# EVIDENCE OF TWO SOURCES OF FALSE POSITIVE RESULTS IN ANALYSIS OF ENVIRONMENTAL SAMPLES FOR DIOXINS

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## Introduction

Concentrations of regulatory concern for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, collectively referred to as dioxins, are 2 to 4 orders of magnitude lower than detection limits achievable using available analytical procedures. This discrepancy between regulatory levels and capability of the analytical methods presents challenges to effective site characterization, as any detection of dioxins in a site sample represents a potentially significant exceedance of a regulatory value. Concentrations near the method detection limit are highly uncertain and subject to numerous sources of error, including sporadic contamination introduced during sample handling and analysis, and analytical interferences from coeluting nontarget analytes that cannot be discriminated using standard high resolution mass spectrometry. These situations both represent false positive results for target dioxin congeners which potentially lead to misallocation of resources better directed to other priorities on a contaminated site. Both situations are well documented in the regulatory and technical literature [1,2,3], and the procedure in United States Environmental Protection Agency (EPA) Method 1613B includes requirements and options that address these concerns [4].

## Materials and methods

This paper presents dioxin data for approximately 500 groundwater samples collected between January 2000 and January 2008, as part of the remedial investigation of a former chemical manufacturing facility, and the laboratory and field blanks associated with those sample results. An evaluation of the data is presented to demonstrate that (1) frequency of detections in the laboratory and field blanks far exceeds the 5% expected based on the EPA definition of detection limits; (2) that the frequency and distribution of low level detections in blanks and field samples is largely indistinguishable at levels below the minimum level (ML) presented in EPA Method 1613B; and (3) that data showing dioxin concentrations below the ML may not be reliable for use in regulatory decision making. In addition, evidence is presented to demonstrate the presence of false positive results for 2,3,7,8-TCDD in groundwater samples related to an unknown compound that coelutes with 2,3,7,8-TCDD on less polar DB-5 column, but does not yield a detectable peak on a more polar SP-2330 column.

## Results and discussion:

### Evidence of Laboratory or Field Introduced Contamination

EPA Method 1613B, which uses high resolution gas chromatography coupled with high resolution mass spectrometric detection (HRGC/HRMS) for determination of dioxins, is often considered the most definitive method for analysis of dioxins in environmental samples in the United States. EPA Method 1613B, however, requires laboratories to control the presence of dioxins in procedure blanks only to a concentration known as the Minimum Level (ML), which is defined in the method as "the level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte." The MLs given for dioxin congeners in EPA Method 1613B range from 10 picograms per liter (pg/L) to 100 pg/L, and these MLs are 4 to 5 orders of magnitude higher than required for comparison of data to risk-based regulatory limits for the corresponding congeners. Lack of requirement to control presence of dioxins in procedural blanks at levels less than or equal to the ML has led to general acceptance of low level detections of dioxins in procedure blanks and field blanks as a commonplace occurrence. Consequently, random and uncontrolled presence of dioxins in either laboratory or field equipment associated with collection and analysis of samples for dioxins can result in false positive results for field samples

without corresponding detections in the associated laboratory or field blanks, potentially leading to incorrect decisions about the nature and extent of dioxins in environmental media at a site.

Table 1 presents the frequency of detection (FOD) of the individual 2,3,7,8-substituted congeners in blank samples and field samples from the data set described above. In this table, method blanks refers to laboratory preparation blanks, rinsate blanks refers to field blanks prepared by passing laboratory purified water through sampling equipment, field samples refers to site-specific groundwater samples, and field samples (validated) refers to field sample results after correction for detection of target congeners in blank samples. As shown in Table 1, the FOD in blank samples and field samples was highly similar in this data set, and correction for apparent blank contribution did not appreciably change the FOD of many congeners in the field samples. These data show that about 50% of blank samples and 50% of field samples had detectable levels of dioxins, and that this FOD persisted after correction for congeners present in blank samples. Figure 1 presents box plots of the 2,3,7,8-TCDD equivalent (TEQ) concentrations of dioxins detected in the method blanks, rinsate blanks and field samples, along with a reference line representing the EPA Method 1613B ML of 10 pg/L for 2,3,7,8-TCDD.

Figure 1 demonstrates the overlap in the distribution of dioxin concentrations in blank samples and field samples, and illustrates the need for caution in interpretation of dioxin results to avoid making decisions based on false positive results.

