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Fingerprint Analysis of Contaminant Data: A Forensic Tool for Evaluating Environmental Contamination

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1.0 Introduction

Several studies have been conducted on behalf of the U.S. Environmental Protection Agency (EPA) to identify detection monitoring parameters for specific industries.[1,2,3,4,5] One outcome of these studies was the evolution of an empirical multi-variant contaminant fingerprinting process. This process, Fingerprint Analysis of Leachate Contaminants (FALCON), was developed through the EPA's Technical Support Center (TSC) in response to the need for identifying the source of contaminant plumes. FALCON combines data for several contaminants to develop a distinctive graphical fingerprint or multi-parameter chemical signature. These fingerprint patterns can be used to characterize the source of a contaminant plume, differentiate the contaminant plume from background conditions at the source, and monitor the migration of leachate into the environment. It can be applied to both organic and inorganic contaminants and is effective over a wide range of contaminant concentrations. This data evaluation process is analogous to using fingerprints to identify individuals. However, rather than using the size and location of ridges and swirls on the fingertip, the relative abundance of selected constituents is used to develop distinctive chemical signatures.

The objective of this paper is to demonstrate that FALCON is a quantitative, defensible fingerprinting process. A description of the stepwise FALCON technique is provided in *Section 2.0*. Examples are presented to illustrate the range of situations in which fingerprinting can be applied to characterize the occurrence and distribution of environmental contaminants. These examples were developed using routine monitoring data obtained from a variety of ongoing site characterization and monitoring programs. Case studies of FALCON applications are presented in *Section 3.0*.

2.0 FALCON Procedure

The FALCON procedure is a multi-step process of combining data from two or more measurements to create a distinctive ratio or multi-parameter chemical signature that can be used to characterize a contaminant plume from a particular source. The following example, using data from a dioxin-furan contaminated sawmill site, illustrates the individual steps in this fingerprinting process.

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Step 1: Data Review

Data are subjected to an initial review to assess the type and quantity of information available. The data are examined to identify subsets that are representative of the designated source area, background areas, impacted areas, and other potential sources that may be differentiated by fingerprinting. The data are then examined to determine whether there are replicate data to assess the reproducibility of any fingerprint pattern that may be identified. This information may exist as either duplicate analyses, multiple samples from the same area, or samples from the same location over time. The data are also reviewed to ensure each individual set is complete and comparable (there are no missing values, results are expressed in the same concentration units, non-detect limits are specified). Finally, the data are examined for any obvious data quality issues.

Step 2. Data Tabulation

The individual data sets are entered into a spreadsheet to (1) select parameters to be used in the fingerprinting process, (2) prepare graphical plots of the fingerprint patterns, and (3) estimate the statistical reproducibility/comparability of identified fingerprint patterns. In this particular example, the laboratory had reported results for 17 specific dioxin-furan congeners and several "total" congener measurements (e.g., total hexachlorodibenzodioxin). The "total" measurements were excluded from the fingerprint process because the results were vague (specific congeners included in the total were not identified and could not be confirmed with the congener-specific data). Also, Octachlorodibenzodioxin was excluded from the fingerprint because the extremely high concentrations for this specific congener overwhelmed the concentrations for the remaining dioxin-furan congeners. After data review and tabulation, 16 dioxin-furan congeners were selected to develop the sawmill fingerprint. The data from seven soil samples at this site are presented in Table 1. These samples, with a calculated total dioxin-furan congener concentration ranging from 231 nanograms per kilogram (ng/kg) to 1,302,460 ng/kg, were specifically selected to demonstrate the capability of this fingerprinting technique to handle the highly variable contaminant concentrations that can be encountered in a site investigation.

Step 3. Data Normalization

Data used for contaminant fingerprinting are transformed in a multi-step process. First, individual results listed as "not detected" in the original data set are replaced with a numerical value. The convention used in this example is to replace the "ND" result with a value equal to one-half the reported detection limit. Second, a total concentration is calculated for the parameters used in the fingerprint (fingerprint mass). Finally, the reported concentration for each fingerprint constituent in that sample is normalized to the calculated fingerprint mass. Thus, the reported concentrations for the fingerprint constituents are converted to a decimal percentage of the calculated fingerprint mass. The transformed dioxin-furan data for this example are shown in Table 2. The substitution of a numeric value for non-detected constituents and the subsequent data transformation process performs two functions; it permits individual data sets to be plotted on a common y-axis scale for visual inspection of the fingerprint (Step 4) and it permits individual data sets to be statistically compared (Step 5).

Table 1. Dioxin-Furan Monitoring Results for Sawmill Soil Samples*

Dioxin-Furan Congener	Chemical Number	Soil Sampling Locations						
		SM20	SM34	SM41	SM44	SM40	SM46	SM51
2378-TCDD	1	**0.95**	**0.95**	180	1.4	170	16	8.4
12378-PeCDD	2	**2.4**	**2.35**	520	9.8	1800	130	31
123478-HxCDD	3	**2.4**	3.1	1700	12	4000	290	48
123678-HxCDD	4	5.4	13	4900	89	47000	2500	350
123789-HxCDD	5	4.8	11	1400	35	12000	630	100
1234678-HxDD	6	160	300	100000	1100	760000	34000	3900
2378-TCDF	7	**0.95**	0.3	13	3.4	190	140	21
12378-PeCDF	8	**2.4**	**2.35**	13	2.6	280	110	6.1
23478-PeCDF	9	**2.4**	**2.35**	16	**2.3**	540	120	**5.5**
123478-HxCDF	10	**2.4**	**2.35**	30	12	3300	240	45
123678-HxCDF	11	**2.4**	**2.35**	150	11	1600	200	24
123789-HxCDF	12	**2.4**	**2.35**	**2.35**	**2.4**	**280**	9	**7.5**
234678-HxCDF	13	**2.4**	**2.35**	85	8.8	1500	180	17
1234678-HpCDF	14	11	30	23000	210	110000	3300	600
1234789-HpCDF	15	**2.4**	**2.35**	2300	14	9800	290	62
OCDF	16	26	69	43000	450	350000	8400	1300
Sum 1-16		230.7	446.1	177309	1964	1302460	50555	6525.5

* Dioxin-Furan concentrations reported in ng/kg.

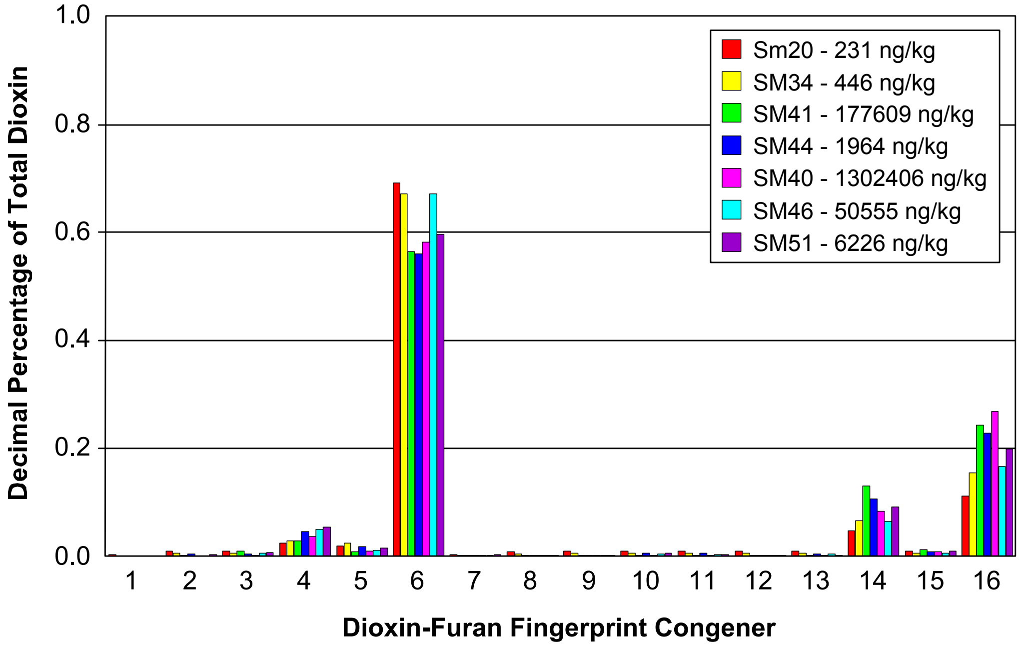
ND values have been replaced with a concentration equal to one-half the ND value (in **bold**).

Table 2. Normalized Dioxin-Furan Monitoring Results for Sawmill Soil Samples

Dioxin-Furan Congener	Chemical Number	Soil Sampling Locations						
		SM20	SM34	SM41	SM44	SM40	SM46	SM51
2378-TCDD	1	**0.0041**	**0.0021**	0.0010	0.0007	0.0001	0.0003	0.0013
12378-PeCDD	2	**0.0104**	**0.0053**	0.0029	0.0050	0.0014	0.0026	0.0048
123478-HxCDD	3	**0.0104**	0.0069	0.0096	0.0061	0.0031	0.0057	0.0074
123678-HxCDD	4	0.0234	0.0291	0.0276	0.0453	0.0361	0.0495	0.0536
123789-HxCDD	5	0.0208	0.0247	0.0079	0.0178	0.0092	0.0125	0.0153
1234678-HxDD	6	0.6935	0.6724	0.5640	0.5602	0.5835	0.6725	0.5977
2378-TCDF	7	**0.0041**	0.0007	0.0001	0.0017	0.0001	0.0028	0.0032
12378-PeCDF	8	**0.0104**	**0.0053**	0.0001	0.0013	0.0002	0.0022	0.0009
23478-PeCDF	9	**0.0104**	**0.0053**	0.0001	**0.0012**	0.0004	0.0024	**0.0008**
123478-HxCDF	10	**0.0104**	**0.0053**	0.0002	0.0061	0.0025	0.0047	0.0069
123678-HxCDF	11	**0.0104**	**0.0053**	0.0008	0.0056	0.0012	0.0040	0.0037
123789-HxCDF	12	**0.0104**	**0.0053**	**0.0000**	**0.0012**	**0.0002**	0.0002	**0.0011**
234678-HxCDF	13	**0.0104**	**0.0053**	0.0005	0.0045	0.0012	0.0036	0.0026
1234678-HpCDF	14	0.0477	0.0672	0.1297	0.1069	0.0845	0.0653	0.0919
1234789-HpCDF	15	**0.0104**	**0.0053**	0.0130	0.0071	0.0075	0.0057	0.0095
OCDF	16	0.1127	0.1547	0.2425	0.2292	0.2687	0.1662	0.1992

Step 4. Graphical Presentation of Fingerprint

The normalized data in Table 2 are plotted as a series of histograms. The x-axis in these plots is an ordered presentation of the individual fingerprint constituents. The actual order along the x-axis is not critical but it must be consistent in each of the histograms. The y-axis is a plot of the relative abundance of each constituent expressed as a decimal percentage of the calculated fingerprint mass. The data transformation process in Step 3 defines a common y-axis scale of 0.0 to 1.0 decimal percent for each data set since no constituent can be less than 0 percent of the fingerprint mass, no constituent can represent more than 100 percent of the fingerprint mass, and the sum of all constituents must be equal to 100 percent of the fingerprint mass. Therefore, each sample histogram can be plotted on the same scale even though the reported concentrations may vary by orders of magnitude. A visual inspection of Figure 1 demonstrates that the seven data sets presented in Table 1 define a single fingerprint pattern characterized by approximately 60 percent constituent 6, approximately 20 percent constituent 16, approximately 10 percent constituent 14, approximately 4 percent of constituent 4 and trace amounts of the remaining 12 constituents. The dioxin-furan congener number along the x-axis of Figure 1 corresponds to the chemical number listed in Tables 1 and 2.



