Dioxin '97, Indianapolis, Indiana, USA

LONG DURATION MEASUREMENT OF PCDDs/PCDFs IN AMBIENT AIR -
METHOD PERFORMANCE DATA

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Abstract

Long duration sampling periods of 30 days have been utilized to measure PCDDs/PCDFs in ambient air. This extended sampling duration beyond the typical 48-hour sampling session offers enhanced method detection limits and extended temporal coverage, during which time active monitoring may more reliably support the establishment of average baseline ambient PCDDs/PCDFs levels.

Since its adoption by the State of Connecticut Department of Environmental Protection following completion of a method validation study completed by ENSR, over 100 ambient air samples have been collected employing this long duration approach. This paper presents method performance data (collocated sampler data, field surrogate recoveries, separate front half/back half analyses of sample collection media) generated from 1993 through 1997 using this method.

Introduction

Numerous studies have been completed in recent years to measure PCDDs/PCDFs in ambient air. Typically, these programs have relied upon sampling durations of 24 to 48 hours, as specified in EPA Method TO-9[1]. ENSR completed a method validation program in 1993 under contract to the State of Connecticut Department of Environmental Protection (CT DEP) to evaluate the use of extending sampling periods (30 days) for the measurement of PCDDs/PCDFs in ambient air.

This long duration ambient monitoring approach offers several key benefits over the 48-hour sampling period typically employed for ambient monitoring of semivolatile compounds, including the following:

- Enhanced method detection limits. Increased sample volumes of approximately 8,000 m^3 resulting from the extended sampling duration (in lieu of approximately 650 m^3 from the typical 48-hour sampling period) enhances method detection limits by an order of magnitude to approximately 1 to 5 fg/m^3 per congener.

- Extended temporal coverage. The 30-day sampling approach provides active ambient monitoring coverage for extended period with collection of a minimum of ambient air samples. The extended sampling period improves the ability to characterize baseline ambient PCDDs/PCDFs concentrations and enhances the demonstration of compliance with Connecticut's annualized standard.

Following review of the 1993 method validation program results, the methodology was formally adopted for use by the CT DEP to support legislation requiring ongoing ambient monitoring in the vicinity of Resource Recovery Facilities in Connecticut. This legislation requires demonstration of compliance with the Acceptable Ambient Concentration of 1.0 pg/m^3 (expressed as annualized EPA 1987 TEQs)[2]. Since 1993, ENSR has utilized the long duration approach to collect over 100 ambient samples to support the Connecticut ambient standard as well as establish baseline ambient PCDDs/PCDFs levels in other regions of the United States.

This paper summarizes key performance criteria for the long duration method for measuring PCDDs/PCDFs in ambient air, and relies upon review of data from over 100 field samples collected throughout the past four years using this approach. Key parameters subjected for evaluation include the following:

- collocated sampler data (precision assessment)
- field surrogate recoveries (accuracy assessment)
- method detection limit evaluation
- analyte migration (breakthrough) evaluation.

Experimental Methods

Sample collection methodology[3,4] was adapted from EPA Method TO-09 for the collection of PCDDs/PCDFs in ambient air, modified for long duration (30-day) sampling. This approach relies upon General Metals Works PS-1 samplers, modified to accept a teflon-coated glass fiber 8" x 10" rectangular filter in lieu of the standard 10.14 cm diameter circular filter. This change to a larger filter accommodates the higher particulate loadings expected from the increased sample volumes collected during the 30-day sampling period. The particulate filter and polyurethane foam plug allow for collection of particulate-associated and gaseous phase PCDDs/PCDFs, respectively.

PS-1 samplers were calibrated in the field prior to and following each 30-day sampling session using a calibrated orifice and water manometer. Samplers were set to operate at a nominal flowrate of 150 to 200 liters per minute to produce an approximate sample volume of 7,000 to 8,000 m^3 over the 30-day extended sampling period.

Sampling media were prepared in advance of field sampling at the analytical laboratory by Soxhlet extraction with toluene (16 to 24 hours), followed by application of the following five isotopically labeled PCDDs/PCDFs to each PUF sorbent module for use as field surrogates:

$^{37}Cl_4$-TCDD (100 pg)
$^{13}C_{12}$-PeCDF (100 pg)
$^{13}C_{12}$-HxCDF (200 pg)
$^{13}C_{12}$-HxCDD (200 pg)
$^{13}C_{12}$-HpCDF (500 pg)

Following sample collection, samples were delivered to the analytical laboratory under strict chain-of-custody. For a majority of samples, the filter and PUF were Soxhlet extracted together with toluene for a 16-hour period. Sample extracts were then split, with one portion analyzed via High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) based upon EPA Method 8290 and the other portion archived. A subset of samples underwent separate front half/back half analysis of front half = filter plus front half PUF section; back half = back half of PUF) to provide an assessment of target analyte migration through the sample collection system.