**Evidence for Presence of Interferences Related to Substances that Coelute with 2,3,7,8-TCDD**

In addition to the sporadic and irreproducible detections of various dioxin congeners in locations inconsistent with the hydrogeochemical model for the site (CSM), there were apparent detections of 2,3,7,8-TCDD that were reproducible, but also occurred in locations inconsistent with the CSM. Given that the entire site lies in an industrial area with multiple historical chemical manufacturing and processing facilities as neighbors, a number of the sample extracts were subjected to reanalysis using a gas chromatographic column with a dissimilar stationary phase to evaluate the possible presence of interferences from substances that coelute with 2,3,7,8-TCDD. Figure 2 shows the original analysis of an extract from one of these samples using the DB5-MS column, and Figure 3 shows the reanalysis of the same extract using a more polar SP-2330 column. As is evident from examination of these figures, the analysis using the DB5-MS column appears to demonstrate the presence of 2,3,7,8-TCDD, but the presence of 2,3,7,8-TCDD is refuted by the lack of a detected peak at the right retention time for 2,3,7,8-TCDD in reanalysis using the SP-2330 column. This second column confirmation procedure has now been incorporated for all dioxin analyses performed at the site, and to date, 2,3,7,8-TCDD has been confirmed in samples where its presence would be expected from the CSM, but has not been confirmed in samples where its presence would be inconsistent with the CSM. To date, no attempt has been made to apply second column confirmation to congeners other than 2,3,7,8-TCDF (required by the method), or 2,3,7,8-TCDD (project specific requirement), so no generalizations can be made as to whether other interferences that effect other congeners may be present, but the potential for such interferences despite use of high resolution mass spectrometric detection is well documented in the literature.

**Table 1: Frequency of Detection of Dioxin Congeners and TEQ in Blank samples and Field Samples**

| | Method Blanks | Field Rinsate Blanks | Field Samples (unvalidated) | Field Samples (validated) |
|---|---|---|---|---|
| OCDD | 23.50% | 40.40% | 47.30% | 29.30% |
| OCDF | 16.60% | 23.80% | 17.80% | 14.30% |
| 1,2,3,4,6,7,8-HpCDD | 16.60% | 21.40% | 15.30% | 12.50% |
| 1,2,3,4,6,7,8-HpCDF | 11.70% | 7.10% | 15.30% | 14.10% |
| 1,2,3,4,7,8,9-HpCDF | 7.80% | 7.10% | 3.60% | 3.60% |
| 1,2,3,4,7,8-HxCDD | 3.90% | 7.10% | 4.70% | 3.80% |
| 1,2,3,4,7,8-HxCDF | 15.60% | 9.50% | 17.20% | 12.90% |
| 1,2,3,6,7,8-HxCDD | 6.80% | 7.10% | 5.90% | 5.10% |
| 1,2,3,6,7,8-HxCDF | 7.80% | 7.10% | 11.40% | 9.20% |
| 1,2,3,7,8,9-HxCDD | 10.70% | 7.10% | 7.10% | 5.90% |
| 1,2,3,7,8,9-HxCDF | 9.80% | 4.70% | 5.70% | 4.90% |
| 1,2,3,7,8-PeCDD | 5.80% | 4.70% | 7.50% | 6.30% |
| 1,2,3,7,8-PeCDF | 10.70% | 4.70% | 10.80% | 9.80% |
| 2,3,4,6,7,8-HxCDF | 8.80% | 7.10% | 9.80% | 8.40% |
| 2,3,4,7,8-PeCDF | 10.70% | 7.10% | 11.20% | 10.00% |
| 2,3,7,8-TCDD | 12.70% | 14.20% | 15.70% | 15.10% |
| 2,3,7,8-TCDF | 12.70% | 4.70% | 12.10% | 11.20% |
| Total TEQ | 50.00% | 54.70% | 52.20% | 49.30% |