Regression Analysis Comparison of Sawmill Fingerprint Pattern

	SM20	SM34	SM41	SM44	SM40	SM46	SM51
SM20		0.994	0.912	0.930	0.913	0.989	0.962
SM34			0.950	0.965	0.951	0.998	0.986
SM41				0.997	0.992	0.956	0.985
SM44					0.995	0.971	0.994
SM40						0.959	0.985
SM46							0.991
SM51							

Average regression analysis comparison = 0.970.

Figure 1. Graphical representation and regression analysis comparison of a dioxin-furan fingerprint pattern at a sawmill.

Step 5. Statistical Assessment of Pattern Reproducibility

A statistical estimate of the comparability of the individual histograms is calculated using regression analysis. Each histogram is individually compared with the remaining histograms to calculate an r^2 value (regression coefficient squared). The calculated r^2 values fall into the range of 0.00 (the two patterns are totally dissimilar) to 1.00 (the two patterns are identical) and provides a decimal estimate of the reproducibility or comparability of two patterns. This example produced 21 histogram comparisons (SM20 vs. SM34, SM20 vs. SM41, etc.) with calculated r^2 values ranging from 0.912 to 0.998 that are summarized in the Regression Analysis Table in Figure 1. The estimated reproducibility of the dioxin-furan fingerprint shown in Figure 1 is 0.970 ± 0.027 (97 ± 3 percent). Despite the highly variable dioxin-furan concentrations that spanned four orders of magnitude across the sawmill site and the variable number of non-detected congeners within each set, the FALCON process identified a single, reproducible chemical signature that characterizes the dioxin-furan contamination at this facility.

Step 6. Evaluate Remaining Data

Once a source fingerprint has been identified, regression analysis can be used to compare the dioxin-furan congener distribution at other monitoring locations with the source fingerprint.

These results can be used to:

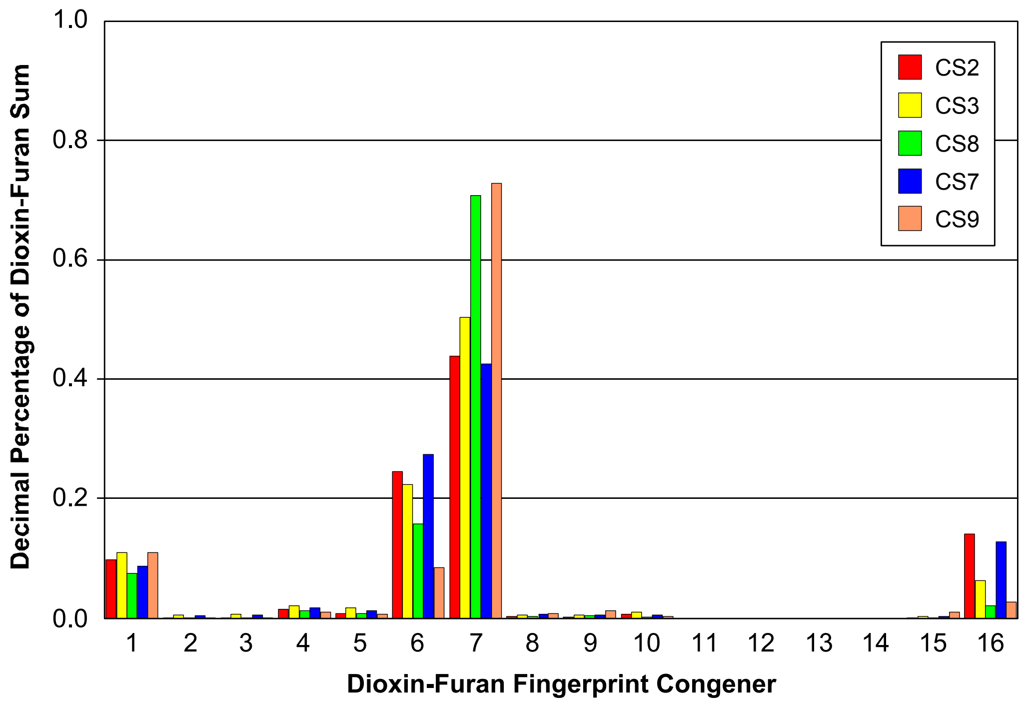
1. differentiate the source from background conditions,
2. demonstrate whether contamination detected at some distance from a site is related to the source,
3. map contaminant migration away from a source,
4. differentiate multiple sources of the same contaminant, and
5. estimate the mixing ratio of two plumes.

3.0 Contaminant Fingerprinting Case Studies

Case studies are presented to illustrate the versatility of FALCON in a variety of contamination scenarios. Data used in these case studies were generated using standard analytical techniques in ongoing site investigation, characterization, and monitoring programs. The intent of these case studies is not to provide detailed site investigation histories for each example, but simply to illustrate the variety of situations in which the FALCON fingerprinting process can be applied to characterize the occurrence and distribution of contaminants.

3.1 Source Characterization of Organic Contaminants - Pulp Mill Case Study

Fingerprinting was conducted to differentiate the impacts of a pulp mill from other potential dioxin-furan sources along the lower Roanoke River in eastern North Carolina. The waste stream from this mill passed through a baffled settling pond and discharged to a tributary of the Roanoke River. Samples were collected from the tributary sediments known to be impacted by the pulp mill. Data from these samples were carried through the FALCON process and produced the dioxin-furan fingerprint pattern shown in Figure 2 (the fingerprint constituents listed by number along the x-axis are identified in Table 1). The 16 dioxin-furan congeners used in this example defined a pattern characterized by 40 to 70 percent constituent 7 (2378-Tetrachlorodibenzofuran), 10 to 25 percent constituent 6 (1234678-Heptachlorodibenzodioxin), 10 percent constituent 1 (2378-Tetrachlorodibenzodioxin), and 2 to 17 percent constituent 16 (Octachlorodibenzofuran (OCDF)).



Regression Analysis for Pulp Mill Fingerprint

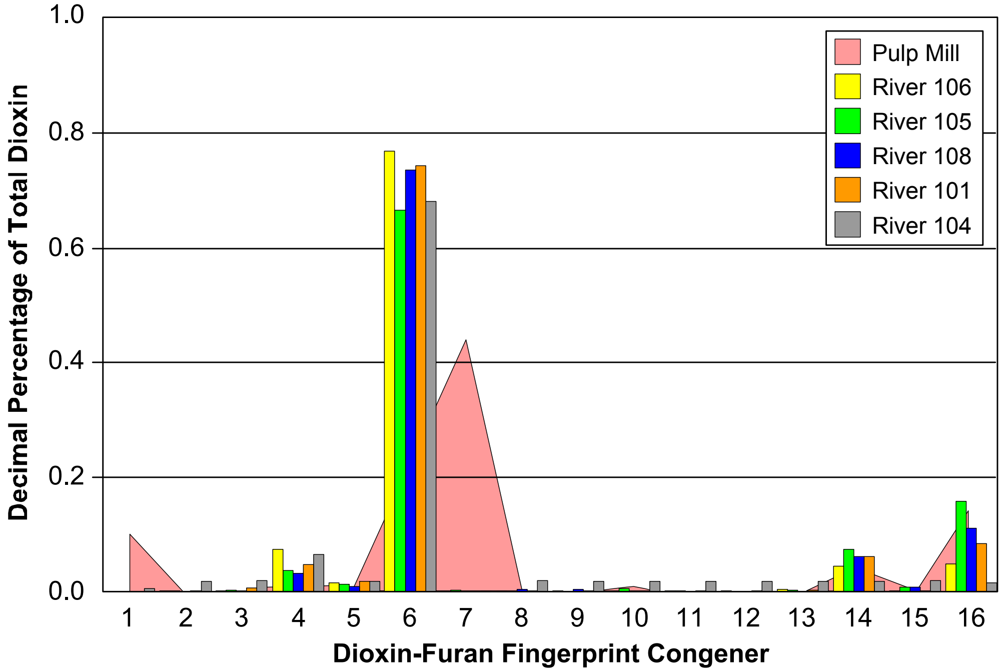
	CS2	CS3	CS8	CS7	CS9
CS2		0.958	0.849	0.993	0.791
CS3			0.948	0.951	0.902
CS8				0.826	0.985
CS7					0.754
CS9					

Average regression analysis comparison = 0.896.

Figure 2. Dioxin-furan fingerprint pattern for a pulp mill effluent.

There were several site-specific factors that influenced the variability of the individual peak heights and the fingerprint pattern for this source. First, the discharge practice to the tributary was terminated in 1987. Changing hydrologic conditions over time (spring runoff, storm events, and tidal cycles) and bioturbation could have affected the dioxin residuals in the sediments. Second, wood fiber accumulation in the sediments complicated the sample collection process. However, despite the possible influence of these factors, the graphical fingerprint for the pulp mill had an estimated reproducibility that ranged from 0.754 (75 percent) to 0.993 (99 percent) with an average value of 0.896 ± 0.08 (90 ± 8 percent).

Roanoke sediment samples were collected upriver from the confluence with the tributary that had been impacted by the pulp mill. These samples defined a second dioxin-furan fingerprint that is contrasted with the pulp mill fingerprint in Figure 3. The upriver sediment fingerprint is presented as a series of histograms and the pulp mill fingerprint is presented as an area plot that was calculated as the average of the tributary samples shown in Figure 2. The upriver sediment fingerprint is characterized by 67 to 78 percent constituent 6 (1234678-HpCDD), 1 to 17 percent constituent 16 (OCDF), 1 to 8 percent constituent 14 (1234678-Heptachlorodibenzofuran), 3 to 6 percent constituent 4, and trace amount of 12 other congeners. The reproducibility of the upriver fingerprint pattern ranged from 0.996 (99+ percent) to 0.999 (99^+ percent) with an average value of 0.998 ± 0.005 (99+ ± 0.5 percent).



