducted in the trenches.
P10	Sample P10 is located near the USFWS Visitor Center in Section 2. This sample represents soils in areas which are frequently visited by the public.

Figure 6. Soil Sampling Locations at Historic Use Areas of RMA



Ten historic use areas (P-1 to P-10) at RMA were identified where historic waste disposal had occurred, and five surface soil samples were collected from each of these locations. These samples were then combined to yield one composite surface soil sample from each of the historic use areas.

soil was collected was within ½ inch of the target (i.e., a bottom depth of no less than 1.5 inches and no greater than 2.5 inches). Loose debris and most gravel or pebbles were removed from the soil sampling site. The surface soil was placed directly into a clean 16-ounce amber glass jar, filled to capacity (about 500 grams of soil), sealed with a teflon-lined lid, and stored in these bottles at room temperature in the dark until shipped. Sealed plastic coolers with frozen ice-packs and water temperature tubes were used to help ensure that no excess heating occurred during transportation to the processing laboratory.

2.2 Sample Preparation

All soil samples collected in the field were submitted under chain-of-custody to Columbia Analytical Services (CAS) in Kelso, WA, for sample preparation. Each unprocessed ("raw") sample was air-dried at about 37°C and weighed, followed by coarse-sieving through a #10 (2 millimeter) stainless steel screen. The soil fraction passing the coarse screen was referred to as the “bulk” soil fraction.

Composite Samples

For samples that were to be composited, about 100 grams of mixed bulk soil from each of the five sub-locations were combined to produce a composite bulk soil sample of about 500 grams. After thorough hand-mixing of the composite bulk soil, approximately 26 grams of the bulk composite sample was placed in a clean amber glass jar, labeled, and stored for possible future analysis. The remainder of the composited bulk sample was further sieved through a 60-mesh (250 micrometer) stainless steel screen in order to isolate soil particles less than 250 micrometers in diameter. The soil passing through this screen was referred to as the "fine" fraction. The fine fraction was prepared for analysis because fine soil particles are more likely be ingested by humans (hand to mouth contact) and ecological receptors (preening feathers, grooming fur) than coarse particles, and hence constitute the most relevant media for use in evaluating health risk. In addition, fine particles have greater surface area to mass ratios than coarse particles, and because dioxins adhere to surfaces, there might be a tendency for dioxins to be enriched in the fine fraction compared to the bulk fraction.

The fine-sieved soil samples were thoroughly mixed, and placed into four new amber sample bottles, with each bottle containing about 26 grams of the fine-sieved soil. These four aliquots of fine-sieved soil were intended to be as identical as possible, for use in reanalysis (if needed) and for establishing intra-laboratory precision and inter-laboratory reproducibility for quality control purposes. All processed soil samples were sent under chain of custody to the

USEPA Regional Laboratory in Golden, CO, for secure storage in dark cabinets, and for organization of samples for later shipments to the analytical laboratory in Kansas City, MO.

Grab Samples

Grab soil samples were prepared as described above for the composite samples, except that each sample was prepared individually and was not mixed with any other soil sample.

2.3 Sample Analysis

Following sample preparation as described above, samples were submitted by USEPA Region 8 under chain of custody to Midwest Research Institute (MRI) for congener-specific analysis of the 7 PCDDs, 10 PCDFs, and 12 PCBs listed in **Table 1**. Samples were typically shipped in stratified random lots of 18 that included a mixture of field samples and blind quality control samples (see Section 2.5). For each set of 18 samples, the laboratory added two laboratory control samples and analyzed the group of 20 as a "lot". Any samples that were broken during shipment or at the laboratory were re-submitted for analysis (sample mass permitting).

The analytical method used in this study (MRI Method 110026) is presented in Appendix E1. The method was developed by MRI with input from EPA for use at RMA. It is based on EPA Methods 1613B, 1668, and 8290, with several modifications (increased sample mass, calibration curve extended to lower levels, more stringent performance criteria) designed to improve analytical performance at the trace levels of dioxins expected in ambient soils. In brief, the congeners were determined using an isotope dilution method via high resolution gas chromatography/mass spectrometry (HRGC/HRMS). Samples were fortified with known quantities of ^{13}C-labeled PCDD/PCDF/PCB isomers and extracted with organic solvents, using two columns so that all 17 PCDDs/PDCFs and all 12 PCBs could be retained for analysis. Before cleanup of the extracts, the analytes were dissolved in hexane and fortified with ^{37}Cl-labeled *2,3,7,8*-tetrachlorodibenzo-*p*-dioxin as an internal standard. Finally, the extracts were sequentially partitioned against concentrated acid and base solutions.

In this program, the Method Detection Limit (MDL) for a congener was defined as an analyte signal that was 2.5 times the background signal ("noise") for that congener in that sample, and the Method Quantitation Limit (MQL) was defined as a signal that was 10-times the signal noise for that sample. Because "noise " levels varied from sample to sample and from congener to congener, MDLs and MQLs also varied from sample to sample and from congener to congener. For PCDD/PCDF congeners, most MDL values were between 0.2 and 1.0 ppt, and most MQL values were between 0.8 and 4.1 ppt. For PCB congeners, most MDLs were between 0.5 and 8.4 ppt, and most MQLs were between 1.9 and 34 ppt. All congener concentrations were rounded to the nearest 0.1 ppt.

Congener concentration values were used for Principal Components Analysis (PCA) as described in Section 4.5, and for calculation of TCDD-equivalent concentration values, as described below.

2.4 Calculation of TCDD-Equivalents (TEQ) in Soil

The aggregate (summed) toxicity of a mixture of different dioxins in an exposure medium such as soil is a complex function of the following variables:

a) the concentration of each congener in the medium
b) the chronic average daily intake of the medium by the receptor
c) the absorption of each congener from that medium
d) the distribution, metabolism, and elimination of the congeners
e) the binding affinity of the congeners for the Ah receptor
f) the biological response to Ah receptor binding

Thus, proper calculation of health risk from exposure to soil that contains a mixture of congeners must take all of these variables into account. However, because detailed toxicokinetic and toxicodynamic data are not available for most congeners, screening-level evaluations of dioxin concentrations in soil samples are usually performed by calculating the concentration of TCDD-Equivalents (TEQ) present in the soil as the TEF-weighted sum of each of the 29 dioxin-like congeners (17 dioxins and furans, plus 12 PCBs), as follows:

$$\text{TEQ (total)} = \sum_{i=1}^{29} (C_i \cdot \text{TEF}_i)$$

In cases where interest is focused on the contribution of PCDDs and PCDFs only (i.e., PCBs not included), the value is calculated as:

$$\text{TEQ (D / F)} = \sum_{i=1}^{17} (C_i \cdot \text{TEF}_i)$$

After summation, all TEQ values are rounded to the nearest 0.1 ppt.

It is important to re-emphasize that this application of TEFs to the calculation of soil TEQ values is appropriate only for screening level purposes. This is because TEFs are derived from, and thus should only be applied to, biological endpoints (e.g., Ah receptor binding, embryotoxicity). The soil TEQ approach is analogous to assuming equal absorption and delivery of all congeners to target cells, and does not account for the effect of differential absorption, metabolism, distribution, and excretion of different congeners from soil. Risk assessors should account for these uncertainties in the interpretation of the soil TEQ values.

2.5 Statistical Analysis

Comparisons Between Data Sets

Comparisons between data sets consisting of similar sample types (i.e., all grab samples or all composite samples) were performed using Kruskal-Wallis one-way analysis of variance (ANOVA) on ranks to compare multiple data sets, and the Mann Whitney Rank Sum Test to compare individual pairs of data sets. These non-parametric approaches were used because most of the data sets were right-skewed and failed tests of normality. Quantitative statistical comparisons were not performed for data sets that were composed of mixed or dissimilar sample types (some grabs, some composites), since compositing is expected to alter (decrease) the variance of the composites compared to the grab samples.

Principal Components Analysis

Evaluation of dioxin congener patterns in different data sets (e.g., on-site soils vs off-site soils) was performed using Principal Components Analysis (PCA) (Jackson. 1991, Rencher 1991, Wilkinson et al. 1996). In brief, PCA is a method for analyzing a set of potentially correlated independent inputs (congener concentrations in soil) and calculating one or more new metrics (the principal components) that capture the inherent variability in the inputs while reducing the number of independent variables. Further details on the use of PCA in this project are provided in Section 4.5.

Regression Analysis

Although PCA is a powerful statistical tool, it does have some limitations in the evaluation of complex data sets. Therefore, a different statistical approach involving multiple pairwise regression analysis was investigated as a means for characterizing congener patterns based on the consistency (or lack of consistency) in mass ratios between pairs of congeners. Further details on this approach are provided in Section 4.5.

2.6 Quality Assurance

A number of steps were taken to obtain information that would allow an assessment of the quality and reliability of the data collected, so that assessments of the usability of the data could be made and defended. As noted above, the analytical laboratory routinely processed and analyzed "lots" of 20 samples at a time. Of these 20 samples, two were laboratory QC samples, including one laboratory control sample (LCS) and one matrix blank (white sand). Therefore, 18 samples were usually available for samples submitted by EPA. In general, the 18 samples were comprised of 14 field samples plus four blind Quality Control (QC) samples, as described below.

Performance Evaluation Samples

Performance Evaluation (PE) samples are samples of a medium that contain known (certified) quantities of analyte and that are submitted blind and in random order along with authentic field samples to the analytical laboratory. In this study, three different types of soil PE samples were used, referred to as "clean", "low", and "medium". In most cases, one aliquot of each of these three PE samples was submitted to the laboratory as part of each batch of 18 soil samples.

These PE samples were obtained from USEPA's Quality Assurance Technical Support (QATS) laboratory. The "clean" soil (also referred to as "native western soil") was obtained from an uncontaminated location at the Idaho National Engineering and Environmental Laboratory (INEEL). The concentration of TEQ is this sample is not certified, but is reported to be less than 2 ppt TEQ. The QATS laboratory prepared the certified PE samples by spiking the "clean" soil with known levels of PCDDs and PCDFs, and submitting these samples for multiple rounds of congener-specific analysis. Based on the certified concentration values (the average across 12-20 independent analyses) for each dioxin-like PCDD/PCDF congener, the TEQ values certified by the QATS laboratory were 35 ppt and 59 ppt for the low and medium unseived samples, respectively (see **Table 4**). However, these certified TEQ values were calculated using older TEF values. If the TEQ content is recalculated using the QATS-certified concentration values for each congener and the TEF values recommended by WHO (Van den Berg et al. 1998), the resultant values are 40 ppt and 70 ppt TEQ, respectively (also shown in **Table 4**). Because all of the TEQ calculations in this report are based on the TEF values of Van den Berg et al.

Table 4. Nominal TEQ(D/F) Concentrations in Soil Performance Evaluation Samples

QATS PE Sample (a)	Nominal TEQ(D/F) (ppt)	
	Certified Value Established by EPA QATS (b)	Recalculated Value Based on WHO TEFs (c)
Native western soil	< 2	--
Low standard	35	39.9 ± 2.8
Medium standard	59	70.4 ± 5.7

(a) All PE samples were obtained from EPA's Quality Assurance Technical Support (QATS) laboratory.

(b) Certified values are based on multiple analyses by participating analytical laboratories using variations of EPA Method 8290, and calculating TEQ using older TEF values.

(c) Recalculated TEQ values (mean ± standard deviation) are based on consensus concentration values (mean ± standard deviation) for each congener measured using variations of EPA Method 8290, and calculated using current TEF values (Van den Berg et al. 1998).

(1998), the recalculated values are considered to be the most appropriate for evaluating accuracy of the analytical laboratory.

Field Splits and Duplicates

A field duplicate is a second sample of soil collected at the same time and the same place as a primary field sample. In this case, field duplicates were collected by alternating scoops of soil into two bottles with separate and random sample identification numbers. A field split is a sample that is generated by dividing a single field sample into two parts. As described above, in this study every field sample was dried and sieved, and this fine material was divided into four essentially identical aliquots (field splits) of 26 grams each. One of these samples was submitted as the primary field sample, and USEPA Region 8 selected additional random samples to submit as split samples. In these cases, a second bottle of these samples was assigned a new random sample identification number and submitted in random order for analysis by MRI, generally within the same "batch", so as to not have the split results be confounded by inter-batch variability. Analysis of field duplicate and field split samples provided data on the variability within and between related samples. One sample of this type (either field split or field duplicate) was submitted to the laboratory (blind) with each set of 14 field soil samples.

Laboratory Quality Control Samples

Internal laboratory quality control samples are samples prepared and run by the laboratory in a non-blind fashion to monitor the performance of the analytical method. Laboratory QC samples included Method Blanks (white sand as a surrogate for clean soil), Laboratory Control Samples (similar to PE samples, but the identity and nominal concentration are known to the laboratory), and optionally Method Duplicates (investigative samples that are split prior to sample preparation at the analytical laboratory). As noted above, two samples in each batch were used by the laboratory for internal laboratory QC samples.

2.7 Data Validation/Verification

Validation of analytical results was conducted according to SOP 803 (revision 1) of the QAPP (USEPA 1999) (see Appendix E2). This validation method was tailored to match the site-specific method used to analyze the 29 dioxin-like congeners in soils (see Appendix E1). An independent contract chemist team, with expertise in validation of trace PCDD, PCDF, and PCB analytical results, conducted the analytical reviews. Full validation was performed for all on-post samples and a number of off-post samples, along with full verification of all sample results.

Contract-required Method Quantitation Limits (CRQLs) and QA/QC performance were reviewed against pre-defined performance criteria for Precision, Accuracy, Representativeness, Comparability, and Completeness (PARCC) to ensure that results were reliable and usable for the objective identified in the QAPP. Narratives were produced for each analytical lot to describe the results of the data and also the validation for that lot. Each measured concentration value was assigned a data usability flag, if needed, using the data quality flag codes presented in **Table 5**. In accordance with USEPA data usability guidelines (USEPA 1992), these flags were used for producing two alternative data sets:

1) a <u>semi-quantitative</u> set of results in which congeners that yielded signals below the sample-specific detection limit (MDL) for that congener (signal/noise ratio less than 2.5) were evaluated by assuming a concentration value equal to ½ the detection limit for that congener, and other flagged data were adjusted according to the rules shown in **Table 5**. This is referred to in this report as the "**Full**" data set (i.e., all 29 dioxin-like congeners are included).

2) a <u>quantitative</u> set of results based only on those congeners that had no disqualifying flags (D, NJ, R), and had a result greater than the MDL (see **Table 5**). This is referred to in this report as the "**Quant**" data set.

These two types of results (Full, Quant) were calculated to help evaluate the relative contribution to TEQ of congeners with estimated and quantifiable concentration values, and to use the quantitative subset of results to statistically evaluate the profiles of congeners in soils (see Section 4.5). These methods were applied both to the PCDD/PCDF congeners alone, and to the total data set (including PCBs). Thus, there are a total of four different measures of TEQ considered in this report, as summarized below:

Designation	Congeners Included		Treatment of Low Values	
	PCDDs/PCDFs	PCBs	Value < MDL	Value > MDL but < MQL
Full TEQ(D/F)	17	0	Use ½ MDL	Use value
Full TEQ(total)	17	12	Use ½ MDL	Use value
Quant TEQ(D/F)	17	0	Don't use	Use ½ MQL
Quant TEQ(total)	17	12	Don't use	Use ½ MQL

Table 5. Definition, Application, and Uses of Analytical Data Flags

Validation Flags	Meaning of Flags for Dioxin Analyses in Soils and Tissues by the MRI Lab	Data Usability (a)	
		Full data set used (*semi-quantitative*)	**Quantitative** (qualified sub-set used)
E	Estimated Maximum Potential Concentration; the relative ion abundance ratios did not meet the acceptance limits.	use value	use ½ value
D	EMPC is caused by polychlorinated **D**iphenyl ether interference.	use ½ value	don't use
B	Analyte was detected in associated Method **B**lank, sample concentration <5x MB concentration.	use value	use ½ value
C	Concentration is above upper **C**alibration Standard; result is an estimate, flagged C by lab and J added by validator.	use value	use value
I	Recovery of 13C-labeled **I**sotopic analyte outside of criteria	use value	use value
J	Estimated: e.g., isotopic standard is outside CCAL range, native analyte recovery in LCS is outside criteria, etc.	use value	use ½ value
NJ	Presumptive evidence for the presence of an analyte with an estimated value; if used for 2378-TCDF, see "U" below.	use ½ value	don't use
S	Peak is **S**aturated; result, if calculated, is flagged by the validator as an estimate - "J".	use value	use value
U	**U**nconfirmed: column is not specific for 2,3,7,8-TCDF; confirmation not requested. Validator now uses "NJ" flag.	use value	use ½ value
R	**R**ejected: result is invalid and not usable.	use ½ MDL	don't use
***use of MRI Laboratory's reported "LT" (less than) values* <MQL (10 x Signal:Noise)**			
LT *applied **first** to data, then apply flags!*	"LT" is not a true "flag", but if a LT result is a "**detect**" **above the MDL** (2.5 x Signal:Noise = lab EDL), then	use value	use ½ value
	"LT" is not a true "flag", but if a LT result is a "**non-detect**" **below the MDL** (2.5 x Signal:Noise = lab EDL), then	use ½ EDL	don't use

(a) In accord with concepts in the 1992 USEPA Data Usability for Risk Assessment in Superfund guidance (USEPA 1992), data quality flags are used to produce two data-sets: 1) a "**Full**" set of semi-quantitative results with an **actual** or a **proxy** value for each of the measured congeners; and 2) a more "Quantitative" but limited set of results that has more certain identification and more accurate quantities of congeners which have **no disqualifying flags** (D, NJ, R or LT), but can use **limited proxies** (E, B, J or U). This distinction is made to better understand and limit artifactual impacts of the *less certain **estimated** values* on TEQs, analyzing the degree of this sensitivity to trace-level "noise" by comparing TEQs from these two data sets. In addition, congener profile pattern analysis should only use the analytes that are quantifiable (above the MQL).