**Figure 1: Box Plot Showing Distribution of TEQ Concentrations in Blanks and Field Samples**

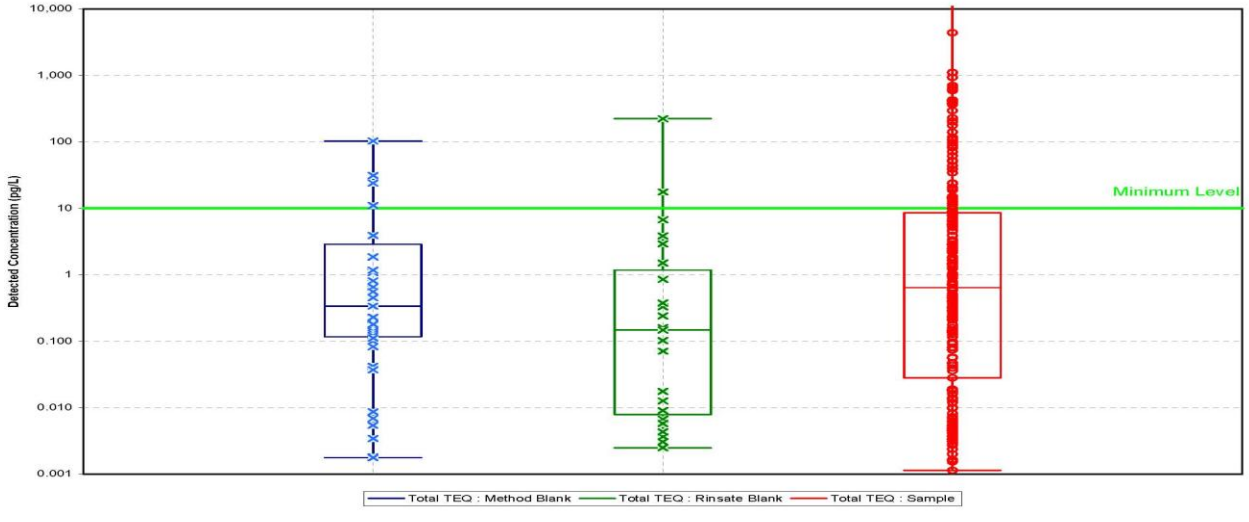


**Figure 2: Results of Original Extract Analysis on a Less Polar DB-5MS Column**

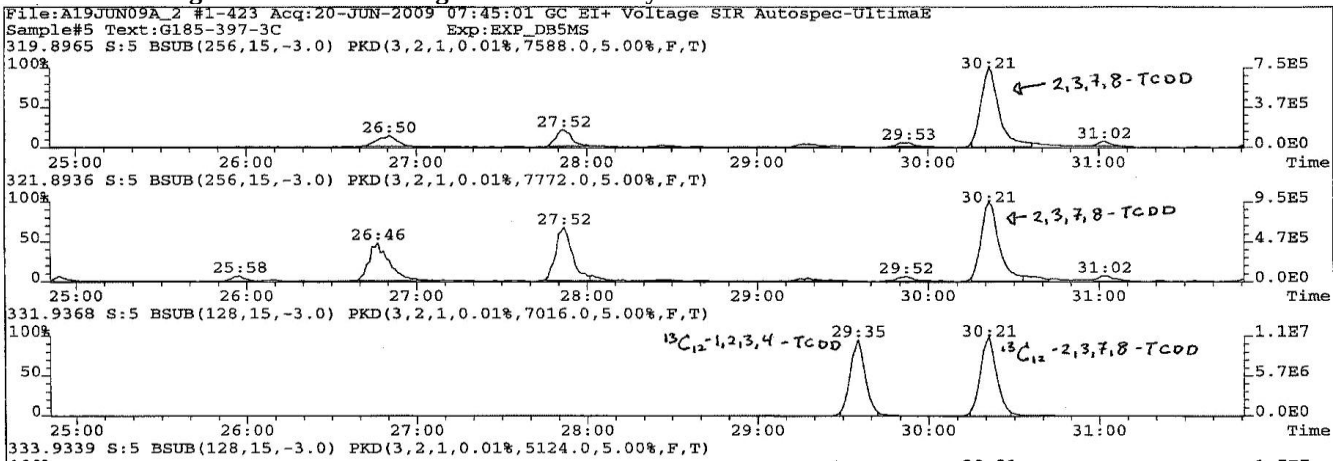
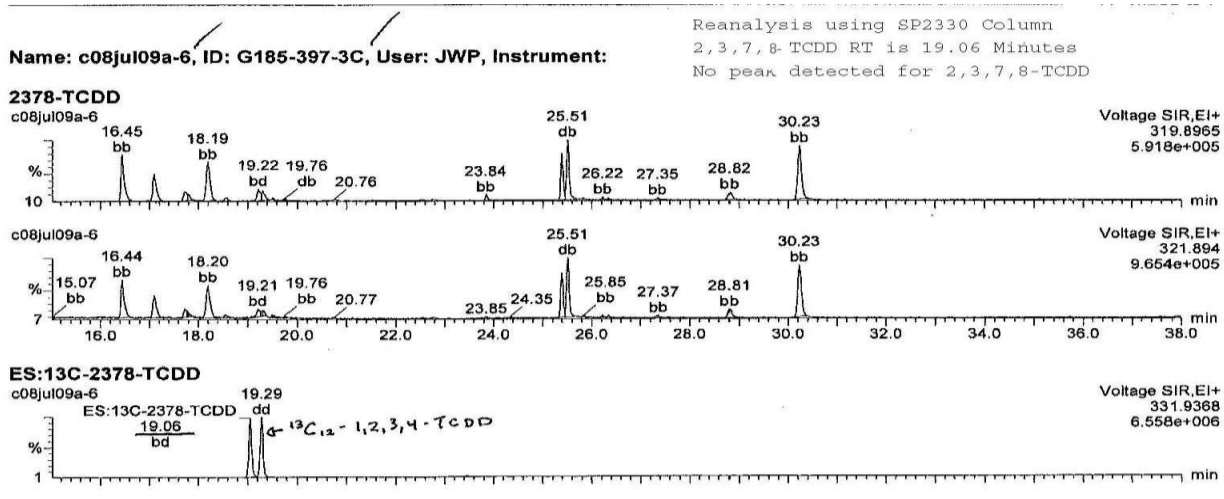



**Figure 3: Results of Extract Reanalysis on a More Polar SP-2330 Column**




**References:**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3. EPA; Guidelines Establishing Test Procedures for the Analysis of Pollutants; EPA Method 1613; Final Rule, Federal Register, Part III, 40 CFR Part 136, September 15, 1997.
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