Regression Analysis of Dioxin-Furan Fingerprint Patterns

	River 106	River 105	River 108	River 101	River 104
Pulp Mill	0.063	0.062	0.062	0.061	0.061
River 106		1.000	0.998	0.999	0.998
River 105			0.996	0.998	0.997
River 108				1.000	0.999
River 101					0.999
River 104					

Comparison between mill and upriver sediments = 0.062.
Estimated reproducibility of upriver sediment pattern = 0.998.

Figure 3. Comparison of upriver sediment dioxin-furan fingerprint with the pulp mill dioxin-furan fingerprint.

The presentation in Figure 3 (histogram vs. area plot) permits a rapid visual comparison of the two identified fingerprint patterns at this site. The dioxin-furan fingerprint pattern for the pulp mill impacted tributary and the dioxin-furan fingerprint for the upriver Roanoke sediments can be differentiated both visually and statistically. The Roanoke upriver fingerprint is characterized by a single dominant peak for constituent 6 (1234678-HpCDD) and several minor peaks for constituent 4 (123678-HxCDD), constituent 14 (1234678-HpCDF), and constituent 16 (OCDF). The pulp mill fingerprint is characterized by a major peak for constituent 7 (2378-TCDF), and lesser peaks for constituent 1 (2378-TCDD), constituent 6 (1234678-HpCDD), and constituent 16 (OCDF). The upriver sediment pattern can be distinguished from the pulp mill pattern by the greater relative abundance of constituent 6 (67 to 78 percent versus 10 to 25 percent), the virtual absence of constituent 7 (<1 percent versus 42 to 73 percent), and the virtual absence of constituent 1 (< 1 percent versus 10 percent). For the purpose of this paper, an average pulp mill fingerprint was calculated based on the results presented in Figure 2. This "average" pulp mill fingerprint was compared with each of the Roanoke upriver sediment samples using regression analysis. As summarized in the regression table associated with Figure 3, the comparability of the upriver dioxin-furan fingerprint with the pulp mill dioxin fingerprint ranged from 0.061 (6 percent) to 0.063 (6 percent). A t-Test analysis of the set of r^2 values for the pulp mill and Roanoke sediments comparisons with the set of r^2 values for the Roanoke sediment reproducibility comparisons demonstrates that the pulp mill dioxin has a significantly different fingerprint pattern at $p = 0.05$. In this case study, FALCON identified a reproducible (90 ± 8 percent) dioxin-furan fingerprint for the pulp mill source (Figure 2), a second highly reproducible (99 ± 0.5 percent) dioxin-furan fingerprint for the upriver source(s) (Figure 3), and the two fingerprint patterns could be easily differentiated both graphically and statistically.

Any dioxin-furan contamination washed out of the tributary will mix with dioxin-furan contamination from the upriver source(s). This will create an unknown mixture of upriver dioxin-furan with pulp mill dioxin-furan in sediments collected below the tributary confluence. Using the two identified FALCON fingerprints, it is possible to calculate the expected congener distribution pattern for possible mixtures of the two source fingerprints. The relative abundance of each congener is known for 100 percent upriver sediment (Figure 3), is known for 100 percent pulp mill waste (Figure 2), and the expected congener distribution was calculated for mixtures of 90 percent upriver sediment plus 10 percent pulp mill waste, 80 percent upriver sediment plus 20 percent pulp mill waste, continuing to 10 percent upriver sediment plus 90 percent pulp mill waste. These results are presented in Table 3 in which each vertical column represents the expected dioxin-furan congener distribution (fingerprint) for the indicated sediment-pulp mill mixture.

If there were no pulp mill dioxin-furan in the lower river sediments, each downriver station would be expected to have a congener distribution pattern similar to the upriver fingerprint (Table 3, 100 percent upriver and 0 percent pulp mill). Therefore, constituent 6 would have a relative abundance of 0.813 (81 percent), constituent 7 would have a relative abundance of 0.016 (2 percent), and the remaining congeners would have the relative abundance indicated. However, if contaminated tributary sediments were entering the river, there would be a characteristic shift in the relative abundance of each congener with increasing amounts of pulp mill dioxin-furan. Thus, the relative abundance of congener 6 would gradually decrease from 0.812 (81 percent) to 0.196 (20 percent) and the relative abundance of congener 7 would simultaneously increase from 0.016 (2 percent) to 0.546 (55 percent) as the mixture changes from 100 percent upriver sediment and 0 percent pulp mill waste to 0 percent upriver sediment and 100 percent pulp mill waste. The relative abundance of each remaining congener in the fingerprint would also be expected to change as indicated in Table 3.

The actual fingerprint pattern in each downriver sample can be compared to the calculated fingerprint patterns in Table 3 using regression analysis. This will produce a range of values for each sample as shown in Table 4. The fingerprint comparison with the best match (maximum r^2 value) provides an estimate of the dioxin-furan mixture at that location. The following examples from Table 4 illustrate the assessment process.

1. The sample from upriver Station R101 produced a match of 0.999 (99+ percent) with the upriver fingerprint. However, this sample only produced a match of 0.924 (92 percent) with the 70 percent upriver - 30 percent pulp mill mixture, a match of 0.437 (44 percent) with the 30 percent upriver - 70 percent pulp mill mixture, and a 0.061 (6 percent) match with the pulp mill fingerprint. Since the maximum fingerprint match for this sample occurred with the 100 percent - 0 percent pulp mill mixture, this location was considered to be 100 percent upriver dioxin-furan.

2. The sample from downriver Station R118 produced a match of 0.904 (90 percent) with the upriver fingerprint and also produced a match of 0.905 (90 percent) with the 90 percent upriver sediment - 10 percent tributary sediment mixture. This sample produced a match of 0.859 (86 percent) with the 70 percent upriver - 30 percent pulp mill mixture, 0.511 (51 percent) with the 30 percent upriver - 70 percent pulp mill mixture, and only 0.198 (20 percent) with the pulp mill fingerprint. Since the maximum fingerprint match for this sample occurred for both the 100 percent upriver sediment - 0 percent tributary sediment mixture and the 90 percent upriver sediment - 10 percent tributary sediment mixture, this location was considered to be 95 percent upriver dioxin-furan and 5 percent pulp mill dioxin-furan.

3. The sample from downriver Station R125 produced a match of 0.718 (72 percent) with the upriver fingerprint. The fingerprint match increased to 0.846 (85 percent) with the 80 percent upriver sediment -

20 percent pulp mill mixture and reached a maximum value of 0.966 (97 percent) with the 50 percent upriver - 50 percent pulp mill mixture. The fingerprint match decreased to 0.846 (85 percent) with the 20 percent upriver - 80 percent pulp mill mixture and 0.662 (66 percent) with the pulp mill fingerprint. This location was considered to have 50 percent upriver dioxin-furan and 50 percent pulp mill dioxin-furan.

4. The sample from downriver station R140 produced a match of only 0.052 (5 percent) with the upriver fingerprint. The fingerprint match increased to 0.231 (23 percent) with the 70 percent upriver - 30 percent pulp mill mixture, 0.696 (70 percent) with the 30 percent upriver - 70 percent pulp mill mixture, and reached a maximum of 0.944 (94 percent) with the pulp mill fingerprint. Since the maximum fingerprint match occurred with the pulp mill source fingerprint, this location was considered to be 100 percent pulp mill dioxin-furan.

The fingerprint analysis results for the lower Roanoke sediment samples are presented in Table 4.

Each of the samples produced a maximum fingerprint match (highlighted and bolded) of 0.832 (83 percent), or higher, with one of the calculated fingerprint patterns. An inspection of Table 4 shows that 90 to 100 percent of the dioxin-furan contamination upriver from the mill could be attributed to upriver sources. However, the influence of the mill is evident downriver from the facility. Samples from downriver stations R120, R127, R128, R143, and R144 have a fingerprint indicating 70 percent upriver dioxin-furan and 30 percent pulp mill dioxin furan. Samples from R133 and R145 have a fingerprint consistent with a 30 percent upriver - 70 percent pulp mill mixture, and samples from R121 and R140 produced a maximum match with the pulp mill source fingerprint (0 percent upriver and 100 percent pulp mill). The spatial variability of the pulp mill dioxin in the downriver samples was attributed to site-specific hydrologic factors such as storm events, channel scouring, tidal effects and eddying. Overall, fingerprinting results from more than 40 downriver locations (only a portion of which are presented in Table 4) indicate that approximately 35 to 40 percent of the dioxin-furan contamination downriver from the tributary confluence could be attributed to the pulp mill. This example demonstrates that the FALCON fingerprinting technique is able to (1) develop a characteristic, reproducible fingerprint for the dioxin-furan source (pulp mill), (2) differentiate pulp mill dioxin-furan from background and/or upriver sources of the same contaminants, (3) quantitatively estimate the mixing that has occurred between pulp mill dioxin-furan and upriver sources, and (4) track the migration of the pulp mill dioxin-furan several miles from the source.

Table 3. Calculated Dioxin-Furan Congener Distributions for Mixtures of Roanoke Sediments and Pulp Mill Effluent

Congener #	100% Upriver 0% pulp mill	90% Upriver 10% pulp mill	80% Upriver 20% pulp mill	70% Upriver 30% pulp mill	60% Upriver 40% pulp mill	50% Upriver 50% pulp mill	40% Upriver 60% pulp mill	30% Upriver 70% pulp mill	20% Upriver 80% pulp mill	10% Upriver 90% pulp mill	0% Upriver 100% pulp mill
1	0.003	0.011	0.019	0.028	0.036	0.044	0.052	0.060	0.068	0.076	0.085
2	0.005	0.005	0.004	0.004	0.004	0.003	0.003	0.003	0.002	0.002	0.002
3	0.006	0.006	0.005	0.005	0.005	0.004	0.004	0.003	0.003	0.003	0.002
4	0.018	0.017	0.016	0.016	0.015	0.015	0.014	0.014	0.013	0.012	0.012
5	0.022	0.021	0.019	0.018	0.017	0.016	0.014	0.013	0.012	0.011	0.009
6	0.813	0.751	0.690	0.628	0.566	0.504	0.443	0.381	0.319	0.258	0.196
7	0.017	0.069	0.122	0.175	0.228	0.281	0.334	0.387	0.440	0.493	0.546
8	0.007	0.006	0.006	0.006	0.005	0.005	0.005	0.004	0.004	0.004	0.003
9	0.007	0.007	0.007	0.007	0.006	0.006	0.006	0.006	0.006	0.005	0.005
10	0.008	0.007	0.007	0.007	0.006	0.006	0.006	0.005	0.005	0.004	0.004
11	0.008	0.007	0.007	0.006	0.005	0.005	0.004	0.003	0.003	0.002	0.002
12	0.009	0.008	0.007	0.006	0.006	0.005	0.004	0.004	0.003	0.002	0.001
13	0.008	0.007	0.006	0.006	0.005	0.004	0.004	0.003	0.003	0.002	0.001
14	0.048	0.047	0.046	0.044	0.043	0.042	0.040	0.039	0.037	0.036	0.035
15	0.008	0.007	0.006	0.006	0.005	0.005	0.004	0.003	0.003	0.002	0.001
16	0.034	0.040	0.046	0.053	0.059	0.065	0.071	0.077	0.084	0.090	0.096

Values represent the estimated abundance of each dioxin-furan congener as a decimal percentage of the fingerprint mass in the sediment-pulp mill mixture.