Results and Discussion

Collocated Sampler Data. As an assessment of precision of the combined sampling and analysis regime, collocated sampler pairs were utilized throughout the long duration ambient monitoring studies. Collocated samplers were setup and contemporaneously operated within 2 meters of one another. The long duration data set includes 12 collocated sampler pairs collected at various U.S. locations during all seasons of the year.

Figure 1 graphs average precision (expressed as percent difference between collocated sample data pairs) for each of the fifteen 2,3,7,8-substituted congeners and the tetra through octa congener classes. The figure shows an average precision of 12% for the long duration method (n = 12 sample pairs; 300 data pairs). This compares to the method precision of 20.3% reported by Maisel and Hunt for 48-hour ambient PCDDs/PCDFs sampling periods[5]. The improved precision offered by the long duration method may be a result of the higher frequency of detection and higher measured quantities of target analytes realized through use of the 30-day sampling period.

Field Surrogate Data. Field surrogate data serves two purposes to the program. First, it provides for an assessment of method accuracy. Known quantities of isotopically labeled PCDDs/PCDFs are prespiked prior to field sampling; recovery of these compounds provides an indication of method accuracy.

Second, the field surrogates provide information on target analyte retention within the sample collection system. Analyte migration through the sample collection system (e.g. breakthrough), a potential problem with the high sample volumes utilized in the method, may be monitored through review of field surrogate recovery data. Field surrogates are expected to act as native species; recovery of field surrogates near 100% provides an indication that the native species are also retained within the sample collection system.

Figure 2 graphically displays average field surrogate recoveries for 128 samples collected using the long duration ambient PCDDs/PCDFs sampling approach. As noted in the

figure, recoveries averaged between 97% and 111% for each of five isotopically labeled surrogates. Minimum and maximum recoveries are also noted. As an indication of recovery variability, the figure also lists relative standard deviation for each field surrogate. These results show acceptable accuracy and affirms that analyte migration through the sample collection system does not appear to occur (as indicated by average field surrogate recoveries of approximately 100%).

Separate front half/back half analyses. An additional QA/QC element of the program included separate analysis of front half (consisting of filter and front half of foam plug) and back half (back half of foam plug) sample portions from 16 of 128 ambient samples. As with evaluation of field surrogate recoveries, separate front half/back half analysis provides an indication of migration of the target analytes through the sampling system. Though no definitive breakthrough criteria have been established for the collection of semivolatile compounds using filter/sorbent media, detection of significant quantities of target parameter on the back-half portion may indicate a potential for analyte breakthrough.

Of particular interest are samples collected during warm weather (e.g. summertime), which may promote analyte migration through the sample collection system. Evaluation of front half/back half analyses conducted on the seven summertime samples shows the following average back half : front half ratios:

Total TCDFs	29%	Total TCDDs	20%
Total PeCDFs	2.8%	Total PeCDDs	0%
Total HxCDFs	2.4%	Total HxCDDs	0%
Total HpCDFs	3.6%	Total HpCDDs	3.5%.

Interestingly, these ratios closely follow the published vapor pressures, with TCDFs and TCDDs showing the highest presence in back half analyses while also considered the first and second most volatile PCDD/F congener classes, respectively[4]. Summertime samples (n=29) showed average recoveries of 95% for the labeled TCDD field surrogates for these samples collected during warm weather (average temperature approximately 75 deg F). Because of this summertime field surrogate recovery data, analyte breakthrough was deemed unlikely for all target compounds, including the more volatile TCDD and TCDF species.

Two of sixteen samples did show unexpected results; one wintertime sample and one fall sample indicated the presence of target analytes in back half analyses for 24 of 25 PCDD/F target parameters. However, because recoveries of field surrogates spiked in the front half foam of these two samples varied from 92% to 123%, breakthrough of target compounds was deemed unlikely.

Conclusions

The following conclusions are offered regarding the long duration approach for measuring PCDDs/PCDFs in ambient air:

Dioxin '97, Indianapolis, Indiana, USA

- Enhanced method detection limits of approximately 1-5 fg/m^3 were achieved through collection of sample volumes near 8,000 m^3.

- Long duration method improves likelihood of measuring all target PCDDs/PCDFs in ambient air, including 2,3,7,8-TCDD.

- Collocated sampler data shows method precision (expressed as average percent difference between collocated sample data pairs) of approximately 12%.

- Target analyte migration through the sample collection system was noted for the lower molecular weight, more volatile congener classes (TCDFs, TCDDs) in summertime (warm temperature) samples. However, normal field surrogate recovery data (average recoveries approach 100%) for field samples collected during summer indicate that "breakthrough" of target analytes is unlikely using the long duration approach.

Acknowledgements

Literature Cited

[1] EPA-600/4-84-041, <u>Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.</u> Method TO-9, Revision 1. 1986.

[2] State of Connecticut, Public Act 86-332. 1986.