In general, the Full TEQ(D/F) results (indicated by the shaded row) were considered to be the most relevant for screening potential health risks from dioxins, since EPA risk assessment guidance generally recommend assuming a value of ½ the detection limit for analytes below the detection limit (USEPA 1989).

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3.0 RESULTS

Detailed analytical results for field samples collected during this program are presented in Appendices A1 to A4, and detailed results for all of the QC samples run as part of this study are presented in Appendix A5. Graphical representations are presented in Appendix B. The results are summarized below.

3.1 Data Quality Assessment

3.1.1 Data Validation

A full validation of the data for all on-post samples and a partial validation with full verification of all off-post samples analyzed during this project was performed in accord with the procedures detailed in the Data Validation SOP (Appendix E2). The data validation effort identified only one sample that failed to meet the pre-established QC acceptance criteria. The sample was from WTP sub-parcel B (sample 911), and was noted to have elevated detection limits (mostly for furans). These detection limits were considerably outside the target MDLs for the study and were roughly 10-fold higher than MDLs for the same congeners in other soil samples in the same lot. Therefore, a duplicate 26 gram aliquot of this soil sample was re-submitted in the usual blind and random manner for analysis. The results from analysis of this sample (assigned the number 911-R) yielded MDLs for the congeners that were substantially improved when compared to the original analysis, and so the results for 911-R were used for the WTP study in place of the rejected results for sample 911. All other samples were judged to meet the pre-defined performance criteria, and did not require re-analysis.

3.1.2 Quality Control Samples

Method Blanks

Full TEQ(D/F) and Full TEQ(Total) values for 22 method blanks (matrix = white sand) both averaged 0.4 ppt (range = 0.1-1.7 ppt). These data indicate that there was no significant source of PCDD, PCDF, or PCB contamination during sample processing or analysis within the analytical laboratory.

Splits and Duplicates

The results for field split and field duplicate soil sample pairs were generally in good agreement, as shown in **Figure 7**. Summary statistics for Full TEQ(D/F) are presented in **Table 6**, stratified into two bins depending on the TEQ concentration, as described in the QAPP (USEPA 1999). In brief, the Full TEQ(D/F) value is about 5 ppt for a sample where each PCDD/PCDF congener is present at the average MQL for that congener. For samples with TEQ values relatively close to this value (< 25 ppt TEQ), precision was evaluated on an absolute basis. For these samples, the average absolute difference between sample pairs was about 1.5 ppt TEQ for splits to 1.7 ppt TEQ for duplicates, well within the acceptability criterion of one MQL (about 5 ppt TEQ) that was established by the QAPP (USEPA 1999). For samples with TEQ values above 25 ppt (i.e., greater than 5-times the MQL), precision was evaluated using the Relative Percent Difference (RPD). For these samples, the RPD ranged from 6% to 21%, also well within the acceptance criterion of 30% established by the QAPP (USEPA 1999). These results indicate good precision was achieved for trace levels of dioxins in soil samples.

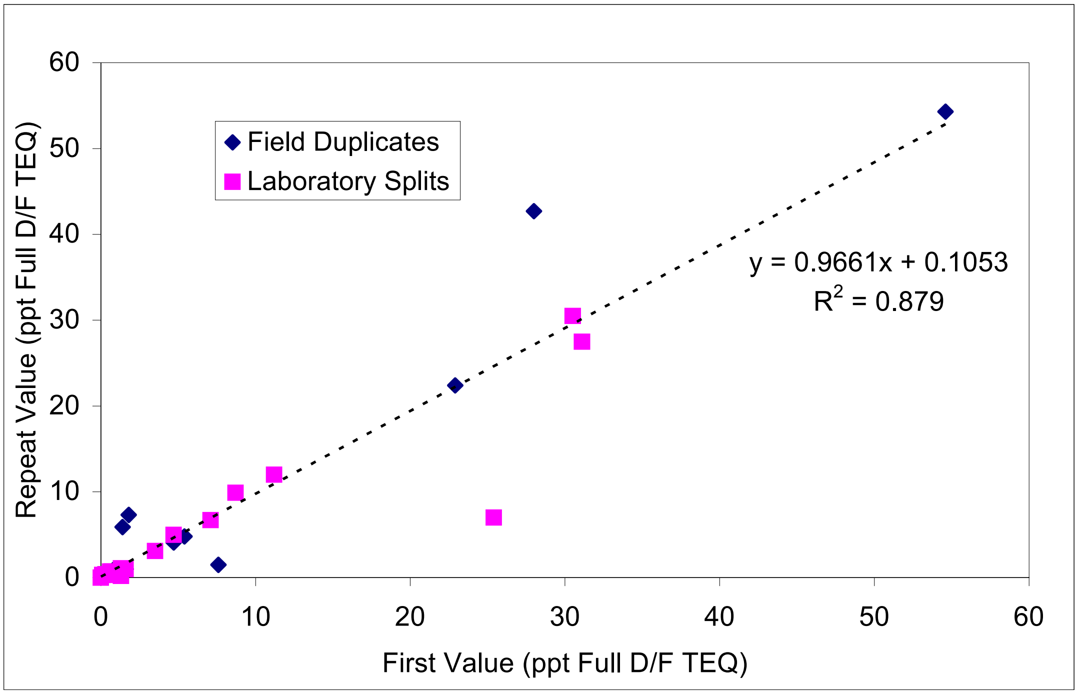
Performance Evaluation Samples

Table 7 presents summary statistics for performance evaluation (PE) soil samples obtained from the USEPA QATS laboratory. These data are also shown graphically in the upper portion of **Figure 8**, plotted as a function of Sample Delivery Group. As seen, the Full TEQ(D/F) values measured in this study tend to be slightly higher than recalculated TEQ(D/F) values for the low and medium QATS samples (see **Table 4**), but are quite close to the Quant TEQ(D/F) values. This slight difference between the measured and the recalculated nominal value is not unexpected, since the certified congener concentrations used to recalculate the expected TEQ values are based on data from many different laboratories using a variety of different instrument and analytical techniques, each with a differing set of detection limits. In some cases, non-detects were treated as zero rather than ½ the detection limit, tending to bias the recalculated nominal value slightly low. In any event, as shown in **Figure 8** (upper panel), all except three of the results for the PE samples are within the acceptance criteria (mean ± 2.5 standard deviations) of the recalculated values. Precision between multiple analyses of the PE samples was good, with coefficients of variation (standard deviation divided by the mean) generally less than 20%.

The bottom panel of **Figure 8** shows results for clean, low and medium QATS PE samples that were sieved before analysis. Because the certified value and the recalculated nominal value apply to the un-sieved sample only, there are no expected or nominal values for

Figure 7. Comparison of Duplicate and Split Results for Fine-Sieved Soil

Linear Scale



Log_{10} Scale

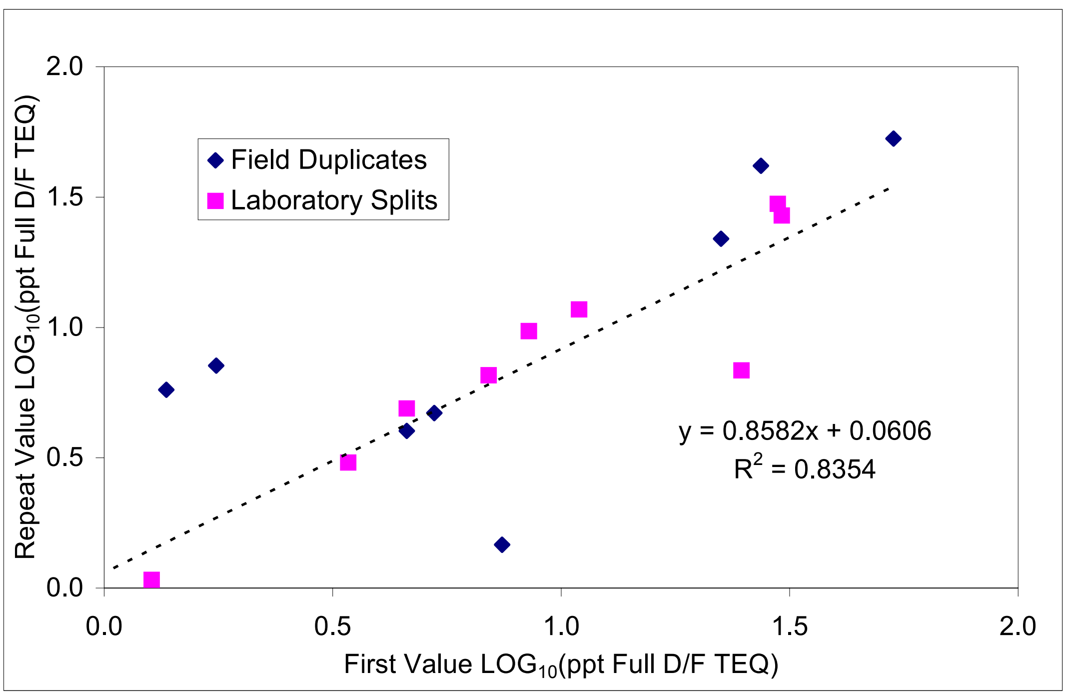


Table 6. Evaluation of Precision in Full TEQ(D/F) Estimates for Fine Fraction Soil Samples

Type	Full TEQ(D/F) ≤ 25 ppt		Full TEQ(D/F) > 25 ppt	
	N	Average Difference (ppt)	N	Average RPD (%)
Field Duplicates	11	1.7	2	21%
Laboratory Splits	16	1.5	2	6%

All values are for fine-sieved (< 250 um) surface soil particles.

In accord with the Project Plan (USEPA 1999), results near the quantitation limit (about 5 ppt TEQ) were evaluated based on the absolute difference between results rather than the Relative Percent Difference (RPD) since the RPD becomes unstable at low concentrations (< 25 ppt).

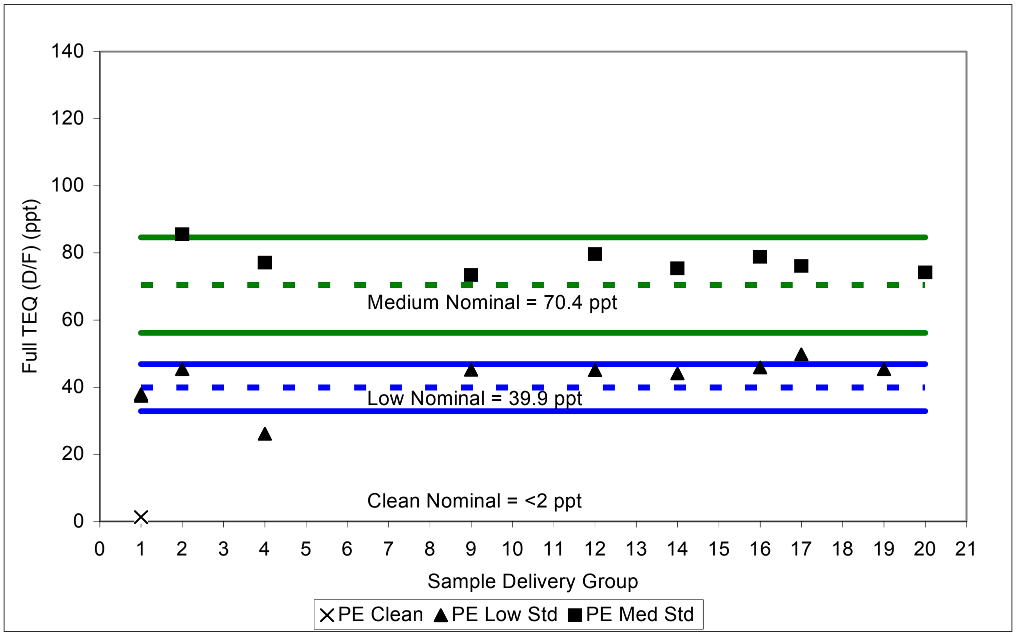
Table 7. Evaluation of Accuracy Using Unsieved Performance Evaluation Soil Samples

QATS PE Sample	Recalculated (a) Nominal TEQ Concentration (ppt)	N	TEQ(D/F) (ppt) (avg ± stdev)	
			Full	Quant
Clean (Native Western Soil)	<2	1	1.3	0.3
Low Standard	39.9	10	42.2 ± 6.8 (106%±17%)	39.9 ± 8.3 (100%±21%)
Medium Standard	70.4	8	77.5 ± 3.9 (110%±6%)	74.0 ± 2.9 (105%±4%)

(a) Recalculated TEQ values for QATS Low and Medium standards were calculated from QATS-certified congener concentrations using WHO consensus TEFs (see Table 4). Certified congener concentrations were not available for the Clean sample.

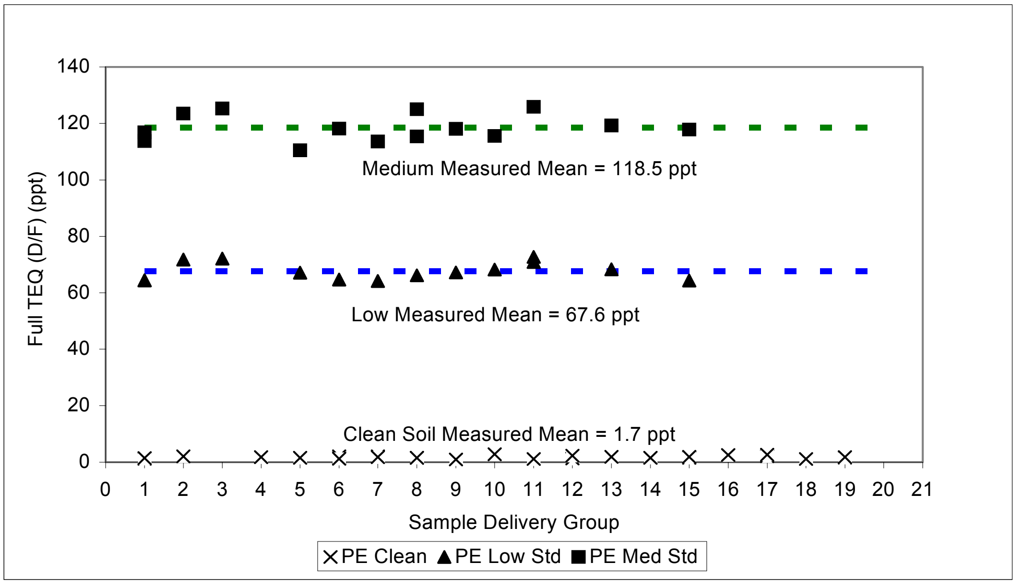
Figure 8. Analytical Results for Performance Evaluation Samples

PANEL A: Unsieved



Confidence bounds based on mean ± 2.5 standard deviations.

PANEL B: Sieved



In Panel A, the dashed green line indicates the consensus value expected for the medium PE standard, and the solid green lines indicate the upper and lower acceptance criteria. Likewise, the dashed blue line indicates the consensus value expected for the low PE standard, and the solid blue lines indicate the upper and lower acceptance criteria. In Panel B, the dashed lines indicate the average concentration measured for each type of PE standard.

these sieved samples. Nevertheless, it is apparent that the values hold steady over time, indicating that the dioxins in the sample are stable (i.e., do not degrade), that the analytical method has high reproducibility, and that the quality of the analyses were consistent throughout the program. The mean and standard deviation of the Full TEQ(D/F) for the sieved clean samples was 1.7 ± 0.5 ppt, indicating that there was no source of contamination during the sample processing or the sample analysis steps.