Table 4. Regression Analysis Comparison of Roanoke Sediment Samples with Calculated Dioxin-Furan Fingerprints Patterns

River Location	Station	Upriver Fingerprint	Calculated composition of upriver sediment - pulp mill mixtures									Pulp Mill Fingerprint
		100 URS to 0 TS	90 URS to 10 TS	80 URS to 20 TS	70 URS to 30 TS	60 URS to 40 TS	50 URS to 50 TS	40 URS to 60 TS	30 URS to 70 TS	20 URS to 80 TS	10 URS to 90 TS	0 URS to 100 TS
Upriver	R101	**0.999**	0.991	0.968	0.924	0.850	0.741	0.599	0.437	0.279	0.149	0.061
	R103	0.888	**0.892**	0.883	0.856	0.807	0.733	0.637	0.527	0.414	0.307	0.215
	R106	**0.859**	0.854	0.835	0.798	0.740	0.659	0.560	0.451	0.341	0.242	0.160
	R107	**0.863**	**0.857**	0.838	0.800	0.770	0.658	0.558	0.447	0.338	0.239	0.157
	R109	**0.904**	**0.897**	0.875	0.833	0.769	0.682	0.576	0.460	0.346	0.243	0.158
	R110	**0.900**	**0.894**	0.874	0.834	0.772	0.686	0.582	0.467	0.352	0.249	0.164
	R115	**0.998**	**0.994**	0.975	0.935	0.866	0.761	0.622	0.460	0.300	0.167	0.073
	Pulp Mill											
Downriver	R116	**0.911**	0.909	0.892	0.857	0.798	0.715	0.612	0.497	0.381	0.274	0.185
	R117	0.867	**0.883**	0.844	0.807	0.749	0.668	0.568	0.457	0.347	0.247	0.164
	R118	**0.904**	**0.905**	0.891	0.859	0.804	0.724	0.624	0.511	0.395	0.288	0.198
	R119	0.916	**0.927**	**0.924**	0.903	0.859	0.789	0.695	0.584	0.467	0.355	0.256
	R120	0.851	0.891	0.924	**0.942**	**0.940**	0.911	0.853	0.769	0.666	0.556	0.450
	R121	0.155	0.216	0.294	0.389	0.497	0.641	0.729	0.829	0.905	0.952	**0.972**
	R122	0.500	0.572	0.655	0.748	0.842	0.926	**0.982**	**0.993**	0.950	0.863	0.749
	R125	0.718	0.783	0.846	0.904	0.946	**0.966**	0.957	0.915	0.846	0.758	0.662
	R126	0.755	0.807	0.856	0.895	**0.917**	**0.914**	0.883	0.823	0.740	0.644	0.545
	R127	0.832	0.874	0.908	**0.929**	**0.931**	0.905	0.851	0.770	0.671	0.564	0.459
	R128	0.890	0.927	0.956	**0.969**	0.960	0.924	0.858	0.766	0.657	0.542	0.433
	R131	0.798	0.844	0.883	0.910	**0.919**	0.901	0.856	0.783	0.689	0.586	0.484
	R132	**0.839**	**0.837**	0.821	0.788	0.734	0.658	0.563	0.456	0.349	0.252	0.170
	R133	0.511	0.589	0.674	0.762	0.845	0.915	0.961	**0.977**	0.960	0.915	0.851
	R134	0.943	0.967	**0.979**	0.974	0.945	0.888	0.803	0.695	0.576	0.457	0.348
	R135	0.819	**0.832**	**0.834**	0.820	0.785	0.726	0.645	0.548	0.443	0.341	0.251
	R138	0.745	0.808	0.869	0.923	0.960	**0.974**	0.958	0.910	0.935	0.742	0.642
	R139	0.842	**0.851**	**0.849**	0.830	0.789	0.725	0.638	0.536	0.428	0.325	0.235
	R140	0.052	0.093	0.152	0.231	0.331	0.448	0.574	0.696	0.803	0.887	**0.944**
	R141	0.799	0.845	0.884	0.912	**0.920**	0.904	0.858	0.785	0.692	0.589	0.487
	R142	0.730	0.789	0.845	0.894	0.926	**0.936**	0.916	0.866	0.791	0.700	0.602
	R143	0.738	0.776	0.809	**0.829**	**0.832**	0.811	0.765	0.694	0.607	0.512	0.418
	R144	0.824	0.857	0.882	**0.909**	0.882	0.847	0.785	0.698	0.597	0.491	0.390
	R145	0.524	0.598	0.677	0.758	0.833	0.894	0.930	**0.937**	0.912	0.862	0.795
	R146	0.655	0.714	0.773	0.826	**0.965**	0.884	0.876	0.838	0.776	0.695	0.608

Tabulated results are regression analysis comparisons between actual sediment composition and calculated sediment-tributary mixtures.

URS = upriver sediments TS = tributary sediments **0.9305 = maximum fingerprint matches**

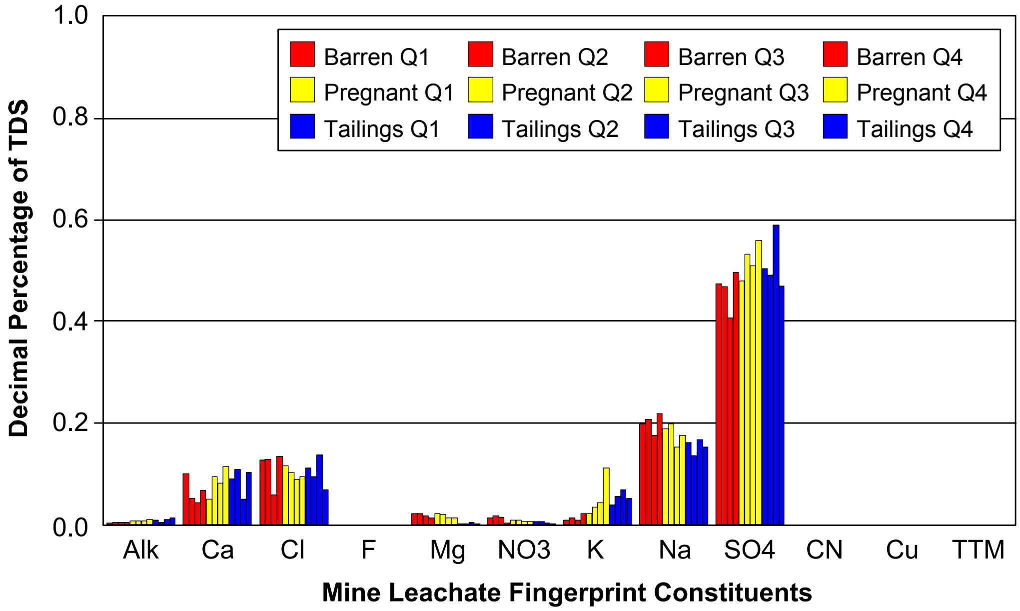
3.2 Inorganic Source Characterization and Leachate Migration Mapping - Gold Mine Case Study

An industry that displayed significant growth in the last quarter of the twentieth century was gold mining utilizing cyanide leaching technology. This process[1] uses a recirculating cyanide solution to extract gold, and other metals, from the ore being processed. An alkaline cyanide solution is prepared in an area referred to as a barren pond. This solution is sprayed on a crushed ore pile to extract gold by complexation as it percolates through the ore. The gold-rich leachate from this process is collected in a second pond referred to as the pregnant pond. Gold and other metals are recovered from the leachate and the cyanide solution is pumped back to the barren pond to repeat the process.

The State of Nevada currently requires heap leaching facilities to conduct quarterly monitoring for 12 geochemical parameters, 28 trace metals, and cyanide at several specified locations (barren pond, pregnant pond, tailings pond, and ground water monitoring wells).[1] Monitoring data from 35 heap leaching facilities were reviewed to develop a better understanding of the composition of mine leachates and to identify a shortened list of potential detection monitoring parameters for this industry.[1] This study demonstrated that nine geochemical parameters were always the most abundant constituents in mine leachates and their relative abundance (expressed as a percentage of total dissolved solids) was a constant at each mine despite the highly variable concentrations. These parameters were alkalinity, calcium, chloride, fluoride, magnesium, nitrate, potassium, sodium, and sulfate.

Data for the nine geochemical parameters specified above from the barren pond, the pregnant pond, and tailings reclaim water at a Nevada heap leaching facility were carried through the fingerprinting process described in *Section 2.0* and plotted as shown in Figure 4. Despite the variability displayed by the individual parameters (e.g., sulfate ranged from 969 to 1720 mg/L, and sodium ranged from 464 to 985 mg/L), the selected parameters define a distinctive chemical signature in which sulfate represents approximately 50 percent of the total dissolved solids concentration, sodium represents approximately 18 percent of the total dissolved solids concentration, chloride represents approximately 10 percent of the total dissolved solids concentration, and the remaining constituents are trace constituents of this pattern. Although cyanide (CN), copper (Cu), and total trace metals (the sum of all trace metal concentrations, TTM) are not significant components of the mine leachate fingerprint, they have been included in Figure 4 for comparison. A separate attempt at using trace metals for fingerprinting mine leachates did not define a distinctive fingerprint.[1]

The reproducibility of the mine leachate fingerprint at this facility is demonstrated in two ways. First, based on quarterly samples, the leachate fingerprint had a reproducibility over time of 0.980 (98 percent) at the barren pond, 0.986 (99 percent) at the pregnant pond, and 0.985 (99 percent) at the tailings reclaim pond. Second, the barren pond, the pregnant pond and the tailings reclaim area are all part of a recirculating system at the mine and a similar fingerprint pattern might be expected at each of these locations. As demonstrated by the regression analysis comparisons tabulated in Figure 4, the monitoring data from these different locations defined a consistent source fingerprint with an average reproducibility of 0.984 (98 percent). Therefore, data over time at a single location (quarterly monitoring data) and data from different locations within the leaching circuit define a reproducible geochemical fingerprint at this facility.