[3] ENSR Corporation, "Ambient Monitoring for PCDDs/PCDFs in Connecticut - Fall 1993 through Summer 1994," Final Report prepared under contract to the State of Connecticut, Department of Environmental Protection. September 1995.

[4] ENSR Corporation, "Ambient Monitoring for PCDDs/PCDFs in Connecticut - 1995 Program," Final Report prepared under contract to the State of Connecticut, Department of Environmental Protection. September 1996.

[5] Maisel, B.E.; Hunt, G.T. "The Role of Quality Assurance/Quality Control in the Interpretation of Ambient PCDDs/PCDFs Data." Proceedings of the 1989 EPA/AWMA International Symposium on the Measurement of Toxic and Related Air Pollutants. May 1989.
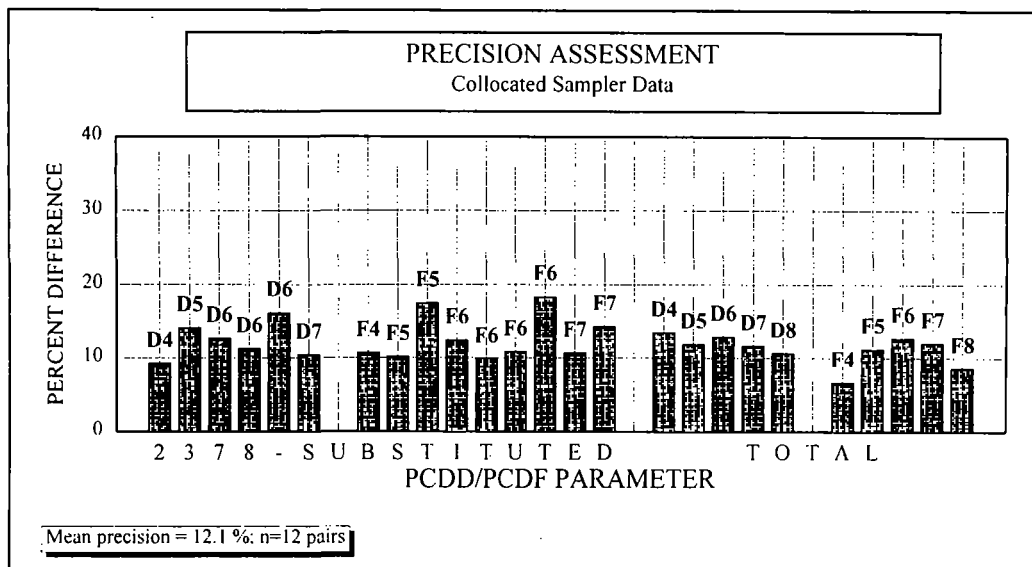
PRECISION ASSESSMENT
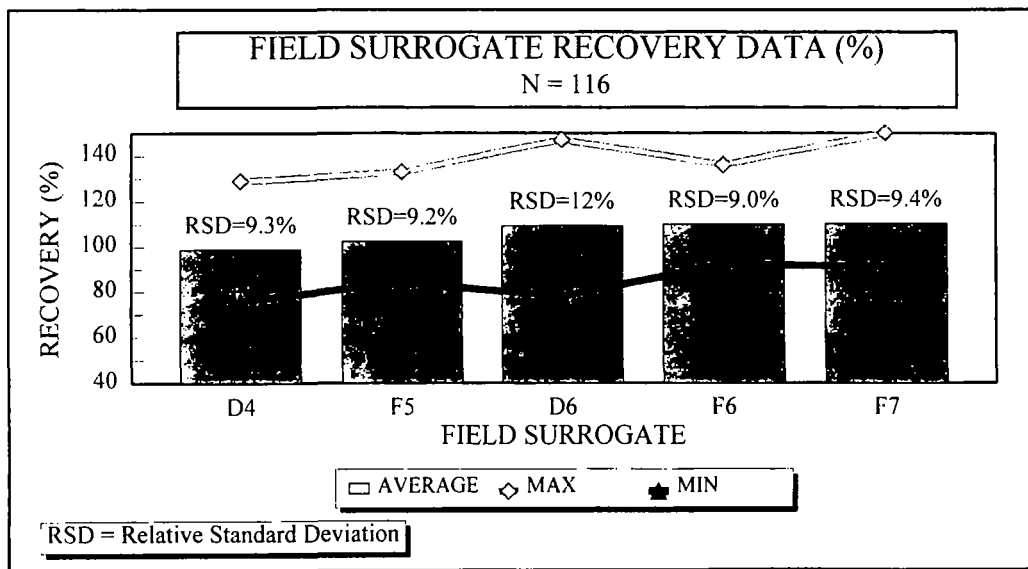### Collocated Sampler Data

FIGURE 1

FIELD SURROGATE RECOVERY DATA (%)
N = 116

FIGURE 2