MRI Laboratory Control Spikes

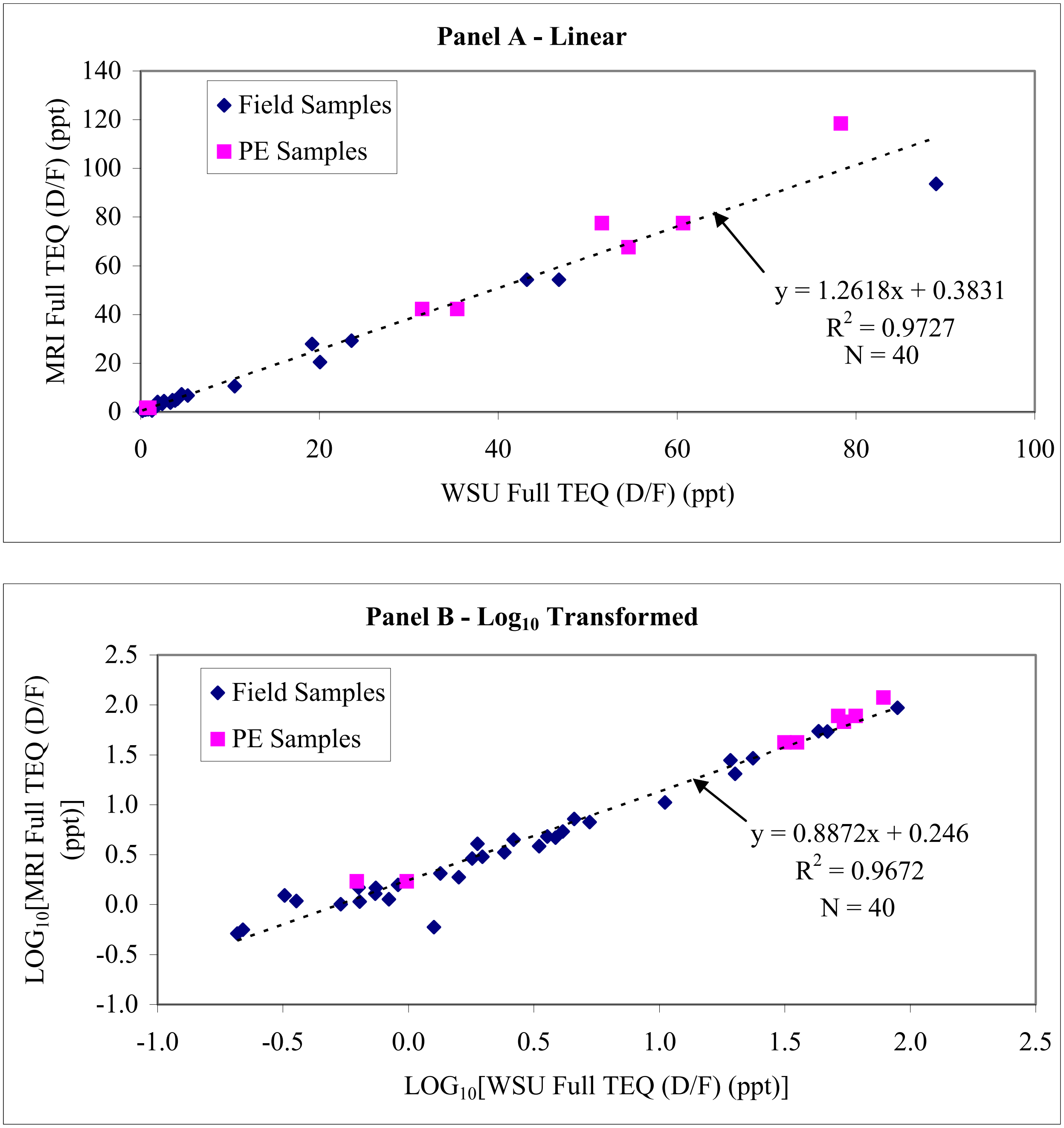
Twenty-one different laboratory control spikes (LCS) were analyzed in association with the field samples from this project. Spike concentrations were 20 ppt for TCDD and TCDF, 100 ppt for each of the penta-, hexa- and hepta-CDDs and -CDFs, and 200 ppt for OCDD, OCDF, and each of the PCBs. Based on this spiking mixture, the nominal TEQ(D/F) is 250 ppt, and the nominal TEQ(Total) is 272.5 ppt. Recovery of individual PCDD/PCDF congeners averaged across all samples ranged from 75% to 109%, with an average of 93% across all samples and all PCDD/PCDF congeners. Recovery of individual PCBs averaged across all samples ranged from 105% to 127%, with an average of 110% across all samples and all PCB congeners. When expressed as Full TEQ, recovery across different samples ranged from 91% to 103% (mean = 98%) for TEQ(D/F), and from 92% to 104% (mean = 98%) for TEQ(Total). This indicates that matrix interference is not likely to be of concern, and that accuracy of the method is good.

Inter-laboratory Comparison

To further evaluate the analytical performance of the primary analytical laboratory (MRI), a subset of 40 samples were sent to a second laboratory at Wright State University (WSU) for independent blind analysis. This sample set included 32 field samples (identical aliquots of the samples analyzed by MRI). These samples were selected from the off-post, South Plants, and WTP areas based on available MRI results to encompass a wide range of concentration values so that analytical performance could be compared across the spectrum of measured concentrations. In addition, eight QATS PE samples (three medium, three low and two clean soils) were submitted to help assess the quality and reliability of the data provided by WSU. The WSU laboratory was provided with the same modified analytical method procedure as that used by MRI.

Figure 9 compares the analytical results of WSU and MRI based on the Full TEQ (D/F). As seen in the upper panel, the TEQ values are generally consistent between the two laboratories

Figure 9. Inter-Laboratory Comparison (WSU vs MRI) for Dioxin Levels in Fine-Sieved Soil



For PE samples, MRI value is based on the mean of multiple analyses.

(slope = 1.26; R^2 = 0.97). For field samples, the inter-laboratory difference in Full TEQ (D/F) ranged from 0.02 to 11.2 ppt, with an average of 1.9 ppt across all samples.

Graphical comparisons of the concentrations measured by each laboratory (MRI and WSU) for each PCDD/PCDF congener in field samples are presented in Appendix F. **Table 8** summarizes the parameters of the best fit straight line through the paired data sets in both linear space and $\log_e$ space:

Linear space: MRI = a + b·WSU
Log Space: ln(MRI) = a + b·ln(WSU)

where:

MRI = full concentration value of congener measured by MRI
WSU = full concentration value of congener measured by WSU

In linear space, the intercept is close to zero for most congeners, and the average slope across all congeners is close to one, indicating generally good inter-laboratory agreement based on individual congener concentration values. Likewise, in $\log_e$ space, the average intercept is close to zero and the average slope is close to one, which also indicates the relationship between inter-laboratory analyses is linear and that the average concentration ratio is close to one. There appears to be a systematic difference between laboratories for a few congeners (e.g., OCDD, OCDF). However, whatever the basis for this difference, it has very little impact on the calculated TEQ values (as discussed above). These results indicate that the modified (trace-level enhanced) method for dioxin congener analyses was reproducible, and that the test results are reliable.

3.1.3 PARCC Criteria

Overall adequacy of a data set is evaluated in terms of five criteria: precision, accuracy, representativeness, completeness and comparability (PARCC). Findings regarding each of these criteria are summarized below.

Table 8. Inter-Laboratory Comparison of Full Congener Concentrations for Fine-Sieved Soils

D/F Congener	Linear			Log Transformed		
	Slope	**Y-Int**	**R2**	**Slope**	**Y-Int**	**R2**
2,3,7,8-TCDF	--	--	--	--	--	--
2,3,7,8-TCDD	0.67	0.1	0.192	0.79	-0.2	0.295
1,2,3,7,8-PeCDF	1.43	0.3	0.996	1.02	0.2	0.972
2,3,4,7,8-PeCDF	1.62	0.7	0.920	0.98	0.3	0.858
1,2,3,7,8-PeCDD	1.45	0.1	0.995	1.14	0.1	0.955
1,2,3,4,7,8-HxCDF	0.97	0.5	0.997	1.11	-0.2	0.867
1,2,3,6,7,8-HxCDF	0.92	0.6	0.995	1.05	-0.1	0.871
2,3,4,6,7,8-HxCDF	2.36	0.0	0.877	1.14	0.2	0.651
1,2,3,7,8,9-HxCDF	0.71	0.7	0.905	1.07	-0.2	0.909
1,2,3,4,7,8-HxCDD	0.90	0.2	0.984	0.99	0.0	0.920
1,2,3,6,7,8-HxCDD	1.03	-0.4	0.985	0.98	0.0	0.935
1,2,3,7,8,9-HxCDD	0.55	-0.4	0.726	1.06	-0.5	0.868
1,2,3,4,6,7,8-HpCDF	0.58	13.4	0.850	0.85	0.2	0.804
1,2,3,4,7,8,9-HpCDF	1.02	1.0	0.996	0.96	0.1	0.889
1,2,3,4,6,7,8-HpCDD	0.70	28.0	0.917	0.93	0.2	0.973
OCDF	0.47	82.4	0.726	0.95	0.1	0.921
OCDD	0.29	248	0.824	0.75	0.6	0.930
Average	**0.98**	**23.5**	**0.868**	**0.99**	**0.0**	**0.851**

Values shown are the best fit parameters for linear regression lines through the paired field samples (MRI on the y-axis vs WSU on the x-axis), either in linear space or in $\log_e$ space.

Precision:	All split and duplicate samples analyzed during the project were within the acceptance criteria that were established by the QAPP (USEPA 1999). In addition, there was good reproducibility for each of the three classes of PE samples (clean, low, medium) over time. Based on this, it is concluded that the precision of the analytical method used in this program was adequate.
Accuracy	Full TEQ(D/F) and Quant TEQ(D/F) values for PE samples were both close to the expected values based on the certified congener concentration estimates reported by the QATS laboratory and the WHO consensus TEFs. Values for Quant TEQ(D/F) were closer than for Full TEQ(D/F), probably because many of the laboratories that helped establish the certified values treated non-detects as zero. In addition, there was good inter-laboratory agreement between MRI and an independent laboratory (Wright State University) on Full TEQ(D/F) values. Based on these observations, it is concluded that the accuracy of the analytical method used in this program was adequate.
Representativeness	The soil sampling design selected for this study (stratified random sampling) ensured that the data set collected is spatially representative of the study area. Purposeful samples (those collected at specific locations that are suspected to be potential source areas) are not interpreted as being representative of the entire area, but only of the location from which the purposeful samples were collected.
Completeness	A total of 405 soil samples were analyzed during this project, including all field and QA samples. This corresponds to a total of 11,745 possible congener-specific values. Of this total, 43 (0.4%) congener-specific values were missing (mainly due to insufficient material to support PCB analysis), and 12 (0.1%) congener-specific values were R-qualified as unreliable. Thus, a total of 11,690 (99.5%) reliable congener-specific values were obtained. This exceeds the minimum completeness criterion of 90% established in the QAPP (USEPA 1999).
Comparability	Comparability of all data collected within the study was achieved by using highly standardized methods for all sample collection and analysis. It should be noted that the results from this study may not be entirely

comparable with results from other studies due to differences in methods used for sample collection, sample analysis, and computation of TEQ.

3.2 TEQ Values in Off-Post Field Samples

As noted above, a total of 165 off-post field samples were collected during this study. Appendix D presents maps showing the results for all 165 of these samples, stratified by land use.

Of the 165 off-post samples, sufficient sample mass was available to sieve and analyze the fine fraction for 162 samples. Visual inspection of the raw data (Appendix A1) for these 162 samples suggest that two data points in the data set (the maximum value for the commercial and the residential land use data groups) might be outliers that are not representative of the rest of the group. This was evaluated by a simple outlier test (based on the mean plus 2.5 standard deviations of the log-transformed values), which indicated that these two data points were very unlikely (less than a 1% probability) to have been drawn from the same distribution as the remainder of the points in each group. The basis for these two apparent outliers is not known, but might be due to the presence of a minor point source at these two sampling locations. Based on the conclusion that these two samples are not representative of their respective land uses, they were excluded from further analysis. Panel A of **Table 9** shows the summary statistics for the data set after exclusion of these two data points.

As seen in **Table 9** (Panel A), there is a fairly wide range of Full TEQ(D/F) values observed in the set of Denver area surface soils (fine fraction) obtained in this study, ranging from a minimum of less than 0.1 ppt TEQ up to a maximum of 57.7 ppt TEQ. Mean values for TEQ (both Full and Quant) are lowest for open space and agricultural sampling locations, with somewhat higher values observed in industrial, commercial and residential areas. The distribution of Full TEQ(D/F) values for each land use all tend to be right skewed, and the log-transformed data all pass the Kolmogorov-Smirnov test for normality ($p > 0.05$). This indicates that the data may be reasonably approximated by lognormal probability density functions.

Panel B of **Table 9** presents the results for the three samples that had insufficient mass to prepare the fine fraction. These results are for the bulk (2 mm) fraction. See Section 4.6.2 for additional information on the relationship between TEQ concentrations in bulk and fine soil samples.

Table 9. Summary Statistics for Off-Post Field Soil Samples

PANEL A. TEQ Values in Off-Post Fine Samples (Excluding Outliers)

			Full TEQ (ppt)			Quant TEQ (ppt)		
Land Use	**N**	**Stat**	**D/F**	**PCB**	**Total**	**D/F**	**PCB**	**Total**
Agricultural	27	Mean	**1.5**	**0.3**	**1.8**	**1.0**	**0.3**	**1.3**
		StdDev	1.9	0.4	2.1	1.4	0.4	1.6
		Min	0.0	0.0	0.0	0.0	0.0	0.0
		Max	7.6	1.6	7.8	4.7	1.6	5.6
Commercial	30	Mean	**6.4**	**2.1**	**8.5**	**5.3**	**2.0**	**7.3**
		StdDev	11.3	7.2	17.9	9.8	7.2	16.5
		Min	0.3	0.0	0.4	0.1	0.0	0.1
		Max	57.7	39.8	97.5	50.2	39.8	90.0
Industrial	29	Mean	**9.9**	**5.5**	**15.4**	**7.9**	**3.6**	**11.6**
		StdDev	14.3	16.4	22.8	11.1	8.7	14.6
		Min	0.0	0.0	0.0	0.0	0.0	0.0
		Max	54.6	88.1	103.2	42.6	44.2	58.2
Open Space	37	Mean	**1.5**	**1.2**	**2.7**	**1.3**	**0.8**	**2.1**
		StdDev	2.2	4.0	5.3	2.1	2.1	3.8
		Min	0.0	0.0	0.0	0.0	0.0	0.0
		Max	9.0	23.6	28.0	8.3	11.9	16.0
Residential	37	Mean	**7.2**	**1.6**	**8.8**	**5.9**	**1.3**	**7.2**
		StdDev	10.2	2.5	11.7	8.2	2.0	9.3
		Min	0.1	0.0	0.1	0.0	0.0	0.0
		Max	43.0	8.7	51.7	32.3	7.8	36.6
Total	160	Mean	**5.2**	**2.1**	**7.3**	**4.3**	**1.6**	**5.8**
		StdDev	9.8	8.1	14.5	8.0	5.1	11.1
		Min	0.0	0.0	0.0	0.0	0.0	0.0
		Max	57.7	88.1	103.2	50.2	44.2	90.0

PANEL B: TEQ Values in Off-Post Bulk Samples

			Full TEQ (ppt)			Quant TEQ (ppt)		
Land Use	**N**	**Stat**	**D/F**	**PCB**	**Total**	**D/F**	**PCB**	**Total**
Open Space	1	Value	2.5	0.6	3.1	2.1	0.6	2.7
Industrial	1	Value	3.6	1.6	5.2	3.3	0.8	4.1
Residential	1	Value	5.8	1.1	6.9	1.1	0	1.1

PANEL C: TEQ Values in Off-Post Fine Samples (Including Outliers)

			Full TEQ (ppt)			Quant TEQ (ppt)		
Land Use	**N**	**Stat**	**D/F**	**PCB**	**Total**	**D/F**	**PCB**	**Total**
Commercial	31	Mean	**10.7**	**2.1**	**12.8**	**8.8**	**2.0**	**10.8**
		StdDev	26.5	7.0	29.6	21.8	7.1	25.3
		Min	0.3	0.0	0.4	0.1	0.0	0.1
		Max	140.2	39.8	141.2	114.3	39.8	115.3
Residential	38	Mean	**11.0**	**1.6**	**12.7**	**9.4**	**1.3**	**10.7**
		StdDev	26.0	2.5	26.6	22.9	2.0	23.3
		Min	0.1	0.0	0.1	0.0	0.0	0.0
		Max	154.8	8.7	156.1	137.8	7.8	139.0
Total	162	Mean	**7.0**	**2.1**	**9.1**	**5.8**	**1.6**	**7.3**
		StdDev	18.5	8.0	21.3	15.7	5.1	17.5
		Min	0.0	0.0	0.0	0.0	0.0	0.0
		Max	154.8	88.1	156.1	137.8	44.2	139.0

Panel C of **Table 9** shows the results for the commercial and residential off-post data sets with the two outlier points included.