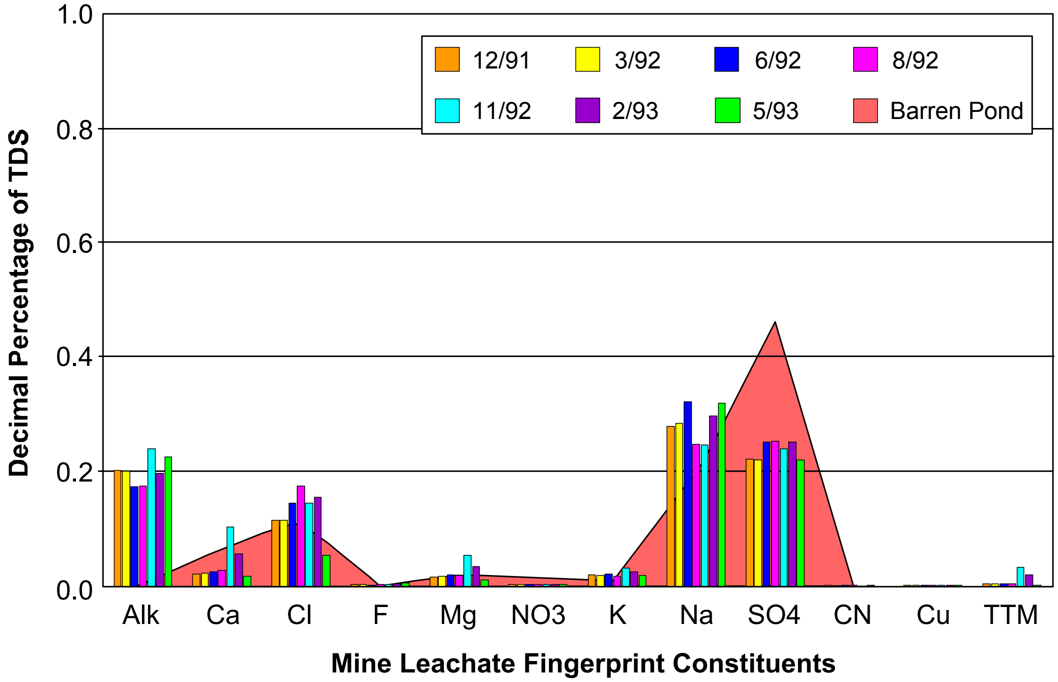
Regression Analysis of Gold Mine Tailings Leachate Fingerprint

	Barren Pond	Pregnant Pond	Tailings Reclaim
Background Ground Water	0.435	0.460	0.406
Barren Pond		0.983	0.972
Pregnant Solution			0.997
Tailings Reclaim			

Estimated reproducibility of mine leachate fingerprint = 0.984.
Comparison between mine leachate and ground water = 0.433.

Figure 4. Geochemical fingerprint at a gold mine using cyanide heap leaching.

A further evaluation of mine site monitoring records demonstrated that the same set of geochemical parameters used to fingerprint leachate at gold mines can also be used to fingerprint ground water in the vicinity of the mine.[1] The ground-water fingerprint developed from two years of quarterly monitoring at an upgradient location is contrasted with the heap leaching fingerprint in Figure 5. The quarterly upgradient ground water data are presented as a series of histograms and the mine leachate fingerprint is presented as an area plot. The first observation is that the ground water data define a single fingerprint pattern characterized by 25 to 30 percent sodium, 20 percent sulfate, 20 percent alkalinity (Alk in the figures), and 10 to 15 percent chloride. The estimated reproducibility of this chemical signature for ground water upgradient of the mine site is 0.941 (94 percent). The second observation is that the ground-water fingerprint developed with the FALCON procedure is visually distinct from the mine leachate fingerprint. Specifically, the mine leachate is enriched in sulfate and depleted in alkalinity when compared to the regional ground water. Despite the fact that the fingerprint constituents are naturally occurring substances and their concentrations are highly variable, the mine leachate and the regional ground water each have a distinctive, reproducible fingerprint that can be differentiated from each other visually and with regression analysis. In this example, there was only a 43 percent comparability between the two fingerprint patterns.



Regression Analysis Matrix for Gold Mine Upgradient Ground Water

	8/91	3/92	6/92	9/92	11/92	2/93	5/93
Barren Pond	0.493	0.489	0.566	0.609	0.475	0.558	0.414
8/91		0.999	0.978	0.948	0.924	0.980	0.963
3/92			0.982	0.944	0.919	0.980	0.966
6/92				0.960	0.882	0.984	0.922
9/92					0.908	0.975	0.835
11/92						0.948	0.857
2/93							0.908
5/93							

Average upgradient fingerprint comparison = 0.941.
Mine fingerprint comparison with upgradient ground water = 0.515.

Figure 5. Comparison of a ground-water fingerprint with the mine leachate fingerprint.

Once a source fingerprint pattern has been established for the mine, it can be used to monitor leachate migration into the environment. This is accomplished by comparing the geochemical pattern at each downgradient monitoring location with either the source fingerprint or the upgradient ground-water fingerprint. If the location was not impacted by fugitive mine leachate, it would be expected to have a geochemical fingerprint that more closely resembled the upgradient fingerprint rather than the mine leachate fingerprint. However, if fugitive leachate was impacting a location, the fingerprint would more closely resemble the mine leachate fingerprint rather than the upgradient fingerprint. Fingerprint analyses for several monitoring wells in the vicinity of a heap leaching facility are summarized in Table 5. An inspection of the results indicates that the wells fall into one of three categories. One category consists of upgradient wells that have a geochemical fingerprint that matches the upgradient fingerprint (80 to 99+ percent) but is different from the mine leachate fingerprint (36 to 63 percent). A second category consists of downgradient wells with a geochemical fingerprint similar to upgradient ground water (84 to 88 percent) and different from the mine leachate fingerprint (48 to 60 percent). The third category consists of wells with a geochemical fingerprint that has a poor match with the upgradient ground-water fingerprint (44 to 75 percent) and a stronger similarity to the mine leachate fingerprint (80 to 93 percent).

The compositional shift from alkalinity-rich and sulfate-poor to sulfate-rich and alkalinity-poor that has occurred in the category three wells is consistent with mine leachate migrating into that area. Once the impacted wells have been identified through the fingerprinting process, the results can be plotted and contoured to delineate specific areas impacted by fugitive mine leachate. This example demonstrates that the FALCON process develops reproducible fingerprints for mine leachate that can be visually and statistically differentiated from background ground-water conditions in the vicinity of the mine. Also, it demonstrates that the mine leachate fingerprint retains its distinctive chemical identity as it migrates through the ground water and can be used as an internal tracer to detect and map its presence some distance from the designated tailings disposal area.

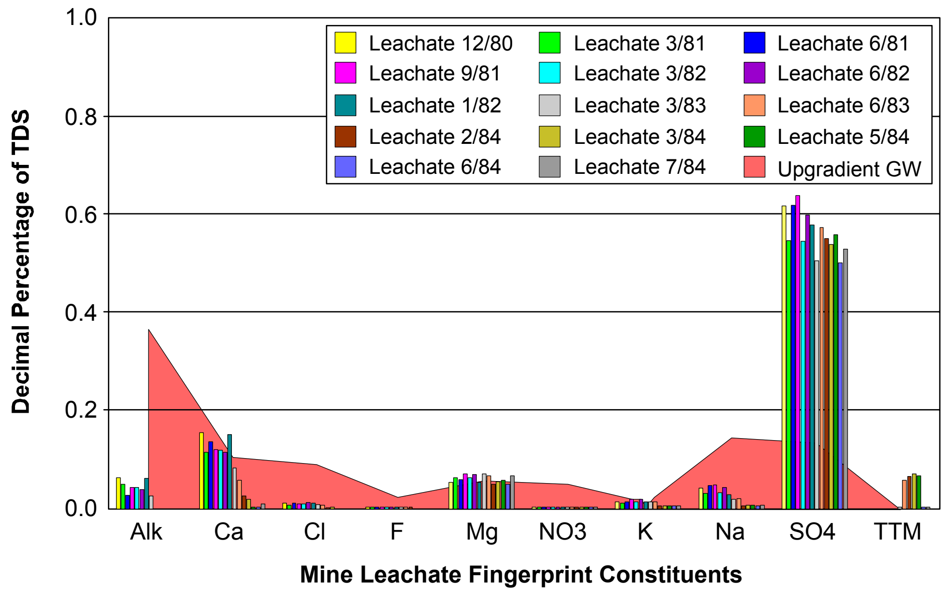
Table 5. Comparison of Ground-water Fingerprints with a Mine Leachate Fingerprint

Classification	Sampling Location	Site Location	Fingerprint Comparison	
			Mine Source	Background GW
Category 1	Well 2	Upgradient	0.433	1.000
	Well 4	Upgradient	0.627	0.937
	Well 22	Upgradient	0.357	0.800
	Mine Site		1.000	0.429
Category 2	Well 37	Downgradient	0.480	0.885
	Well 42	Downgradient	0.492	0.844
	Well 38	Downgradient	0.602	0.880
	Well 45	Downgradient	0.531	0.882
Category 3	Well 1	Downgradient	0.835	0.463
	Well 9	Downgradient	0.898	0.492
	Well 12	Downgradient	0.844	0.747
	Well 15	Downgradient	0.874	0.621
	Well 39	Downgradient	0.866	0.584
	Well 44	Downgradient	0.932	0.441
	Well 40	Downgradient	0.801	0.592
	Well 61	Downgradient	0.885	0.610
	Well 66	Downgradient	0.897	0.381

Tabulated values are regression analysis comparisons between ground water and the indicated fingerprint pattern.

3.3 Early Detection of Leachate Migration - Copper Mine Case Study

A review of monitoring results from several copper mines demonstrated that the same set of geochemical parameters used at gold heap leaching facilities would also be useful for fingerprinting leachates at copper mines.[1] As indicated in Figure 6, tailings pond data over a period of 14 years produced a series of histograms that defined a single chemical fingerprint characterized by 55 to 60 percent sulfate, 15 percent calcium, 10 percent magnesium, 10 percent total trace metals (TTM), and 5 percent alkalinity. Despite variability in the ore being processed and the long period of record, the tailings pond at this facility had a single characteristic fingerprint with an estimated reproducibility of 0.970 (97 percent). In addition, this pattern was distinctively different from the alkalinity-rich, sulfate-poor background ground-water fingerprint in the vicinity of the mine (fingerprint comparison = 0.016 (2 percent)).[1] Fingerprint comparisons were used to identify several downgradient wells that had been impacted by mine leachate as demonstrated in the previous example. The monitoring results from one impacted well at this copper mine provided a set of data that illustrates another possible application of the FALCON procedure. Relative abundance (actual concentration divided by TDS) for the geochemical fingerprint parameters at well 1225 at this site are plotted as a function of time in Figure 7. Between 1970 and 1976, the dominant geochemical parameter in the ground water at this location was alkalinity while sulfate was almost negligible. This alkalinity-rich, sulfate-poor pattern, that is typical of most unimpacted freshwater systems, had a 99 percent match with the ground water upgradient of the mining facility and less than a 5 percent match with the tailings pond leachate at the copper mine. However, the ground water composition at this location began to change around 1976. There was a gradual reduction in the relative abundance of alkalinity and a concurrent increase in the relative abundance of sulfate. This compositional shift, that is consistent with a sulfate-rich, alkalinity poor leachate entering the area, continued through 1984 when the Well 1225 fingerprint produced a 95 percent match with the tailings pond leachate. Even though sulfate and alkalinity are naturally occurring substances, fingerprint analysis clearly identifies mine leachate as the causative factor for the ground-water changes observed at this location. Thus, the fact that the geochemical fingerprint retains its distinctive identity as it migrates through the ground water could have been used to provide an early warning of mine leachate migration.



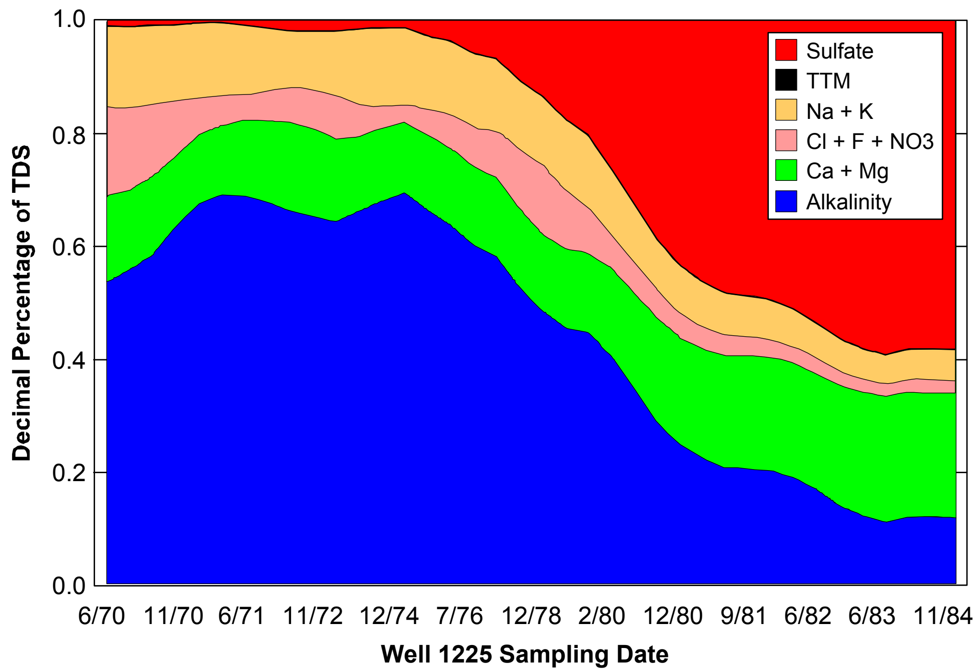
Regression Analysis Matrix for Copper Mine Tailings Pond Fingerprint

Tailings Pond Sampling Date

	12/80	3/81	6/81	9/81	3/82	6/82	12/82	3/83	6/83	2/84	3/84	5/84	6/84	7/84
12/80		0.997	0.995	0.994	0.997	0.994	0.999	0.985	0.952	0.929	0.919	0.911	0.936	0.937
3/81			0.996	0.998	1.000	0.998	0.996	0.995	0.967	0.947	0.939	0.933	0.957	0.959
6/81				0.998	0.998	0.998	0.984	0.992	0.968	0.946	0.936	0.929	0.953	0.954
9/81					0.999	1.000	0.992	0.996	0.973	0.954	0.946	0.941	0.965	0.967
3/82						0.999	0.996	0.995	0.967	0.947	0.938	0.932	0.956	0.958
6/82							0.992	0.997	0.974	0.954	0.946	0.941	0.965	0.968
12/82								0.984	0.949	0.926	0.916	0.908	0.933	0.935
3/83									0.981	0.964	0.958	0.954	0.976	0.980
6/83										0.996	0.994	0.991	0.986	0.986
2/84											0.999	0.998	0.986	0.984
3/8												0.999	0.983	0.982
5/84													0.986	0.985
6/84														0.999
7/84														

Average mine leachate fingerprint reproducibility = 0.970.

Figure 6. Comparison of a copper mine tailings pond fingerprint with the background ground-water fingerprint.



Ground-Water Conditions at Copper Mine Well 1225

Sampling Location	pH Standard Units	Total Metals (mg/L)	Fingerprint Match Decimal Percent
Tailings Pond Leachate	2.0	1963	1.000
Well 1225 10/70	nd*	0.291	0.033
Well 1225 3/71	nd*	0.372	0.027
Well 1225 11/72	nd*	0.467	0.031
Well 1225 6/73	nd*	0.410	0.037
Well 1225 12/74	nd*	0.296	0.017
Well 1225 10/75	nd*	0.341	0.043
Well 1225 7/76	nd*	0.357	0.038
Well 1225 5/78	nd*	0.697	0.018
Well 1225 12/78	nd*	0.383	0.075
Well 1225 11/79	nd*	0.354	0.026
Well 1225 2/80	nd*	0.350	0.375
Well 1225 5/80	nd*	0.342	0.576
Well 1225 8/80	nd*	0.322	0.755
Well 1225 12/80	nd*	0.354	0.717
Well 1225 3/81	nd*	0.295	0.898
Well 1225 6/81	nd*	0.302	0.805
Well 1225 9/81	7.4	0.110	0.731
Well 1225 3/82	7.0	0.030	0.890
Well 1225 6/82	6.7	0.150	0.890
Well 1225 12/82	7.2	1.190	0.946
Well 1225 6/83	7.4	1.110	0.867
Well 1225 12/83	7.4	0.000	0.950
Well 1225 5/84	7.7	0.470	0.920
Well 1225 11/84	7.1	1.570	0.945
Well 1225 5/85	6.9	1.550	0.949

* nd = no data

Figure 7. Geochemical fingerprint analysis of ground water downgradient of a copper mine tailings basin.

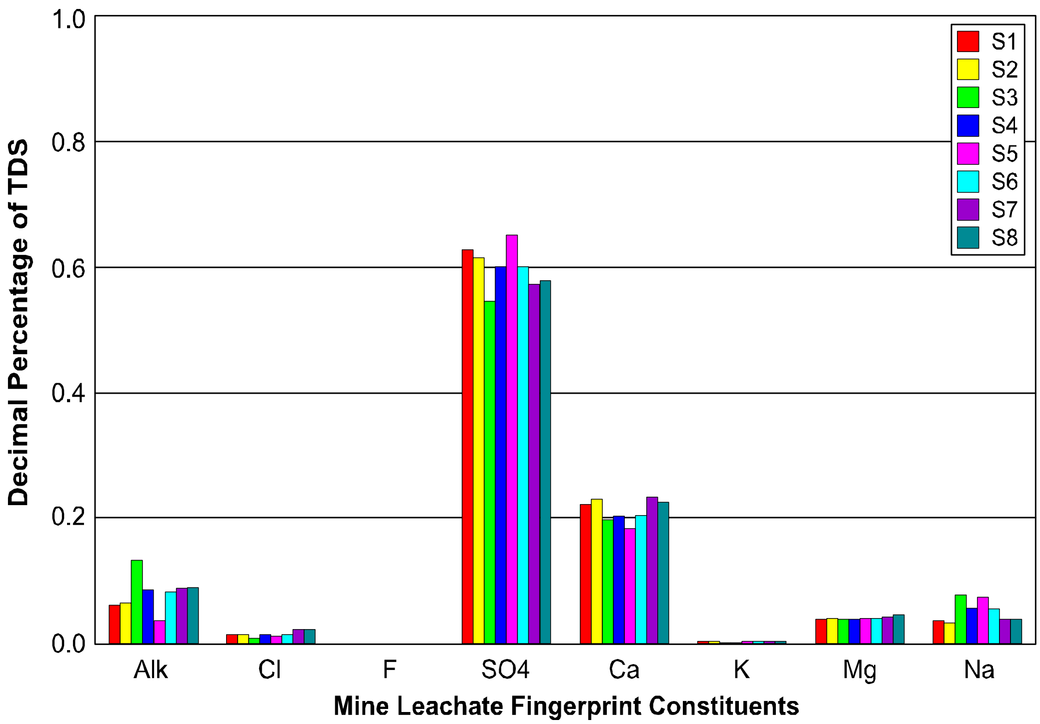
A review of additional monitoring data from this location (Figure 7) provides further insight into the capabilities of FALCON as a mechanism to provide early warning or early detection of leachate migration. The tailings pond at this facility has a total trace metals concentration (sum of 17 trace metals being routinely monitored) of 1963 mg/L and a pH of 2.0. Between 1970 and 1975, while the geochemical fingerprint was essentially identical to upgradient (background) conditions, the total trace metals concentration at this well was in the range of 0.291 to 0.467 mg/L. While the tailings pond fingerprint was being established at Well 1225 between 1976 and 1982, the total trace metals concentration remained in the range of 0.030 to 0.697 mg/L. After the tailing leachate fingerprint was fully established, the total trace metals concentration had only increased slightly to 0.470 to 1.570 mg/L. Also, the pH at this location was still in the range of 6.7 to 7.7 between 1981 and 1985. (The pH data from this set between 1970 and 1981 was missing. However, the pH at upgradient locations and other impacted downgradient locations was in the range of 6.7 to 7.7 between 1970 and 1985.) These field results, and an additional laboratory study[1], demonstrate that the geochemical fingerprint migrates faster through the ground water than other inorganic parameters of environmental concern that may be in mine leachate. Thus, in addition to providing a reliable characterization of mine leachates at their source and acting as an internal tracer, a geochemical fingerprint acts as a good indicator parameter because it migrates faster than mine leachate constituents of higher regulatory concern (pH and trace metals). Fingerprint analysis can provide an early warning so that remedial action can be initiated while a contaminant migration problem is smaller and more manageable.

This example demonstrates that the inorganic fingerprints can be used to characterize mine leachates at their source and to differentiate the leachate from background conditions. In addition, since the fingerprint retains its identity and migrates faster than other contaminants of higher regulatory concern, the fingerprint can function as an effective detection monitoring parameter.

3.4 Ground Water and Surface Water Mixing - Molybdenum Mine Case Study

This facility is located adjacent to the Red River in New Mexico and monitoring was conducted at the mine site, several ground water and seep locations, and the nearby river. The same set of geochemical parameters used in the gold mine and copper mine case studies were also useful at this site. Although the concentrations of the individual fingerprint parameters varied by a factor of 10 across the site, the monitoring results defined a single mine leachate pattern characterized by 60 percent sulfate, 20 percent calcium, 10 percent alkalinity, and small amounts of the remaining geochemical parameters (Figure 8). The regression analysis comparison of eight source samples produced r^2 values ranging from 0.9618 to 0.9999. The estimated reproducibility of this source fingerprint was 0.9894 (99 percent).