Figure 10 is a graphical representation of the distributions of Full TEQ(D/F) in fine soils after the two outliers were excluded. As noted above, samples collected on lands that were ranked as agricultural or open space ("light use") tended to have values somewhat lower than those from commercial or industrial areas. The distribution for residential samples is generally similar to that for commercial properties. In interpreting this finding, it is important to remember that none of the "residential" sampling locations are actually on private residential properties, but rather all are on public properties located in or near residential neighborhoods. In some cases, the current land use is more similar to light commercial/industrial than residential (e.g., pump stations, park-and-ride stations). In addition, because a full land use history is not available for most of these properties, it is possible that some of these public properties may have been used in the past for activities that tended to increase dioxin levels slightly.

As noted above, simple inspection of the off-post data set suggests that the distributions of TEQ levels are somewhat higher in commercial, industrial, and residential areas than in open space or agricultural areas. The distributions of values in each land category were compared using Kruskal-Wallis one-way analysis of variance (ANOVA) on ranks. The results indicated that differences between land uses were statistically significant ($p < 0.01$). Multiple pair-wise comparisons using the Mann-Whitney Rank Sum Test were performed to identify the groups that are statistically different from each other. The results are shown in **Table 10**. As seen, the land use data sets tend to fall into two groups: open space and agricultural lands are not statistically different from each other, but are different from the industrial, commercial and residential data sets. Conversely, the industrial, commercial and residential data sets are not statistically different from each other, but are different from the open space and agricultural data sets. Summary statistics for these combined groups (Open Space/Agricultural, and Commercial/Industrial/Residential) are presented in **Table 11**. Comparison of these two combined groups by the Mann-Whitney Rank Sum Tests indicates that they are statistically different ($p < 0.001$).

As noted above, classification of a sampling location into one of the five different land use categories was based mainly on an inspection of the current conditions at the location, combined with a review of available historic use information for the location. In some cases (35 out of 160), the land use assignment was considered to be somewhat uncertain, and a secondary (alternative) land use category was also identified. **Figure 11** compares the distribution of Full TEQ(D/F) values based on the original and the alternative land use assignments. As seen, the distributions are generally similar, indicating that uncertainty in the

Figure 10. Range of Full TEQ(D/F) Levels in Off-Post Fine-Sieved Soils

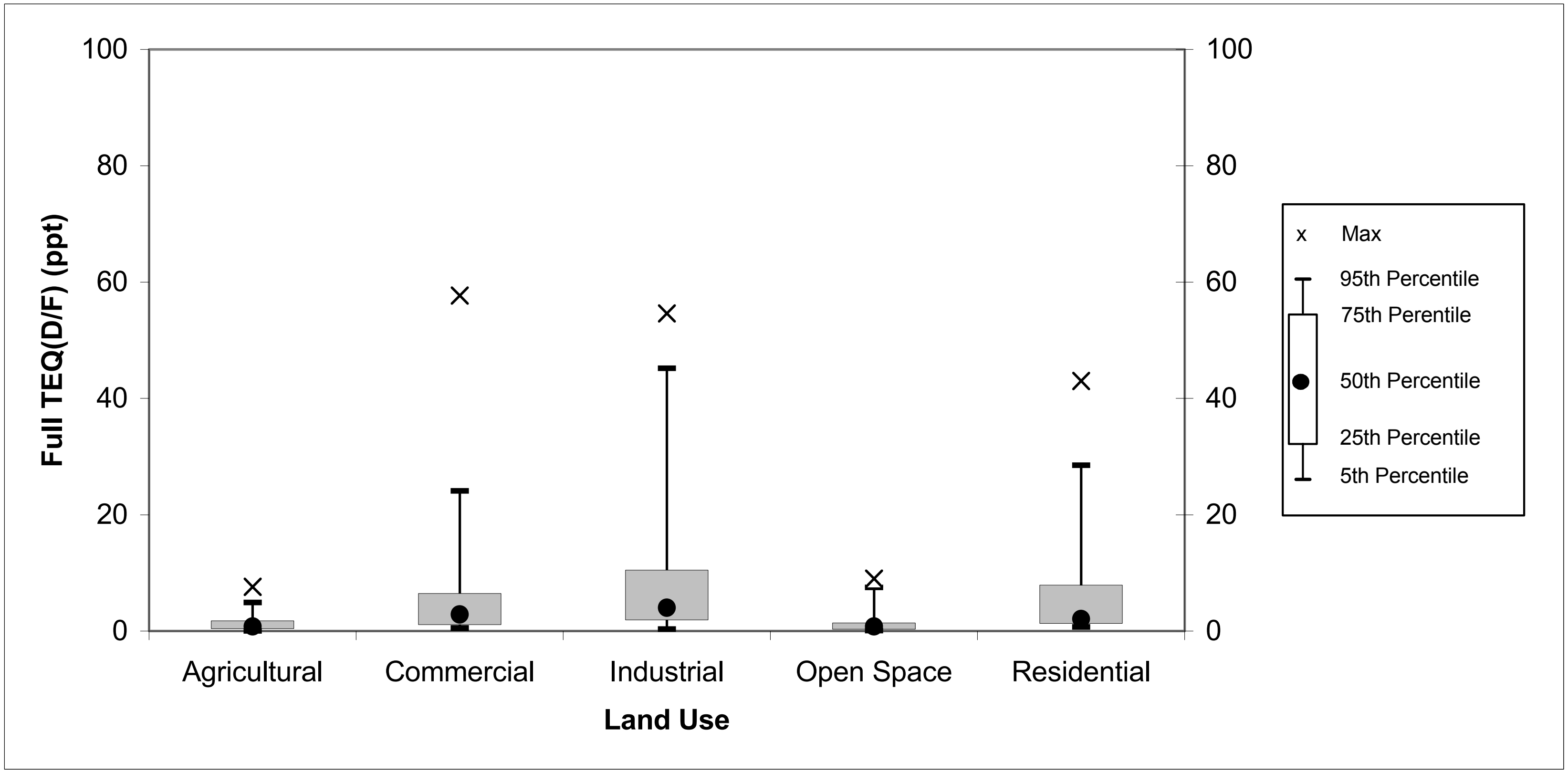


Table 10. Statistical Differences in TEQ Values Between Off-Post Land Uses

Land Use	N	Agricultural	Commercial	Industrial	Open Space	Residential
Agricultural	27					
Commercial	30	Yes (p < 0.01)				
Industrial	29	Yes (p < 0.01)	No (p = 0.264)			
Open Space	37	No (p = 0.664)	Yes (p <0.01)	Yes (p < 0.01)		
Residential	37	Yes (p < 0.01)	No (p = 0.772)	No (p = 0.258)	Yes (p < 0.01)	

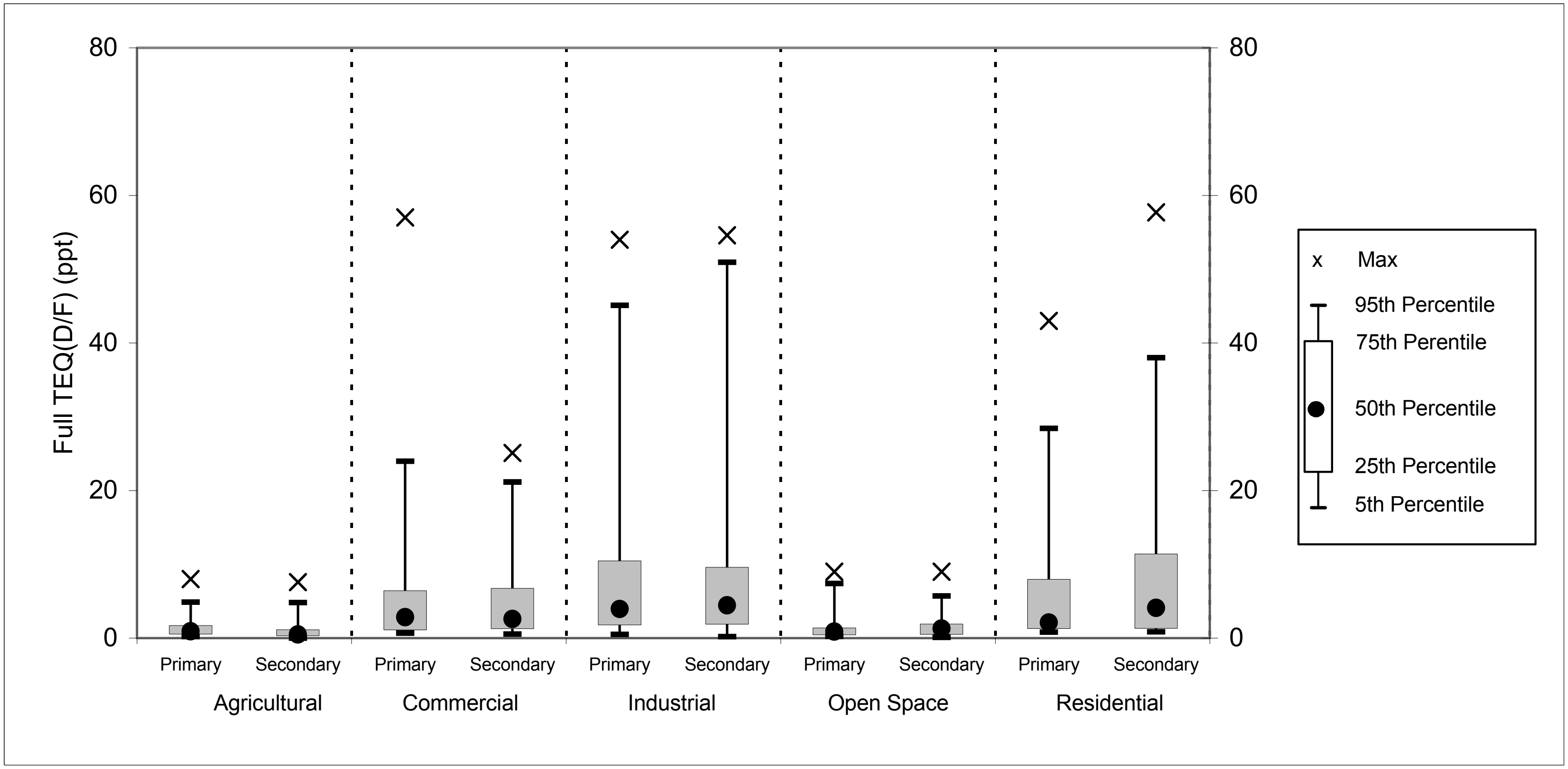
Results based on multiple pair-wise comparisons of the log-transformed data using the Mann-Whitney Rank Sum Test

Table 11. Summary Statistics for Full TEQ(D/F) for Off-Post Fine-Sieved Soils

Statistic	Agricultural and Open Space	Commercial, Industrial and Residential
N	64	96
Mean	1.5	7.7
Stdev	2.1	11.9
5th	0.0	0.4
25th	0.4	1.3
50th	0.8	3.1
75th	1.5	7.6
90th	4.3	22.6
95th	6.9	30.4

All TEQ values are expressed in units of ppt

Figure 11. Effect of Land Use Re-Classification on Full TEQ (D/F) Patterns in Fine-Sieved Soils



appropriate land use assignment of specific sampling locations is not likely to significantly alter the basic findings.

3.3 TEQ Values in On-Post Field Samples

Of the 60 field samples collected for analysis from various areas of the RMA, sufficient mass was available for all samples to sieve and analyze the fine fraction. The results for these 60 samples are shown in **Table 12**, stratified by location.

A map showing the spatial pattern of Full TEQ(D/F) in all on-post fine-sieved samples is presented in **Figure 12**. As seen, dioxin levels tend to be low (1-3 ppt) for most locations at the RMA. However, TEQ levels are slightly elevated in the South Plants area, with values ranging from 10-100 ppt TEQ. The spatial pattern of these elevations is consistent with the hypothesis that low levels of dioxins were released to soils in association with the former chemical manufacturing operations on-post. However, the areal extent of the contamination is relatively small in scope, decreasing rapidly as a function of distance from the central South Plants area.

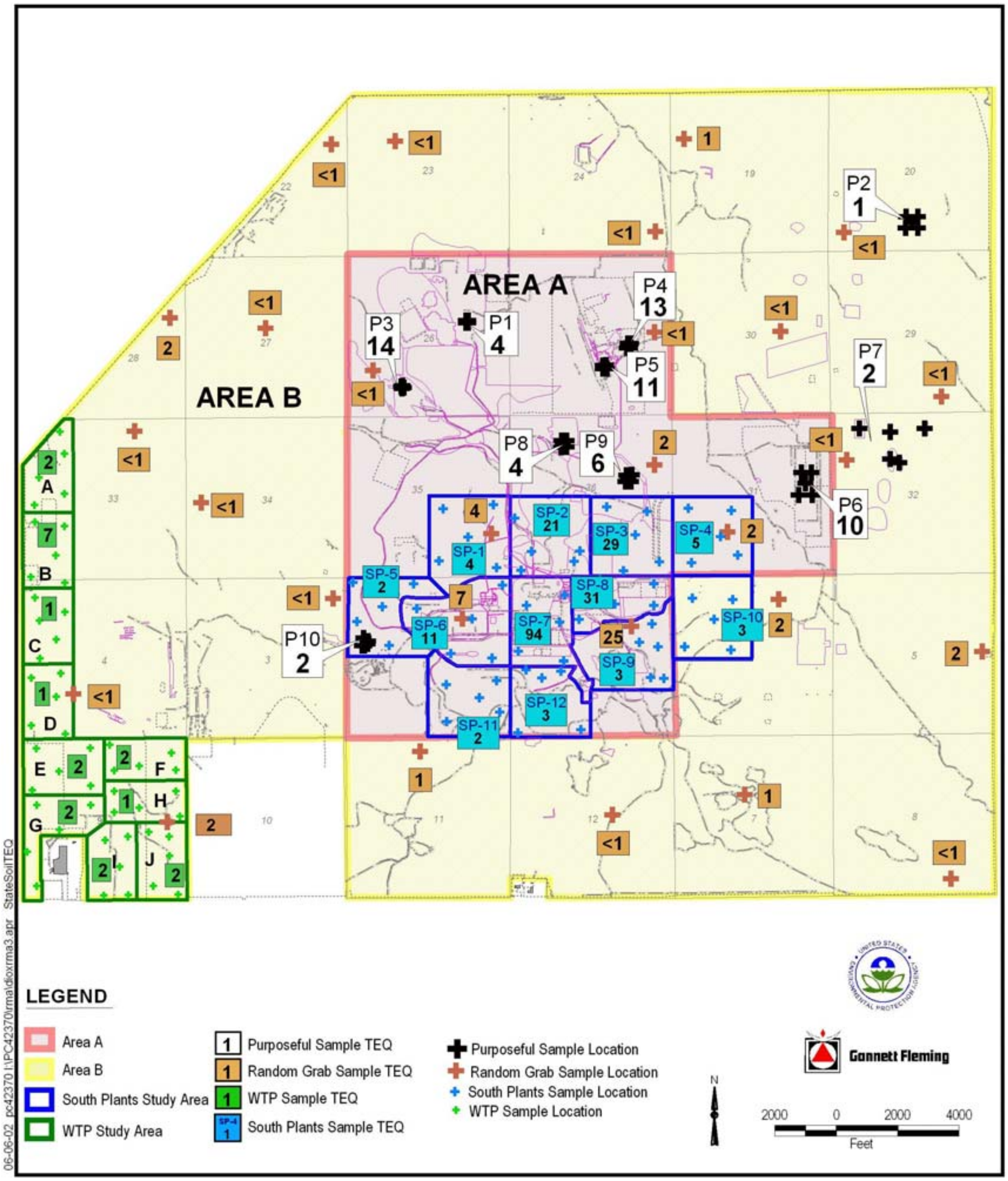
In addition, a few of the historic waste disposal areas have slightly elevated TEQ levels, with the highest values (10-14 ppt) occurring at Stations P-3, P-4, P-5 and P-6. These stations are associated with the following:

> Sample P-3 is located in secondary Basin D in Section 26. This sample is composed of soils impacted by the disposal of liquid wastes from RMA production areas.
>
> Sample P-4 is located just east of the North Plants production facility. This sample is composed of soils potentially impacted by the incineration operations in North Plants.
>
> Sample P-5 is located within the North Plants production facility. This sample is composed of soils potentially impacted by GB operations within North Plants as well as the incineration operations in North Plants.
>
> Sample P-6 is located in the Toxic Storage Yard (TSY) in Section 31. This sample is composed of soils potentially impacted by spills of various materials stored in the TSY.

Table 12. TEQ Summary Statistics for RMA On-Post Fine-Sieved Soil Samples

Sample Category	N	Stat	Full TEQ (ppt)			Quant TEQ (ppt)		
			D/F	PCB	Total	D/F	PCB	Total
South Plants	12	Mean	**17.4**	**2.0**	**19.3**	**15.0**	**1.7**	**16.7**
		StdDev	26.3	2.0	28.2	23.7	1.8	25.4
		Min	1.9	0.4	2.8	1.2	0.2	1.9
		Max	93.8	7.2	101.0	83.9	6.5	90.4
Purposeful	10	Mean	**6.5**	**5.5**	**12.0**	**5.8**	**3.5**	**9.3**
		StdDev	4.8	11.3	13.9	4.8	5.5	8.6
		Min	1.4	0.2	1.6	0.9	0.2	1.1
		Max	13.5	37.5	48.7	12.3	18.8	29.3
RMA Random	28	Mean	**2.0**	**0.4**	**2.5**	**1.8**	**0.3**	**2.2**
		StdDev	4.8	0.4	4.9	4.7	0.3	4.8
		Min	0.0	0.0	0.1	0.0	0.0	0.0
		Max	25.4	1.5	26.1	24.7	1.1	25.2
Western Tier Parcel	10	Mean	**2.2**	**1.1**	**3.3**	**1.3**	**1.1**	**2.3**
		StdDev	1.9	0.7	2.5	2.1	0.7	2.7
		Min	1.2	0.6	1.8	0.4	0.6	1.0
		Max	7.4	2.9	10.3	7.2	2.8	10.0

Figure 12. Map of Full TEQ(D/F) for Fine-Sieved Samples at On-Post Sampling Locations



Another sample that is slightly anomalous is from Zone B of the WTP. The Full TEQ(D/F) value for this sample (7.4 ppt) is higher than for all of the other samples at WTP (1.2-2.3 ppt TEQ), and for most of the other random samples from non-use areas of RMA. The source of the somewhat increased concentrations of PCDDs/PCDFs and PCBs in WTP sub-parcel B is not known; however, an earlier study of organo-chlorine pesticide levels in the WTP by USEPA Region 8 (USEPA 2000b) also detected slight elevations in aldrin and dieldrin concentrations in this same area.

It should be noted that the South Plants and other historic use areas of RMA with the highest dioxin levels are scheduled for soil excavation as part of on-going remediation efforts to reduce or eliminate the presence of organo-chlorine pesticide contamination. Once this remediation is complete, it is expected that dioxin levels throughout RMA will be approximately the same as for open space areas in the Denver Front Range area, and that future use of the RMA as a wildlife refuge will not result in any excess dioxin exposure to refuge workers, volunteers, or site visitors.

4.0 DATA ANALYSIS AND DISCUSSION

4.1 Comparison of TEQ Levels at On-Post and Off-Post Locations

As discussed previously, one of the main objectives of this study was to allow a comparison of dioxin levels at various on-post locations with appropriately matched off-post land uses. However, statistical comparisons of the various on-post data sets with the off-post data sets are complicated by two factors: a) there is a spatial pattern apparent in on-post TEQ values, with values from the central area of the site tending to be higher than the peripheral areas, and b) many of the on-post samples are composites of five sub-samples, while all of the off-post samples are grab samples.

To address the issue of the spatial pattern on-post, the on-post samples were divided into two groups, as shown in **Figure 12**:

> **Area A** (indicated by the pink area) includes most of the samples in the vicinity of South Plants and the near-by historic waste disposal areas (an area of about seven square miles). This area contains 26 total sampling locations, including 11 composite samples from the South Plants area, 8 composite samples from historic use areas, and 7 random grab samples.
>
> **Area B** includes all other on-post samples (N = 34), including 10 composite samples from the WTP, 21 random grab samples, 2 composites from historic use areas, and one composite sample from the eastern end of the South Plants area.

Summary statistics for these two on-post areas are presented in the upper panel of **Table 13**. Comparison of the on-post data with the off-post data is difficult because the off-post samples are random grab samples while the on-post samples are a mixture of biased and random samples and a mixture of grab samples and composites. The lower panel of **Table 13** presents summary statistics for the off-post samples, and compares the data with the two on-post areas. As seen:

- Random grab samples from on-post Area B are not significantly different than any of the rural-type off-post land use samples (open space, agricultural), either alone or together.

Table 13. Comparison of Full TEQ(D/F) Values in Fine-Sieved Soil at Off-Post and On-Post Locations

Panel A: On-Post Summary Statistics

RMA On-Post Area	Sample Type	Summary Statistic			
		N	**Mean (ppt)**	**Min (ppt)**	**Max (ppt)**
Area A	**All**	26	11.8	0.1	93.8
	Grabs	7	5.8	0.1	25.4
	Composites	19	14.1	1.9	93.8
Area B	**All**	34	1.3	0.0	7.4
	Grabs	21	0.8	0.0	1.6
	Composites	13	2.1	1.2	7.4

Panel B: Comparison of On-Post and Off-Post Values

Off-Post Land Use	Off-Post Summary Statistics			Comparison with On-Post Areas		
	N	Mean (ppt)	Max (ppt)	Area A N = 26 total (a)	Area B N = 21 Grabs	p Value (b)
Open Space	37	1.5	9.0	na	nsd	0.482
Agricultural	27	1.5	7.6	na	nsd	0.383
Rural (c)	***64***	***1.5***	***9.0***	***na***	***nsd***	***0.412***
Residential	37	7.2	43.0	na	Area B is lower	<0.001
Commercial	30	6.4	57.7	Area A slightly greater than off-post	na	na
Industrial	29	9.9	54.6		na	na
Heavy Use (d)	***59***	***8.1***	***57.7***		***na***	***na***

na = not applicable because land uses are different
nsd = no significant difference (Mann Whitney Rank Sum Test)

(a) Area A samples are a mixture of grabs and composited and are mainly biased, and can't be statistically compared
(b) Grab samples only
(c) Rural = open space and agricultural combined
(d) Heavy use = Commercial and industrial combined

- Random grab samples from on-post Area B are significantly lower than off-post residential land use samples.

- Samples from on-post Area A are a mixture of grabs and composites and are mainly from biased sampling locations, so rigorous statistical comparisons with random grab samples from off-post commercial/industrial land uses cannot be performed. However, simple inspection of the data suggest that on-post Area A is similar to but perhaps slightly greater than off-post commercial/industrial areas.

4.2 Comparison to Published Data on Ambient TEQ Levels

Data Summary

Limited data are available in the literature on the concentrations of PCDDs and PCDFs in "background" soil (i.e., soil that is not believed to have been impacted by any local point source of dioxin release). Data from studies that measured the concentrations of all of the toxicologically relevant *2,3,7,8*-substituted PCDD and PCDF congeners are summarized in **Table 14**. Results are presented as average parts per trillion (ppt) of TEQ, calculated using the WHO consensus TEF values for mammals (Van den Berg et al. 1998). Non-detects were evaluated by assigning a value of zero, so true values are likely to be somewhat higher. As seen, mean values for rural and urban areas are mainly in the 1-6 ppt range, although some lower and some higher values are reported. The range of individual sample values in a study is generally much wider than the range of mean values between studies. For example, the range of TEQ values in soil reported in the BC Environment (1995) study was from less than 1 ppt to 57 ppt (mean = 4 ppt). Likewise, Rotard et al. (1994) reported a range of 1-6 ppt in grassland and plowland, and from 6-150 ppt in forest soils. Thus, the range of mean values for different studies reported in **Table 14** should not be interpreted as defining the range of concentrations that occur in individual grab samples.

Data Gaps and Limitations

In considering these data, it is important to recognize that a number of factors may limit the accuracy and relevance of the data, including the following:

- Some data are from older studies performed 5-15 years ago. Because dioxin emission rates have been tending to decrease over time, older data are inherently less relevant and less applicable than current data for characterizing ambient TEQ levels in soil.

Table 14. Summary of Literature Studies on Dioxins and Furans in Soils (a)

Land Use Category	Reference	Geographic Location	Number of samples	Comments	MeanTEQ (b) (ppt)
Rural	BC Environment, 1995	British Columbia	53	background	4
	Kjeller et al., 1991	England	3	agricultural, average of 3 samples taken in 1986, excluded all historic samples	2
	MRI, 1992	Connecticut	34	background	6
	Reed et al., 1990	Minnesota	4	semi-rural, background, but near former site of coal-fired power plant	4
	Rogowski and Yake, 1999	Washington	54	agricultural	<1
	Rogowski et al., 1999	Washington	16	rangeland and forest	2
	Rotard et al., 1994	Germany	41	grassland, plowland forest (hardwood, conifer)	3 42
	Schuhmacher et al., 1997	Catalonia, Spain	30	rural samples near where a hazardous waste incinerator is under construction	1
	Rappe and Kjeller, 1987	Europe	3	rural areas from "various parts of Europe"	2
	Tewhey Associates, 1997	Maine	8	background	3
	USEPA, 1996	Ohio	3	background	1
Urban	NIH, 1995	Maryland	37	urban	2
	USEPA, 1996	Ohio	18	urban	21
	Rogowski et al., 1999	Washington	14	urban	4
	Schuhmacher et al., 1997	Catalonia, Spain	10	urban samples near where a hazardous waste incinerator is under construction	5
Industrial	Rappe and Kjeller, 1987	Europe	2	industrial areas from "various parts of Europe"	166

(a) Adapted from USEPA (2000)

(b) TEQ values calculated using WHO consensus TEF values for mammals (Van den Berg et al. 1998). All values rounded to the nearest ppt to account for uncertainties in the measurements.

- In the past (and even in some current studies), Method Quantitation Limits (MQLs) were often higher than background levels in soil, which prevents reliable quantitation of true background levels. In some cases, MQLs were not even reported or defined.
- In some studies, only partial sets of the 17 dioxin/furan Ah-agonist congeners were measured. In these cases, the true TEQ (the sum of the 29 Ah-agonists listed in **Table 1**) is likely to be underestimated.
- Many studies stratified values according to only two land-use categories: rural and urban. Thus, if there are significant differences in background levels as a function of land-use, application of a two category system may obscure important differences.
- Variations occurred in the depth of soil samples collected. Because dioxin levels resulting from atmospheric deposition and/or application of herbicides are likely to be higher in surface soil than subsurface soil, comparisons of results between studies conducted using different soil depths are of uncertain relevance.
- Most soil collections were apparently measured in "bulk" (non-sieved, larger particulate) soil samples. However, both humans and animals are believed to be exposed mainly to the fine fraction (less than 250 micrometers maximum diameter) of soil particles. If dioxin levels are higher in the fine fraction, older "bulk" data may underestimate actual exposure levels.
- Quality control data were not reported in all studies, making it difficult to judge the accuracy and precision of the data.

The data gaps and uncertainties summarized above make it difficult to use the published literature data as a basis for distinguishing elevations in dioxin levels in site soils compared to levels in ambient soils, and these limitations were the fundamental impetus for the Denver Front Range Dioxin Soil Study.

Comparison of Literature Values to Front Range Dioxin Results

Despite the limitations and uncertainties in the published data on the concentrations of PCDDs and PCDFs in "background" soil, it is evident that there is general agreement between the findings from the Front Range Dioxin Soil Study and the available literature values, as summarized below:

Data Source	Average Full TEQ(D/F) (ppt)	
	Rural	Urban
Front Range Dioxin Soil Study	1-2 (a)	6-10 (b)
Published Literature Values	1-6	2-21

(a) Range is for mean values in Open Space and Agricultural areas
(b) Range is for mean values in Commercial, Industrial, and Residential areas

This general agreement suggests that even though regional differences are likely to exist in ambient dioxin levels in soils, these differences appear to be relatively small in scale (probably less than a factor of 5 in most cases), and that reliable data collected from one area may be used as a reasonable approximation for results from other similar but unstudied areas. In this regard, because of the improved analytical methodology and high emphasis on representativeness and quality control, the data sets collected during the Front Range Dioxin Study constitute the most robust, reliable and representative data for comparative purposes with other sites.

4.3 Contribution of PCBs to Total TEQ

As noted previously, some PCBs also possess TCDD-like activity and may contribute to the levels of total TEQ in soil. Thus, measurement of PCBs is important whenever the Total is of interest, or when comparing chemical and bioassay-based measurements of TEQ.

Summary statistics (averaged across samples within a land use category) on the relative contribution of PCBs to Full TEQ(total) are presented in **Table 15**. At off-post locations, PCBs in agricultural and open space soils contribute about 0.3-1.2 ppt TEQ to the Full TEQ(Total), but may contribute about 1.6-5.5 ppt TEQ in commercial, industrial or residential samples. On average across all off-post samples, PCBs contribute about 29% of the total TEQ. Results are generally similar at on-post locations, with PCBs contributing between 0.4 to 1.1 ppt Full TEQ (18-33% of total) in non-impacted areas of the site, with slightly higher values (2.0-5.5 ppt Full TEQ) in the South Plants and historic use areas of the site.

As shown in **Table 15**, elevated PCB levels tend to be associated with elevated PCDD/PCDF levels, although the correlation between the two groups is not strong: the coefficient of determination (R^2) between Full TEQ(D/F) and Full TEQ(PCB) is 0.10 in all off-post samples, 0.06 in all on-post samples, and 0.08 in all samples combined.

Table 15. Contribution of PCBs to Total TEQ in Fine-Sieved Soils

Location	Land Use	Full TEQ (ppt)				Quant TEQ (ppt)			
		D/F	PCB	Total	% PCB Contrib	D/F	PCB	Total	% PCB Contrib
Off-Post	Agricultural	1.5	0.3	1.8	18%	1.0	0.3	1.3	23%
	Commercial	6.4	2.1	8.5	25%	5.3	2.0	7.3	27%
	Industrial	9.9	5.5	15.4	36%	7.9	3.6	11.6	31%
	Open Space	1.5	1.2	2.7	43%	1.3	0.8	2.1	38%
	Residential	7.2	1.6	8.8	18%	5.9	1.3	7.2	18%
	All	*5.2*	*2.1*	*7.3*	*29%*	*4.3*	*1.6*	*5.8*	*27%*
On-Post	Purposeful	6.5	5.5	12.0	46%	5.8	3.5	9.3	38%
	RMA Site Wide	2.0	0.4	2.5	18%	1.8	0.3	2.2	16%
	South Plants	17.4	2.0	19.3	10%	15.0	1.7	16.7	10%
	WTP	2.2	1.1	3.3	33%	1.3	1.1	2.3	46%

4.4 Contribution of Congeners Below the Method Detection Limit

As described in Section 2.6, in the calculation of the Full TEQ value for a sample, all congeners that were below the MDL (signal/noise ratio < 2.5) were evaluated by assuming a concentration value equal to ½ the detection limit, and values between the MDL and the MQL were evaluated using the reported value. This is the approach is that is normally used to evaluate chemicals of concern at CERCLA sites (USEPA 1989). In order to evaluate the relative contribution of congeners that were either not detected, or else were present at such low concentrations that their true concentration could only be estimated, a second calculation of "Quant" TEQ was performed, which excluded congeners that were below the MDL, and used ½ the reported value for concentrations between the MDL and the MQL. A comparison of the Full and Quant TEQ values are shown in **Table 16**. As seen, the average contribution of congeners below the MQL to Full TEQ is about 1.0 ppt (D/F only) to 1.5 ppt (D/F plus PCBs), which corresponds to an average of about 18% to 20% of the total TEQ. This finding supports the conclusion that in this study, Full TEQ results are not unduly influenced by congeners below the MQL or the MDL, even at these relatively low soil levels. At higher soil levels, the relative contribution of congeners below the MQL would be even lower.

4.5 Congener Pattern Analysis

The congener composition (i.e., the relative concentration of the different congeners) of dioxins in a soil sample may provide useful information about the source of the dioxin contamination, and helps to reveal which specific congeners are contributing the majority of the risk. The results of several alternative approaches to congener pattern analysis are presented below.

Summary Statistics

Appendix A shows the relative (percent) contribution of each of the 29 congeners to the total TEQ in each of the field soil samples collected during this study. Summary statistics for the average percent contribution (i.e., the percent contribution within a sample averaged across all samples in a group) are summarized in **Table 17**. For emphasis, congeners which contribute an average of 10% or more to the total TEQ are shaded. In the case of PCDDs/PCDFs (upper panel), most of the Full TEQ at off-post locations is contributed by *1,2,3,7,8*-PeCDD and *1,2,3,4,6,7,8*-HpCDD. At on-post locations, the largest contributors to TEQ include *2,3,4,7,8*-PeCDF, *1,2,3,7,8*-PeCDD, and *1,2,3,4,7,8*-HxCDF. For PCBs (lower panel), PCB-126 is the predominant contributor to Full TEQ at all sampling locations.