Monitoring was conducted at several ground water and surface seep locations between the mine operations and the river. Regression analysis of the geochemical pattern at these locations produced fingerprint comparisons of 94 to 99 percent with the source fingerprint. In addition, surface water data from several gulches that drain from the mine site towards the Red River also produced geochemical fingerprints with a strong similarity to the mine leachate (> 90 percent). Fingerprint analysis indicated that fugitive mine leachate was migrating through the ground water and may be entering the nearby river.



Regression Analysis of Molybdenum Mine Fingerprint

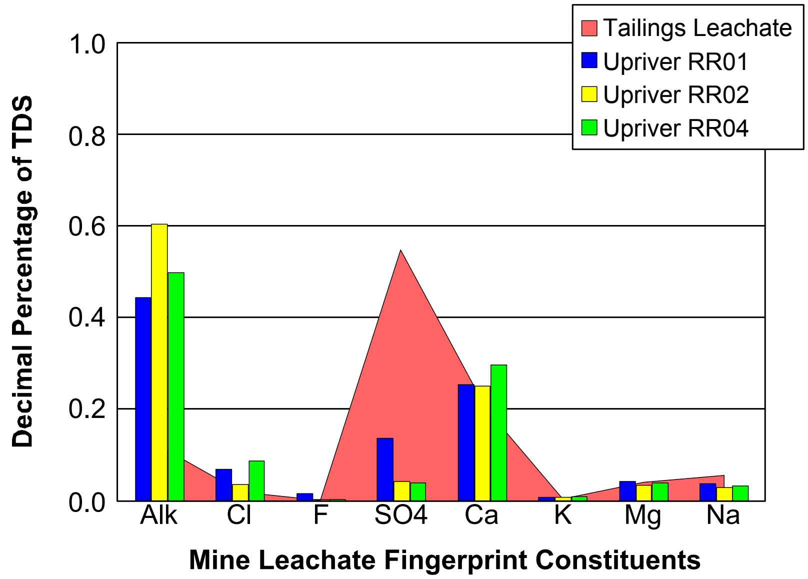
Molybdenum Mine Sampling Locations

	S1	S2	S3	S4	S5	S6	S7	S8
S1		1.000	0.997	0.977	0.996	0.984	0.998	0.997
S2			0.994	0.973	0.994	0.981	0.998	0.995
S3				0.990	1.000	0.987	0.996	0.997
S4					0.989	0.962	0.984	0.989
S5						0.988	0.995	0.996
S6							0.975	0.974
S7								1.000
S8								

Average fingerprint reproducibility = 0.989.

Figure 8. Geochemical fingerprint of molybdenum mine leachate.

The monitoring program at this mine site included 16 sampling stations in the nearby river. Data from three locations upriver from the mine site defined a geochemical fingerprint pattern that is contrasted with the mine leachate fingerprint in Figure 9. The river pattern, presented as a series of histograms, is characterized by 45 to 60 percent alkalinity, approximately 25 percent calcium, approximately 10 percent chloride, and 5 to 15 percent sulfate. This alkalinity-rich, sulfate-poor pattern upriver of the mine is typical of most fresh water systems and can be clearly differentiated from the sulfate-rich, alkalinity-poor mine fingerprint of the mine leachate that is presented as an area plot in Figure 9. The estimated reproducibility of the Red River fingerprint at these three upriver stations was 0.9804 (98 percent) and the comparability with the molybdenum mine fingerprint was only 0.0189 (2 percent). As in previous examples, the two inorganic fingerprint patterns can be readily distinguished from each other both visually and with regression analysis.



Fingerprint Analysis in Red River Near Molybdenum Mine

Station	Location	Background Fingerprint Match	Leachate Fingerprint Match	Percent Leachate in River
RR04	Upriver from mine	0.987	0.011	0
RR02	Upriver from mine	0.988	0.011	0
RR01	Upriver from mine	0.976	0.012	10
RR03	Adjacent to mine	0.906	0.063	20
RR05	Adjacent to mine	0.875	0.082	20
RR06	Adjacent to mine	0.767	0.192	30
RR09	Adjacent to mine	0.912	0.064	20
RR11	Adjacent to mine	0.969	0.015	10
RR08	Adjacent to mine	0.832	0.133	25
RR07	Adjacent to mine	0.856	0.111	20
RR10	Adjacent to mine	0.824	0.140	25
RR12	Adjacent to mine	0.458	0.496	40
RR13	Adjacent to mine	0.698	0.262	30
RR14	Downriver from mine	0.465	0.484	40
RR15	Downriver from mine	0.488	0.467	40
RR16	Downriver from mine	0.469	0.477	40

Figure 9. Comparison of mine leachate fingerprint with the background Red River fingerprint.

An evaluation of the data from the remaining river sampling locations adjacent to and downriver from the mine site demonstrated that the geochemical composition of the river was being altered. At stations adjacent to the mine site (RR03 to RR13), the comparability of the fingerprint with the upriver fingerprint ranged from 46 to 97 percent. At the three stations downriver from the mine site (RR14 to RR16), the comparability with the upriver fingerprint was reduced to 47 to 49 percent. These compositional changes were due to a reduced relative abundance of alkalinity and an increased relative abundance of sulfate as the river flowed past the mining operation. This shift is consistent with a sulfate-rich, alkalinity-poor leachate characteristic of the mining operation (Figure 8) entering the river and is reflected by the increased comparability of the river fingerprint with the mine leachate fingerprint. The upriver stations only had a 1 percent match with the mine leachate fingerprint. However, as the river passed the site, the leachate fingerprint match increased to 6 to 50 percent at adjacent sampling locations and 47 to 48 percent at downriver sampling locations.

Fingerprint analysis indicated that mine leachate was migrating through the ground water and reaching the Red River in sufficient quantity to alter the geochemical composition. An additional capability of the FALCON technique is that the surface water to mine leachate dilution ratio can be estimated. As in the sediment dioxin case study (Section 3.1), the two source fingerprints can be used to calculate the expected composition for various mixtures of river water and mine leachate (i.e., 90 percent river + 10 percent mine leachate, 80 percent river water + 20 percent mine leachate, etc.). The actual inorganic composition at each river location can then be compared to each of the calculated mixtures to produce a range of fingerprint match values as shown in Table 6. For example:

1. The sample from station RR4 produced a fingerprint match of 0.987 (99 percent) with the upriver fingerprint. As the calculated amount of mine leachate in the mixture increased above 0 percent, the fingerprint match decreased. Since the best match (maximum r^2) occurred with the upriver fingerprint, this location was considered to be 100 percent upriver water.

2. The sample from station RR12 produced a fingerprint match of 0.458 (46 percent) with the upriver fingerprint. The fingerprint match increased to 0.772 (77 percent) for the 80 percent upriver + 20 percent mine leachate mixture and reached a maximum of 0.992 (99 percent) for the 60 percent upriver + 40 percent mine leachate mixture. As the calculated amount of mine leachate in the mixture increased above 40 percent, the fingerprint match decreased. This location was considered to be 60 percent upriver water and 40 percent mine leachate.

Each of the remaining samples was evaluated in a similar manner and the calculated fingerprint mixture that produced the best fingerprint match is highlighted and bolded in Table 6. It should be noted that the maximum fingerprint match for each river sample was 0.981 (98 percent), or higher.

As shown in Table 6 and summarized in Figure 9, the three upriver stations produced a best fingerprint match for mixtures that contained 0 to 10 percent mine leachate. The stations adjacent to the mine site produced the best fingerprint match for mixtures that contained 10 to 40 percent mine leachate and the three downriver locations produced the best match for a mixture of 40 percent mine leachate and 60 percent river water. The fluctuations at the adjacent river stations listed in Table 6 (e.g., RR 11 has a lower percentage of leachate than RR6) are due to runoff entering the river from unimpacted tributaries. In this example, the FALCON technique was able to develop a characteristic fingerprint for the mine leachate and differentiate mine leachate from background ground water conditions and surface water. In addition, based on the properties of the fingerprint, it was possible to track the migration of mine leachate through the ground water, into a nearby river, and develop a quantitative estimate of the mixing that was occurring between river water and fugitive mine leachate.

Table 6. Comparison of Red River Geochemical Fingerprints with Secondary Mine Leachate Fingerprints

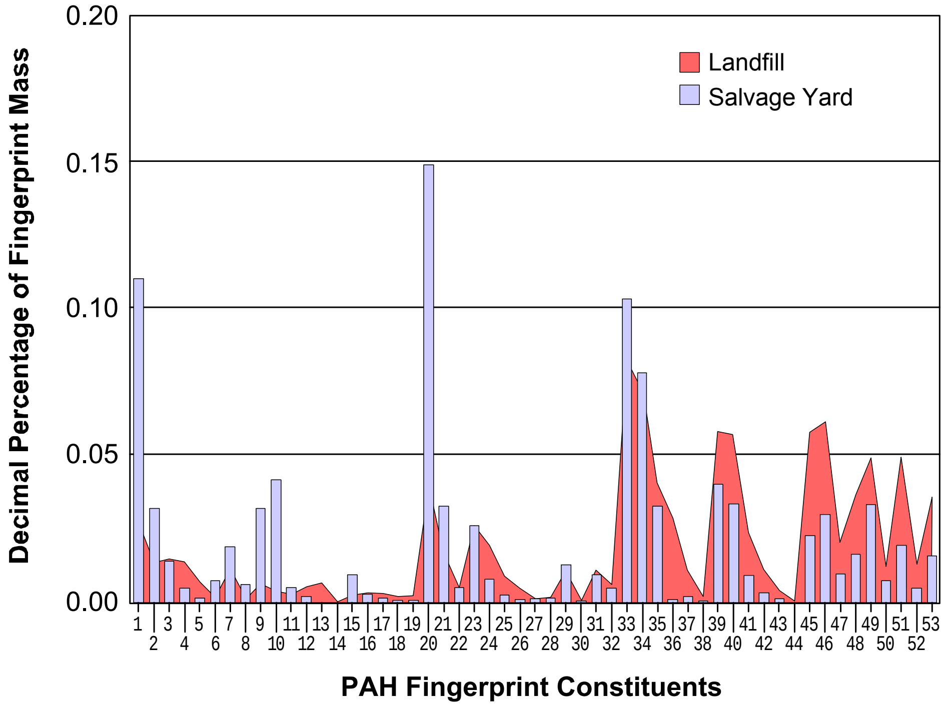
River Location	Station Number	Identified River Fingerprint	Calculated composition of surface water - mine leachate mixtures.									Identified Leachate Fingerprint
		100% UR 0% ML	90% UR 10% ML	80% UR 20% ML	70% UR 30% ML	60% UR 40% ML	50% UR 50% ML	40% UR 60% ML	30% UR 70% ML	20% UR 80% ML	10% UR 90% ML	0% UR 100% ML
Upriver	RR4	**0.987**	0.953	0.847	0.677	0.467	0.268	0.124	0.041	0.001	0.001	0.011
	RR2	**0.988**	0.954	0.848	0.679	0.468	0.269	0.124	0.042	0.006	0.001	0.011
	RR1	0.976	**0.999**	0.968	0.860	0.660	0.475	0.296	0.166	0.084	0.036	0.012
Adjacent	RR3	0.906	0.966	**0.991**	0.937	0.800	0.615	0.432	0.285	0.179	0.109	0.063
	RR5	0.875	0.943	**0.983**	0.945	0.822	0.646	0.466	0.317	0.208	0.132	0.082
	RR6	0.767	0.869	0.967	**0.994**	0.932	0.796	0.631	0.478	0.354	0.261	0.192
	RR9	0.912	0.972	**0.997**	0.943	0.806	0.619	0.435	0.287	0.180	0.109	0.064
	RR11	0.969	**0.995**	0.969	0.866	0.690	0.487	0.307	0.175	0.091	0.041	0.015
	RR8	0.832	0.918	**0.988**	**0.981**	0.887	0.727	0.551	0.397	0.279	0.193	0.133
	RR7	0.856	0.935	**0.993**	0.973	0.865	0.697	0.518	0.365	0.249	0.167	0.111
	RR10	0.824	0.913	**0.986**	**0.984**	0.894	0.737	0.562	0.408	0.288	0.201	0.140
	RR12	0.458	0.592	0.772	0.916	**0.992**	0.979	0.898	0.787	0.676	0.578	0.496
	RR13	0.698	0.813	0.937	**0.996**	0.969	0.859	0.710	0.561	0.435	0.336	0.262
Downriver	RR14	0.465	0.599	0.776	0.917	**0.989**	0.972	0.887	0.775	0.663	0.565	0.484
	RR15	0.488	0.622	0.797	0.933	**0.997**	0.971	0.880	0.762	0.648	0.549	0.467
	RR16	0.469	0.602	0.778	0.916	**0.986**	0.966	0.880	0.767	0.655	0.558	0.477