Table 16. Contribution to TEQ of Congeners Below the Quantitation Limit in Fine-Sieved Soils

Location	Land Use	D/F TEQ (ppt)		Average Contribution of Congeners < MQL (ppt)		Total TEQ (ppt)		Average Contribution of Congeners < MQL (ppt)	
		Full	Quant			Full	Quant		
Off-Post	Agricultural	1.5	1.0	0.5	(33%)	1.8	1.3	0.6	(30%)
	Commercial	6.4	5.3	1.1	(17%)	8.5	7.3	1.2	(14%)
	Industrial	9.9	7.9	1.9	(19%)	15.4	11.6	3.8	(25%)
	Open Space	1.5	1.3	0.2	(15%)	2.7	2.1	0.6	(22%)
	Residential	7.2	5.9	1.2	(17%)	8.8	7.2	1.5	(18%)
	All	***5.2***	***4.3***	***0.9***	***(18%)***	***7.3***	***5.8***	***1.5***	***(20%)***
On-Post	Purposeful	6.5	5.8	0.7	(10%)	12.0	9.3	2.7	(22%)
	RMA Site Wide	2.0	1.8	0.2	(10%)	2.5	2.2	0.3	(12%)
	South Plants	17.4	15.0	2.4	(14%)	19.3	16.7	2.6	(13%)
	WTP	2.2	1.3	0.9	(43%)	3.3	2.3	1.0	(29%)

Table 17. Relative Contribution of Congeners to Full TEQ in Fine-Sieved Soil

Dioxins/Furans

	Off-Post						On-Post		
Analyte	**Agricultural**	**Commercial**	**Industrial**	**Open Space**	**Residential**	**All**	**Area A**	**Area B**	**All**
2,3,7,8-TCDF	1%	1%	0%	1%	0%	1%	2%	1%	1%
2,3,7,8-TCDD	3%	9%	3%	1%	7%	5%	3%	3%	3%
1,2,3,7,8-PeCDF	1%	1%	0%	1%	1%	1%	5%	2%	3%
2,3,4,7,8-PeCDF	**12%**	8%	9%	9%	8%	9%	**11%**	**10%**	**10%**
1,2,3,7,8-PeCDD	**19%**	**20%**	**16%**	**20%**	**19%**	**19%**	7%	**12%**	**10%**
1,2,3,4,7,8-HxCDF	3%	2%	2%	2%	2%	2%	**16%**	6%	**10%**
1,2,3,6,7,8-HxCDF	3%	2%	2%	3%	2%	2%	9%	4%	6%
2,3,4,6,7,8-HxCDF	4%	3%	3%	3%	3%	3%	4%	3%	4%
1,2,3,7,8,9-HxCDF	5%	2%	2%	5%	2%	3%	4%	4%	4%
1,2,3,4,7,8-HxCDD	3%	3%	3%	4%	3%	3%	1%	2%	2%
1,2,3,6,7,8-HxCDD	5%	6%	6%	5%	6%	6%	2%	4%	3%
1,2,3,7,8,9-HxCDD	4%	4%	4%	4%	4%	4%	2%	4%	3%
1,2,3,4,6,7,8-HpCDF	2%	3%	3%	2%	3%	2%	3%	2%	3%
1,2,3,4,7,8,9-HpCDF	0%	1%	0%	0%	0%	0%	2%	1%	1%
1,2,3,4,6,7,8-HpCDD	**13%**	**15%**	**17%**	**12%**	**17%**	**15%**	5%	9%	7%
OCDF	0%	0%	0%	0%	0%	0%	0%	0%	0%
OCDD	1%	1%	1%	1%	1%	1%	0%	1%	1%

PCBs

	Off-Post						On-Post		
Analyte	**Agricultural**	**Commercial**	**Industrial**	**Open Space**	**Residential**	**All**	**Area A**	**Area B**	**All**
PCB-77	0%	0%	0%	0%	0%	0%	0%	0%	0%
PCB-81	0%	0%	0%	0%	0%	0%	0%	0%	0%
PCB-105	0%	1%	1%	1%	1%	1%	1%	1%	1%
PCB-114	0%	0%	0%	0%	0%	0%	0%	0%	0%
PCB-118	1%	1%	1%	1%	1%	1%	1%	1%	1%
PCB-123	0%	0%	0%	0%	0%	0%	0%	0%	0%
PCB-126	**18%**	**17%**	**23%**	**23%**	**18%**	**20%**	**19%**	**29%**	**25%**
PCB-156	1%	1%	1%	1%	1%	1%	1%	1%	1%
PCB-157	0%	0%	0%	0%	0%	0%	0%	0%	0%
PCB-167	0%	0%	0%	0%	0%	0%	0%	0%	0%
PCB-169	0%	0%	0%	0%	0%	0%	0%	0%	0%
PCB-189	0%	0%	0%	0%	0%	0%	0%	0%	0%

Figure 13 summarizes the average quantitative congener concentration pattern in study soils. The upper panel shows congeners in the PCDD/PCDF class, while the lower panel shows congeners in the PCB class. As seen in the upper panel, the congener in the dioxin/furan class occurring at the highest concentration level is usually OCDD, along with varying amounts of OCDF (especially in on-post Area A), *1,2,3,4,6,7,*8-HpCDD, and *1,2,3,4,6,7,8*-HpCDF. As seen in the lower panel, several PCBs are usually present, primarily 105, 118, and 156, with lower levels of 157 and 167.

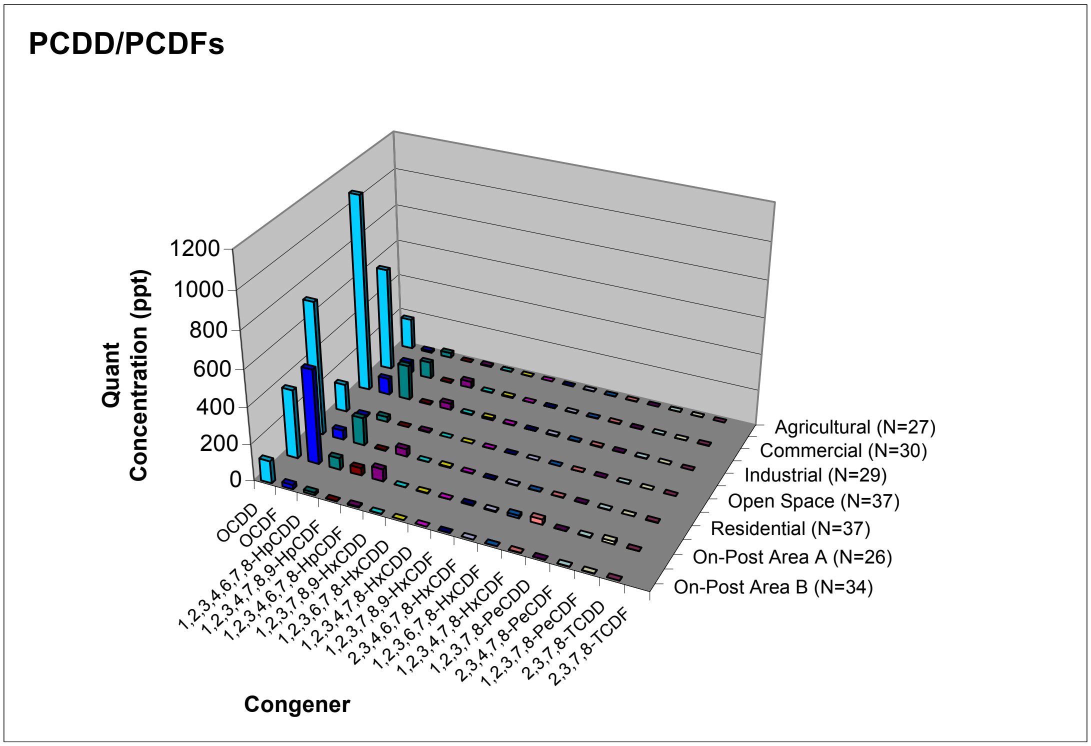
Principal Components Analysis (PCA)

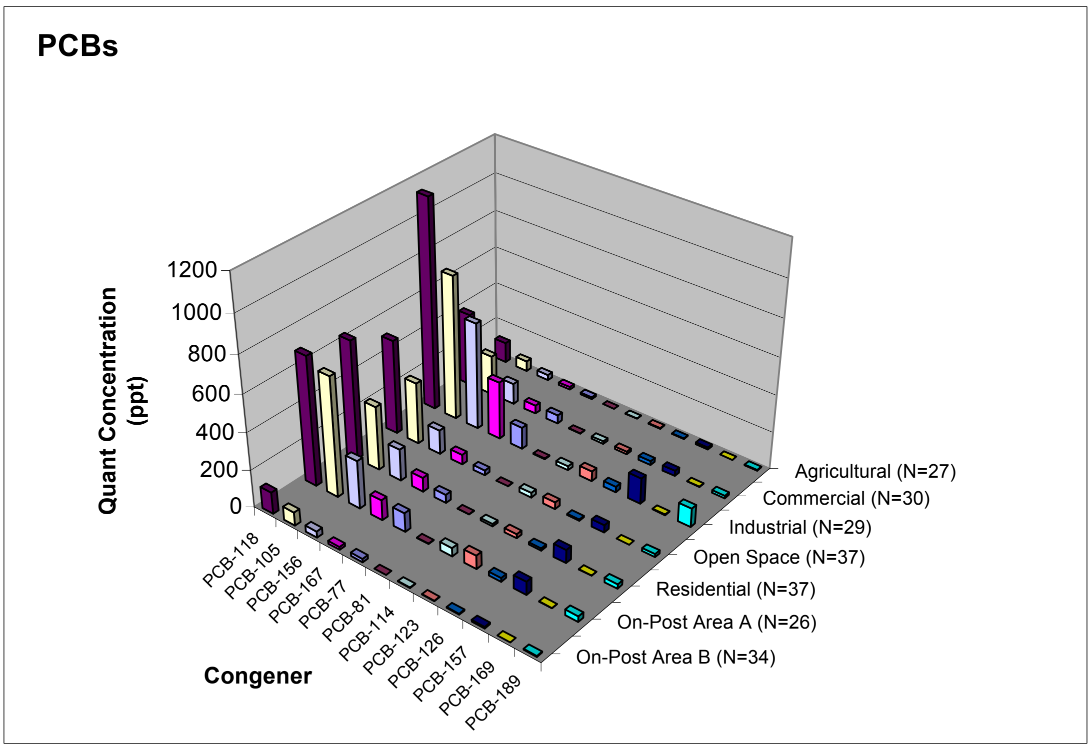
Multivariate statistical analysis was conducted to investigate the congener pattern for PCDDs/PCDFs and PCBs in both the on-post and off-post surface soil samples collected during this study. The detailed results are presented in Jones et al. (2001) (see Appendix G), and the findings are summarized below.

The major statistical approach to the study was Principal Components Analysis (PCA), a data condensation and discovery tool. This PCA method was chosen as it provides the most readily understandable and communicable interpretation of the data. However, PCA is not an analytical statistical tool and so cannot be used to perform hypothesis testing.

To improve the normality of the data and so avoid undue influence from outliers, the data were log-transformed before use. The treatment of values less than the method detection limit can have a major influence on the outcome of pattern recognition techniques. For the purpose of this analysis, ½ of the MDL was used in cases where concentrations were below the MDL and other flag-specific adjustments were applied. Despite considerable efforts, different approaches and options for the analysis the PCA of samples collected in the off-post reference areas indicated only limited differences based on land-use or location. The factor loadings, which indicate the individual PCDDs that determine the factors, were greatest for the higher chlorinated PCDD and PCDF congeners. This indicated that it is these higher chlorinated compounds that show the greatest differences between these samples. The clustering of the samples was relatively diffuse with many samples falling outside the 2 standard deviation confidence interval for the different land-use types. When these outliers were assessed based on location, they were relatively evenly distributed geographically indicating that the samples were not influenced by any unidentified major point sources of PCDD/PCDFs. There was some indication of separation of a small group of samples when plotted against Factor 3. This factor, while it explains only a small amount of the variation in the dataset, is influenced mainly by 2,3,7,8-TCDD and 2,3,7,8-TCDF. Overall the similarity of the samples in the off-post datasets resulted in the

Figure 13. Average Congener Concentration Profile for Fine-Sieved Soils





condensation of the five different land-use designation down to 3 for subsequent analysis; these were 'Rural' (agricultural and open space); 'Light-Use' human influenced (commercial and residential); and 'Industrial' which was retained as the original designation.

The PCA of the on-post samples demonstrated more significant clustering of samples indicating the presence of possible minor sources of PCDD/PCDFs to the on-post samples. It should be remembered that PCA cannot directly assess the magnitude or extent of any possible PCDD/PCDF source, it can only suggest the presence of a source and identify possible influences on samples collected at different distances from the source. From the detailed report on the concentrations of PCDD/PCDFs in the soil samples and the toxicological analysis of them, it is clear that the PCDD/PCDF sources on-post are limited in extent and relatively low level. The PCA of the on-post samples was driven, as determined by the factor loadings, by higher chlorinated PCDFs in contrast to the PCDD dominated pattern observed off-post. The WTP samples formed a relatively discrete cluster with the exception of one sample. This sample was collected near one of the RMA public entrances and so may in all probability received historic uses of chlorinated pesticides and herbicides which were commonly contaminated with PCDD/PCDFs. Random grab samples collected in the RMA site wide study showed a greater degree of variability than those from the WTP. This is to be expected as some of these samples were collected within the boundaries of areas of historic industrial use. The South Plants and the historic use sample groups also showed a relatively diffuse cluster of samples suggesting a relatively great degree of variability within the samples and so the presence of relatively insignificant PCDD/PCDF sources. The presence of a large source of dioxins would be expected to produce a strong clustering of the samples within the group.

For the final PCA analysis the log-transformed data for the on-post and off-post samples were combined into a single dataset. The factor loadings for the combined PCA were similar to those for the two individual datasets. As in the on-post PCA, factor 1 was heavily loaded on the higher chlorinated furans while factor 2 was loaded on the higher chlorinated dioxins and furans. Finally, factor 3 was most influenced by 2,3,7,8-TCDD but less strongly by 2,3,7,8-TCDF than in the individual datasets. These factors resulted in the on-post historical use samples being distinguished from the off-post sample by factor 1. The WTP samples and many of the RMA site wide samples clustered close to the off-post Rural and Light-Use human activity samples. The RMA site wide samples collected in or adjacent to the areas of historic use ordinated with the RMA historic use cluster. The signature profiles for the on-post and off-post Industrial uses were distinct with the on-post samples being influenced by higher chlorinated dioxins and the off-post samples being influenced by higher chlorinated PCDDs and PCDFs.

From the PCA conducted in this report it appears that the PCDD/PCDF profile for samples from the RMA are characterized by a relatively higher abundance of PCDF congeners than for reference area that have a relatively higher abundance of PCDD congeners. The presence of a PCDF "signature" for the RMA samples does not necessarily indicate a major source of these contaminants on-site. Indeed, the relatively diffuse nature of the sample clusters would argue strongly against the presence of a single large source. Instead, the predominance of the PCDF congeners on-post (especially in the central area) is probably indicative of the mixed industrial activities that took place on the site and the fact that since the area was a closed site, the PCDD congeners that predominate off site were not able to be generated or transported onto the site in corresponding amounts.

This analysis indicated that many of the samples collected on the RMA are indistinguishable from the off-post open space reference set. However, some samples collected on the RMA have a similar PCDD/PCDF "signature". The presence of an RMA signature is not indicative of a major contamination source on-site nor does it suggest any toxicological significance to the signature.

A multivariate statistical analysis was also conducted to evaluate the congener pattern of PCBs in on-post and off-post soil samples (see Appendix G). The analysis found that the concentrations of all the 12 PCBs congeners were highly correlated in the data set as a whole as well as when examined by land-use category and location, with essentially all the samples having the same PCB congener profile. This indicates that the source of PCBs in Denver-area soils (both on-post and off-post) is more likely to be an ambient area source than a series of different point sources.

Regression Analysis

In an effort to gain additional information on potential similarities and differences in congener patterns in various categories of on-post and off-post surface soil samples that PCA analysis might not be sensitive enough to detect, USEPA Region 8 also sponsored an exploratory analysis of the data for the WTP and Open Space land uses using a new approach involving regression analysis (DeGrandchamp 2001). This method utilized multiple pairwise regression analysis to derive mass ratios for highly correlated pairs of congeners. In brief, the PCDD/PCDF concentration data for these two data sets were log-transformed and the best fit linear regression lines were determined for each of the 136 different congener pairs. Non-detects were not considered in the regressions, and congener pairs were not evaluated unless there were at least four samples in which each of the two congeners were present above the detection limit. Data points that did not fall close to the regression line were identified as potential outliers, and samples were identified as "atypical" if they contributed multiple congener pairs that were potential outliers. The results of the regression analysis, including the number and identity of congener pairs that showed a strong correlation ($R > 0.7$), along with the slopes and intercepts of the best fit regression lines, constituted a "fingerprint" for each particular data set. Then, the "fingerprints" were compared between the two data sets (Open Space compared to WTP) using a weight of evidence approach. This analysis revealed no major differences between Open Space and WTP, although differences in the identity of some of the correlated pairs was interpreted as suggestive evidence of subtle differences, and several atypical samples were identified in each data set. While potentially promising as an evaluation technique, this approach was not pursued further because the outcome is apparently dependent upon a number of subjective decision rules inherent in the approach, and the underlying statistical basis of the approach is not yet well established.

4.6 Evaluation of Potential Confounders

4.6.1 Effect of Soil TOC Level

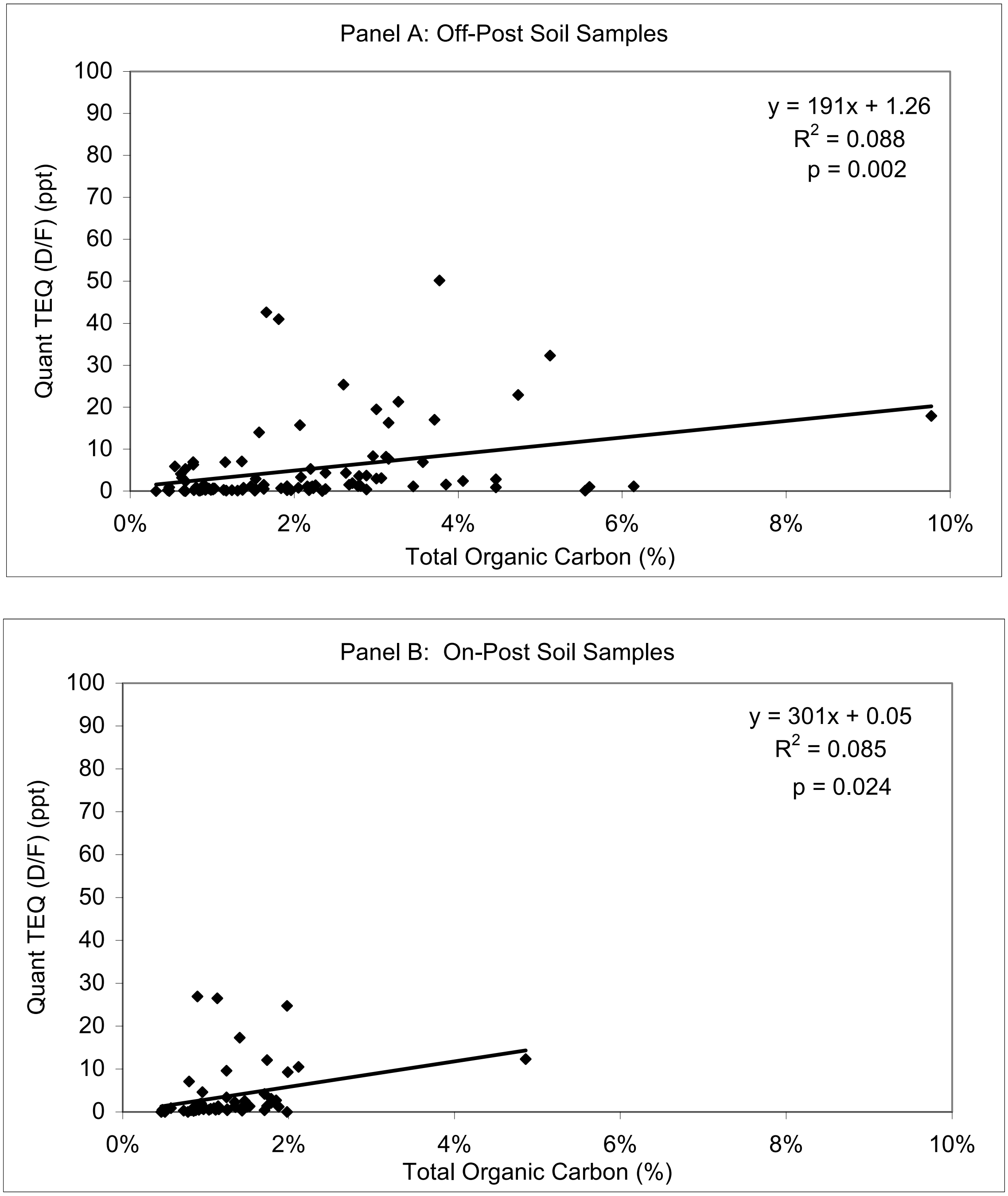
Binding of dioxins to soil particles is a physical process that might be expected to depend on the total organic carbon (TOC) content of the soil (soils with high TOC might bind more dioxins per unit weight than soils with low TOC). Such a dependence of TEQ levels on soil characteristics has been noted by Rogowski et al. (1999), although these data are complicated by use of TEQ values calculated from congener concentrations that were largely below the MDL.

Figure 14 summarizes the relationship between Quant TEQ(D/F) and soil TOC in off-post and on-post soil samples (fine fraction). As shown, the slope of the best-fit linear regression line through the data is statistically different from zero ($p < 0.05$) for both off-post (Panel A) and on-post (Panel B), but the coefficients of determination are quite low ($R^2 = 0.088$ and 0.085, respectively). Similar results are obtained when the Full TEQ(D/F) data are used. These results suggest that the TEQ(D/F) value in a soil sample may depend in part on the TOC of the soil, but that this is not the main determinant of the TEQ value.

4.6.2 Effect of Soil Particle Size

Binding of dioxins to soil particles is a physical process that might be expected to depend on the surface area of the soil particles. That is, soil particles that are small (i.e., fines) might tend to have a higher concentration per unit mass than coarser soil particles, and soils that have a

Figure 14. Correlation of TEQ (D/F) in Fine-Sieved Soils with Total Organic Carbon



P value < 0.05 indicates slope of line is significantly different from zero high percentage of fines might tend to have a higher concentration of dioxins than soils with a high fraction of coarse particles (other factors being equal).

Comparison of Bulk to Fine

As noted earlier, if sufficient sample mass was available, bulk field soil samples were prepared by sieving to isolate the "fine" fraction of particles less than 250 micrometers in diameter, since it is believed that this size fraction is likely to be of greater relevance for human and wildlife exposure than the bulk fraction. However, since most other studies of dioxin concentrations in soil have used un-sieved (bulk) soil, a number of samples of un-sieved (bulk) soil were also analyzed as part of this study to allow a comparison of concentration values in the bulk and fine fractions. The results for Full TEQ(D/F) are shown in **Figure 15**. As seen, the slope of the best fit regression line is slightly less than 1.0, indicating that there is no significant enrichment of TEQ in the fine soil compared to the bulk soil, and that TEQ values based on bulk field soil sample are similar to those based on the fine sieved soil.

In contrast to field samples, there is a clear enrichment in TEQ when the PE samples provided by EPA's QATS laboratory are sieved:

QATS PE Sample Type	N	Average Full TEQ(D/F) (ppt)		
		Bulk	Fine	Ratio
Low	10	42.2	67.6	1.60
Medium	8	77.5	118.5	1.53

The basis for this difference between the field samples and the QATS PE samples is not known, but may be attributable to physical differences in the way that PCDD/PCDF congeners combine with soil particles in the field compared to the methods used to prepare the PE samples in the laboratory.

Correlation of TEQ with Percent Fines

Figure 16 shows the relation between Quant TEQ(D/F) in a soil sample and the mass fraction of the sample that passes a fine screen. As shown, the slope of the best-fit linear regression line is not statistically different from zero in either the off-post (Panel A, $p = 0.39$) or the on-post data set (Panel B, $p = 0.15$), and the coefficient of determination is very low ($R^2 < 0.03$) in both cases. Similar results are obtained when the Full TEQ(D/F) data are evaluated.

Figure 15. Comparison of Full TEQ (D/F) in Bulk and Fine-Sieved Field Soil Samples

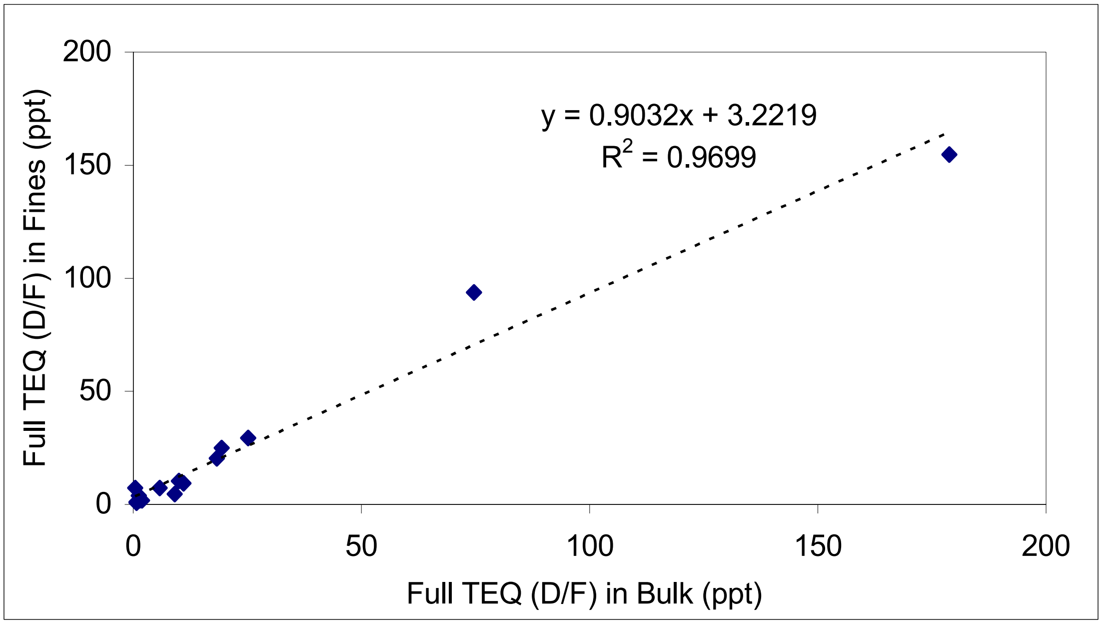
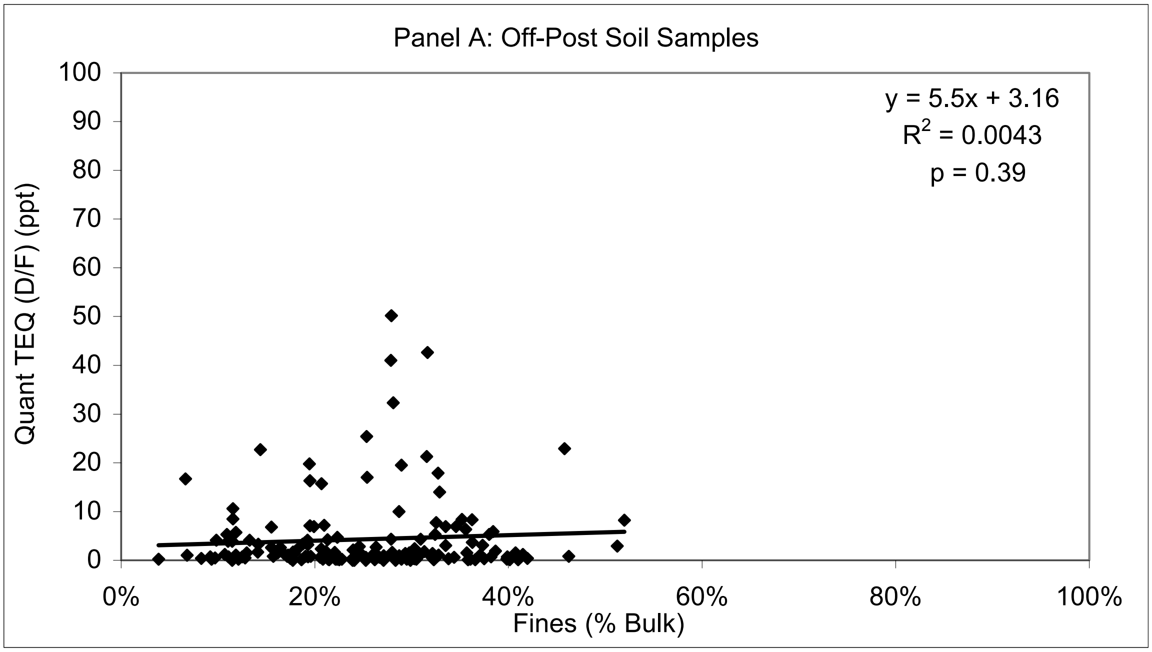
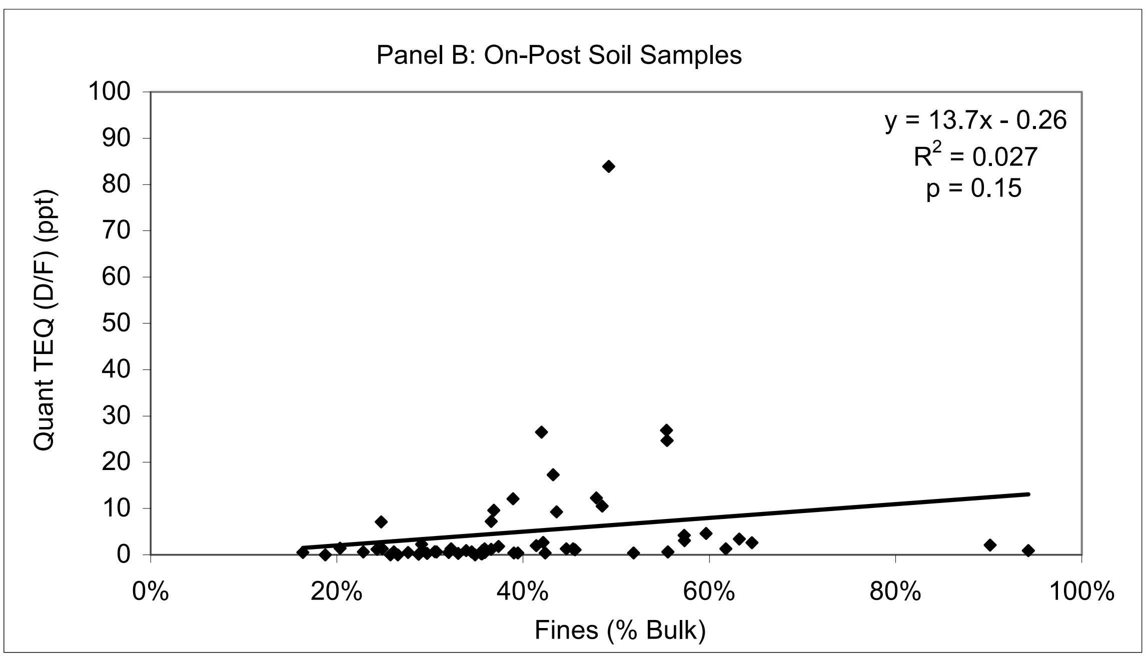


Figure 16. Correlation of TEQ (D/F) with Percent Fines in Soil





P value < 0.05 indicates slope of line is significantly different from zero

These results suggest that soil particle size distribution is not an important determinant of TEQ(D/F) in these samples. This result is consistent with the finding that the concentration of TEQ is not substantially different in the fine soil fraction than the bulk soil fraction for most field samples.