Tabulated results are regression analysis comparisons between river samples and the calculated surface water-mine leachate mixture.

UR = Upriver

ML = Mine Leachate

0.9830 = maximum leachate matches



PAH Fingerprint Analysis of Tributary Sediments

Station	Landfill Match Decimal Percent	Salvage Yard Match Decimal Percent	Total PAH (ng/kg)
T6	0.874	0.657	3951
T3	0.886	0.433	3075003
T4	0.900	0.429	99022
T5	0.901	0.508	91739
T17	0.930	0.203	4845764
T15	0.982	0.380	4135
S9	0.984	0.359	12256
T9	0.990	0.347	14671
T1	0.254	0.964	210573
T2	0.113	0.843	23743530
T10	0.247	0.781	1842
T14	0.154	0.850	58481394
S7	0.379	0.986	332628
S8	0.529	0.859	354305
S10	0.283	0.986	328377
S11	0.138	0.872	174072

Figure 10. Fingerprint analysis of PAH contaminated sediments.

3.5 Mixing of Similar Contaminant Plumes - PAH Case Study

Two potential sources of polycyclic aromatic hydrocarbon (PAH) are separated by a small tributary that drains into a river. One potential source is a landfill that included waste tar among its contents. The second potential source was a salvage yard that processed crude tar wastes to recover creosote, phenol, and other chemicals. Wastes from this salvage yard were disposed of on-site. Sediment sampling of the tributary that runs between these two operations produced total PAH concentrations ranging from less than 5 mg/kg to greater than 50,000 mg/kg.

The FALCON procedure was applied to a set of soil samples collected adjacent to the tributary. This effort identified two PAH fingerprint patterns as shown in Figure 10. For brevity, the 53 standard PAH compounds are not listed by name but simply referred to by compound number. One pattern was characterized by a relatively dominant peak for PAH compound 33, smaller peaks for PAH compounds 39, 40, 45, 46, and 20, and the low abundance of PAH compounds 1 to 19. The distinguishing characteristics of the second fingerprint pattern were the relatively large peaks for PAH compounds 1 and 20, several peaks for PAH compounds 2 to 10, and a relatively lower abundance of PAH compounds 39 to 53. The comparability of the two identified PAH fingerprints was only 0.329 (33 percent).

The PAH distribution in collected tributary sediment samples was compared to the two identified PAH fingerprints. One set of samples (T6, T3, T4, T5, T17, T15, S9 and T9) produced strong matches (0.874 to 0.990) with the fingerprint relatively enriched in compounds 33 to 53 and a poor match (0.203 to 0.657) with the fingerprint enriched in compounds 1 to 19. The second set of samples (T1, T2, T10, T14, S7, S8, S10, and S11) produced a strong match (0.781 to 0.986) with the fingerprint enriched in PAH compounds 1 to 20 and a poor match (0.113 to 0.529) with the fingerprint enriched in PAH compounds 33 to 53. Based on the fingerprint assessment, tributary sediments closest to the bank had a low total PAH concentration and a PAH fingerprint enriched with compounds 1 to 20. The mid-channel sediments had a very high total PAH concentration (two orders of magnitude greater than the sediments closest to the bank) and a PAH distribution relatively enriched in compounds 33 to 53.

4.0 FALCON Capabilities

FALCON is a flexible data analysis technique of combining data from two or more contaminants to develop a distinctive chemical signature. The resultant FALCON fingerprint, based on the relative abundance rather than actual concentrations of the individual contaminants, provides a mechanism to identify the source and monitor the environmental behavior of fugitive emissions and leachates. These source patterns provide a visual characterization of contaminants in liquid and solid matrices and generally have a reproducibility of 90 to 99 percent.

The FALCON process can assist in the evaluation and interpretation of site characterization and monitoring data in several ways:

1. The process produces a characteristic fingerprint that associates a contaminant with a particular source. The data normalization process permits a direct visual comparison of fingerprint patterns despite highly variable contaminant concentrations and the use of regression analysis provides a statistical estimate of the reproducibility or comparability of two patterns. Distinctive fingerprints can be developed to characterize organic and inorganic contamination due to spills, leaks, and landfill leaching. In addition to the dioxin-furan, mine site, and PAH examples illustrated in this report, the FALCON technique has also been used to characterize halogenated organic solvent spills, gasoline and diesel fuel spills, and landfill leachates.

2. The fingerprints can differentiate a source fingerprint from background conditions. As illustrated in the gold mine (Section 3.2), copper mine (Section 3.3), and the molybdenum mine (Section 3.4) examples, each source had a characteristic fingerprint that could be visually and statistically differentiated from background ground water and upriver surface water conditions in the vicinity of each facility.

3. FALCON fingerprints provide a mechanism to differentiate multiple sources of the same contaminants. As illustrated in the dioxin example (Section 3.1) and the PAH example (Section 3.5), distinctive fingerprints can be developed for each source.

4. FALCON fingerprints retain their chemical identity and act as an internal tracer as they migrate through the environment. Therefore, fingerprint patterns at established monitoring locations can be directly compared with the source fingerprint as demonstrated with the gold mine example (Section 3.2) to verify the source of detected contaminants and to map the areas that have been impacted by a specific potentially responsible party.

5. FALCON fingerprints can also be used as a tool to characterize the environmental behavior of contaminant plumes. Fingerprint analysis provided a quantitative estimate of the Roanoke sediment contamination that can be specifically attributed to a pulp mill even though there are multiple sources of dioxin-furan contamination to the river (Section 3.1). The molybdenum mine case study (Section 3.4) demonstrated that a source fingerprint could be tracked through the ground water and used to estimate the rate of mixing between mine leachate and surface water. Thus, in addition to source characterization, the fingerprints can be used to characterize the migration of contaminants between environmental phases (ground water, surface water, and sediments) and to quantify the extent of mixing or dilution that has occurred between two source fingerprints. This capability provides a mechanism to apportion responsibility for environmental degradation between potentially responsible parties.

6. Fingerprints also have a potential application as detection monitoring parameters to provide early warning of leachate migration. This capability is illustrated with the copper mine case study (Section 3.4) in which the tailings pond fingerprint was initially detected and then fully developed before the more hazardous constituents associated with mine leachate were detected downgradient from the mine site. Fingerprint analysis would have provided an early warning to implement a corrective action or remediation program while the developing problem was smaller and more manageable. The factors that would permit the FALCON process to be used in this capacity are (a) the fingerprint characterizes the source and differentiates it from background conditions, (b) the fingerprint retains its chemical identity as it migrates away from the source, and (c) the fingerprint migrates faster than the contaminants of higher regulatory concern.

7. Each of the case studies mentioned in this report were developed with routine monitoring data. It is not necessary to use special analytical techniques, that may not produce data compatible with historical site records, in order to use the FALCON technique.

The previous discussion focused on the use of contaminant fingerprinting to evaluate site-specific data. The FALCON process can also provide the technical basis for the development of industry-specific monitoring strategies. For example, a review of the gold mine (Section 3.2), copper mine (Section 3.3), and molybdenum mine (Section 3.4) case studies reveals that the same small set of geochemical parameters defined a characteristic, reproducible fingerprint at each mine as well as the ground water and surface water in the vicinity of the mine. This observation has been verified by evaluating data from more than 30 additional mines.[1] These results suggest the possibility of a uniform two-phased monitoring program at mining facilities based on the set of geochemical parameters that characterize mine leachates. The first phase would utilize the fingerprint parameters to characterize and detect the leachate. As long as leachate is not detected, contaminants are not entering the ground water and the facility would remain at this monitoring level. However, once the leachate fingerprint is detected, the second phase would be triggered to more fully characterize the slower migrating contaminants that may be present. The factors that support consideration of this approach are that the fingerprint is a reliable indicator of the leachate, the fingerprint retains its identity as it migrates, and the fingerprint migrates faster than other leachate constituents (as illustrated in the copper mine case study, Section 3.3). This approach could reduce monitoring costs and provide a uniform monitoring strategy that would be easier to implement, evaluate, and enforce.

5.0 Summary

FALCON is an empirical data assessment and visualization tool that produces contaminant fingerprint patterns. This technique combines data from two or more parameters to produce visually distinctive and reproducible fingerprints. The resultant fingerprints can be used to:

1. Characterize contaminants at their source,

2. Compare and evaluate background levels of contaminants with anthropogenic sources,

3. Establish an internal tracer to monitor the migration of a contaminant plume through ground water, surface water, and sedimentary environments, and

4. Differentiate two sources of the same contaminant and estimate the relative mixing that has occurred between two contaminant plumes.

Additional information on the FALCON procedure can be obtained from Gareth Pearson, Director of the Technical Support Center, U.S. EPA National Environmental Research Laboratory, Las Vegas, Nevada (pearson.gareth@epa.gov).

6.0 References

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7.0 Notice

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