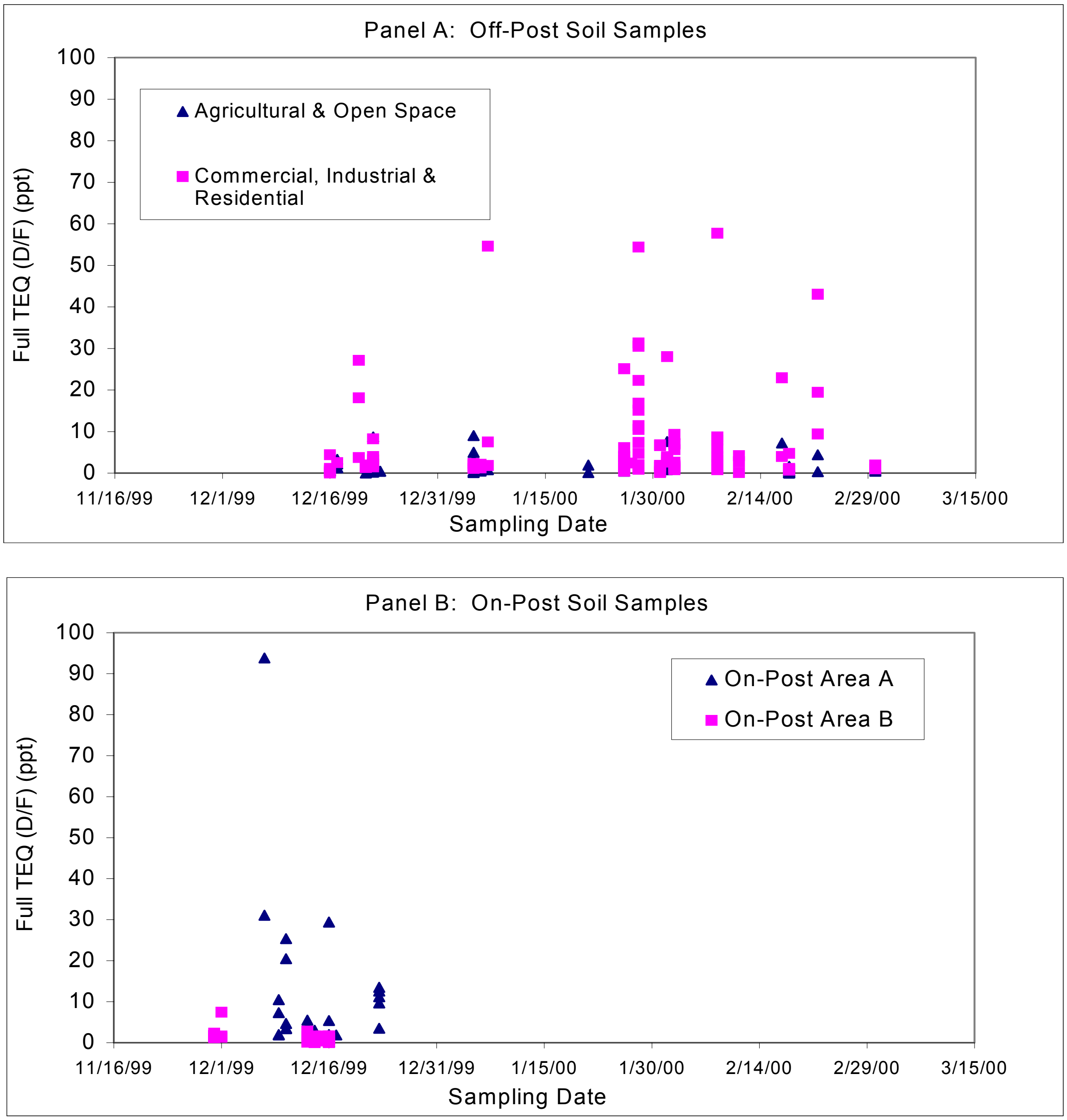
4.6.3 Temporal Variability

Even though dioxins tend to be relatively stable in the environment, it is possible that levels in soil vary as a function of time due to seasonal differences in emission rates and/or environmental transport rates. **Figure 17** shows the Full TEQ(D/F) for the soil samples collected during this study plotted as a function of the sample collection date. As seen, most samples from on-post locations were collected in December, 1999, and a majority of off-post samples were collected in January and February, 2000. Inspection of **Figure 17** does not reveal any clear temporal pattern in TEQ values, with high values occurring in samples collected in each month. Thus, seasonality is not considered to be an important issue in this study. A more extensive study, with repeat samples collected from fixed number of stations over a longer time interval, would be needed to determine if temporal trends in TEQ occur or not.

4.7 Comparison of Soil Data to Data from Biological Tissues (the BAS Study)

A Tier I screening study of dioxin levels in the tissues of several different types of ecological receptor was performed by the RMA Biological Advisory Subcommittee. The detailed project plan (BAS 2000) and study report for this project (BAS 2001) are available at the EPA Region 8 Records Center and are also available at the Region 8 web site (www.epa.gov/Region8/superfund/sites). In brief, this study focused on biological tissue levels of dioxins rather than soil levels because ecological receptors tend to integrate exposures of bioaccumulative compounds over a wide area, and because tissue data can be used to evaluate the likelihood of adverse ecological responses in the exposed receptors. The indicator species selected for study included the American kestrel, the great horned owl, and the common carp. Samples of kestrel eggs, owl liver, and carp eggs were obtained from animals collected at both on-post and off-post (reference) locations. Dioxin levels were measured both by congener-specific chemical analysis (using the same basic method that was used for soils), and by an *in vitro* cell culture bioassay technique. All data were validated and verified by an SOP similar to SOP 803 (see Appendix E2). The principal findings of this study are summarized below:

Figure 17. Correlation of Full TEQ (D/F) in Fine-Sieved Soils with Sample Collection Date



- The concentration of dioxins in kestrel eggs was not different in kestrels that resided on-post compared to those that resided off-post. Further, there was no significant difference between eggs from birds that resided in the central area compared to the peripheral area of RMA. The BAS report concluded that there was no indication of an on-post source of exposure above-background concentrations to American kestrels.

- Results for dioxin levels in owl livers were more difficult to interpret. This is mainly because the owl samples were fortuitous specimens (animals that were found dead or dying), rather than an active collection of spatially representative samples, so the number of samples and the spatial representativeness were limited. For juvenile owls, there was no statistically significant difference in dioxin levels in liver from birds collected on-post compared to off-post, but adult owls collected on-post did have higher levels than for adults collected off-post. However, interpretation of this finding was complicated by the fact that three of the four adult owls collected on-post were severely emaciated (probably because of pesticide toxicity or other disease). Such a weight loss has been observed to cause a redistribution of dioxins into the liver, and this might have contributed to the high levels observed in these animals. When the results were adjusted for the body weight loss, the levels were closer to what was observed in off-post samples, but were still marginally higher. The highest levels of dioxins were found in livers of owls (all ages) that were collected from near the South Plants area of RMA. Because of the relatively small number of samples and the uncertainty caused by the emaciation of the on-post adult owls, the BAS report concluded the results for owl liver were inconclusive.

- For carp eggs, concentration levels were very low (near the detection limit) for samples from both on-post and off-post fish. Because of the very low levels, statistical comparisons of the data were difficult, but the BAS report concluded that there was no indication of a potential on-post source of dioxin exposure to carp.

In summary, the BAS (2001) study found equivocal evidence of a small increase in liver dioxin levels for owls that resided in the vicinity of the South Plants area of RMA, but no evidence of an increase in exposure for kestrels or carp.

The results of the biological sampling program performed by BAS (2001) are fully consistent with the results of the on-post soil sampling studies (USEPA 2001b, c, d). As described above, the on-post soil studies found small elevations in dioxin levels in soil samples from the South Plants area and a few nearby waste disposal areas, but no significant elevations in soil samples from the peripheral areas of RMA. This pattern of soil contamination might reasonably be expected to cause a small increase in exposures of receptors residing in the immediate vicinity of South Plants, but not for receptors residing in the perimeter areas of RMA, precisely as observed in the BAS study (BAS 2001).

4.8 Comparison to Human-Health Based Guidelines

Although the primary purpose of the Denver Front Range Dioxin Study was to characterize the distribution of dioxin levels in surface soil samples from the Front Range area and the RMA (and not to perform a health risk evaluation), it may be of some use to provide a health-based frame of reference by which the measured concentrations of dioxins in soils may be placed in context.

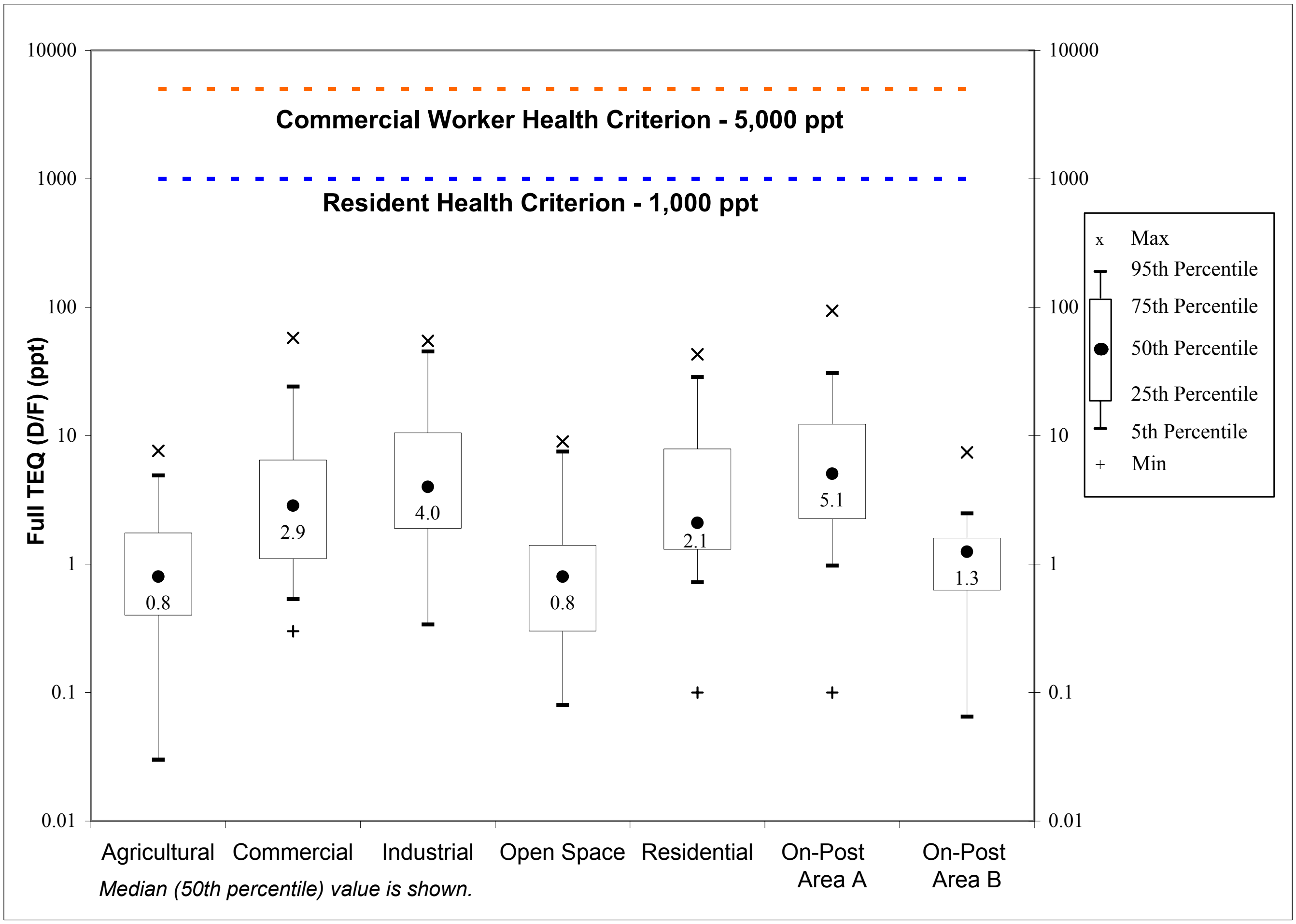
The USEPA Superfund Program has currently established a default screening concentration value of 1,000 ppt (1 ppb) TEQ in surface soil as a concentration that is not of cancer or non-cancer concern for lifetime exposure of residents (USEPA 1998a). For commercial and industrial land uses, USEPA guidelines identify 5,000 to 20,000 ppt (5-20 ppb) TEQ as the screening concentration of concern in surface soil. These soil screening concentrations are based only upon the 17 TCDD-like PCDDs and PCDFs, and are calculated using the TEFs for mammals recently recommended by the WHO (Van den Berg et al. 1998).

The Agency for Toxic Substances and Disease Registry (ATSDR) has also established an interim policy guideline for human (residential) exposure to dioxin and dioxin-like compounds in soil (De Rosa et al. 1997). ATSDR currently identifies a provisional concentration of 50 ppt TEQ in soil as a "screening level," below which no further investigation or characterization will usually be required. ATSDR identifies a concentration of 1,000 ppt TEQ as an "action level," indicating that public health actions such as surveillance, research, health studies, community education, or exposure investigations should be considered. Concentrations between 50 ppt and 1000 ppt TEQ are identified as "evaluation levels," indicating that further investigation of site-specific factors regarding the extent and possible public health implications of the exposure may be warranted.

The USEPA is in the process of completing a comprehensive reassessment of dioxin toxicity, and has tentatively concluded that the carcinogenic and non-carcinogenic potency of dioxins may be somewhat greater than previously believed (USEPA 2000a). However, until a complete peer review and cross-program policy assessment of the impacts of this report can be performed, USEPA recommends that the 1,000 ppt TEQ concentration in surface soil continue to be used as a soil screening level for residential land uses (USEPA 1998a), and that 5,000 ppt TEQ be used as a screening level for commercial workers.

As illustrated graphically in **Figure 18**, none of the samples collected during the Denver Front Range Study approach or exceed the USEPA level of concern for either residents (1,000 ppt TEQ) or commercial workers (5,000 ppt TEQ). Of the 38 off-post soil samples where land use was classified as residential, only one had a TEQ concentration that exceeded the ATSDR "screening level" of 50 ppt TEQ, and none approached the ATSDR "action level" or the EPA screening level of 1,000 ppt TEQ. As discussed previously, this one residential value (155 ppt TEQ) that exceeds the ATSDR "screening level" appears to be an outlier (> 99th percentile), even though no local point source was identified for this sample. In addition, like all the samples in the "residential" land use category, the sample is not from an actual private residence where exposure is estimated to occur for 24 hours per day, 7 days per week. In consideration of these factors, USEPA Region 8 has determined that dioxin levels in Denver Front Range "background" samples do not present a significant human health concern for any land use category.

Figure 18. Full TEQ (D/F) Levels in Fine-Sieved Soils Compared to Health Criteria



If minimum TEQ value is not shown, the value is off-scale low.

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5.0 SUMMARY AND CONCLUSIONS

The results of the Front Range Dioxin Soil Study provide an accurate, sensitive and complete data set on the average and range of PCDD, PCDF and PCB concentrations and TEQ levels which occur in a variety of soil sampling locations in the Denver Front Range area and at the Rocky Mountain Arsenal. The mean value for Full TEQ for dioxins and furans across all off-post samples was about 5 ppt, with individual values ranging from less than 1 ppt TEQ up to a maximum of 58 ppt TEQ[1]. Values from open space and agricultural areas tended to be the lowest (mean Full TEQ(D/F) = 2 ppt), while values from industrial, commercial, and residential areas included some higher values (mean Full TEQ(D/F) = 8 ppt). Full TEQ(D/F) values in soil from the central portion (Area A) of RMA are slightly elevated (mean = 12 ppt, maximum = 94 ppt), a finding that is consistent with the findings of potential slight elevations of dioxin levels in livers of owls residing in this area. However, dioxin levels in the Area A of RMA appear to be generally similar to off-post industrial or commercial areas around Denver. Also, the South Plants and other historic use areas of RMA with the highest dioxin levels are scheduled for soil excavation as part of on-going remediation efforts to reduce or eliminate the presence of organo-chlorine pesticide contamination. Once this remediation is complete, it is expected that dioxin levels throughout RMA will be approximately the same as for open space areas in the Denver Front Range area, and that future use of the RMA as a wildlife refuge will not result in any excess dioxin exposure to refuge workers, volunteers, or site visitors. Soil samples from the peripheral areas of RMA (Area B) are generally low (mean = 1 ppt, maximum = 7 ppt) and are not significantly different from off-post open space or agricultural areas. None of the samples collected either on-post or off-post approached or exceeded the level of health concern for either residents or workers.

In conclusion, this study provides a large and comprehensive data set for concentrations of 29 TCDD-like PCDD, PCDF, and PCB congeners in soil. Advanced analytical techniques achieved lower detection and quantitation limits than most other studies, and extensive quality control data establish that the data are reliable and accurate. Confounders were evaluated and found to be minimal. These strong methods and robust study design provide greater assurance that the data have high quality and usability at trace levels. This study and its design and methods are an excellent template for future studies that may be needed to provide high quality data with adequate quantitative usability for risk assessments.

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[1] Two samples were collected which had TEQ values of 140 and 155 ppt, but these were judged to be outliers that were not representative of typical ambient levels due to non-point sources.

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APPENDICES

All Appendices to this report are provided in electronic format in the attached CD

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APPENDIX A

RAW ANALYTICAL DATA AND CALCULATION OF TEQ VALUES FOR SOIL SAMPLES

A1 Off-Post Field Samples (Study 1)
A2 On-Post Random Sampling Field Samples (Study 2)
A3 On-Post WTP Field Samples (Study 3)
A4 On-Post Historic Use Area Samples (Study 4)
A5 Quality Control Samples (all studies)

APPENDIX B

GRAPHICAL DATA PRESENTATIONS OF SOIL CONCENTRATIONS AND CONTRIBUTIONS TO TEQ

APPENDIX C

DETAILED SOIL SAMPLE LOCATION INFORMATION

Appendix C1 Off-Post Surface Soil Sampling Locations

Appendix C2 On-Post Surface Soil Sampling Locations

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MAPS OF TEQ RESULTS IN SURFACE SOILS

APPENDIX E

STANDARD OPERATING PROCEDURES

E1 Modified Analytical Method with Performance Criteria

E2 Data Validation SOP

APPENDIX F

INTER-LABORATORY COMPARISON OF CONGENER RESULTS

APPENDIX G

PRINCIPAL COMPONENT ANALYSIS (PCA)

G1 PCA for PCDDs/PCDFs

G2 PCA for PCBs