US EPA SITE PROGRAM PERFORMANCE VERIFICATION OF MONITORING AND MEASUREMENT TECHNOLOGIES FOR DIOXIN AND DIOXIN-LIKE COMPOUNDS IN SOIL AND SEDIMENT

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Introduction

Performance testing of innovative environmental technologies is an integral part of the regulatory and research mission of the U.S. Environmental Protection Agency (EPA). The Superfund Innovative Technology Evaluation (SITE) Program was established by the EPA Office of Solid Waste and Emergency Response and the Office of Research and Development under the Superfund Amendments and Reauthorization Act of 1986. The program is designed to meet three primary objectives: (1) identify and remove obstacles to the development and commercial use of innovative technologies, (2) demonstrate promising innovative technologies and gather reliable performance and cost information to support site characterization and remediation activities, and (3) encourage the use of innovative technologies at Superfund sites as well as other waste sites or commercial facilities. The intent of a SITE demonstration is to obtain representative, high-quality performance and cost data on innovative technologies so that potential users can assess a given technology's suitability for a specific application. More information about the SITE Program can be found on the Program's Web site (www.epa.gov/ORD/SITE).

Conventional analytical methods for determining dioxin concentrations are time-consuming and costly. For example, EPA standard methods require solvent extraction of the sample, processing the extract through multiple cleanup columns, and analyzing the cleaned fraction by gas chromatography (GC)/high-resolution mass spectrometry (HRMS). Use of a simple, rapid, cost-effective analytical method would allow field personnel to quickly assess the extent of dioxin contamination at a site and could direct or monitor remediation or risk assessment activities. More rapidly acquired data could be used to provide immediate feedback on potential health risks associated with the site and permit the development of a more focused and cost-effective sampling strategy. More affordable and quicker analytical techniques would not replace HRMS, but would provide an alternative technology for consideration. However, before choosing an alternative to traditional laboratory-based methods, a thorough assessment of how commercially available technologies compare to conventional laboratory-based analytical methods using certified, spiked, and environmental samples is warranted.

Materials and Methods

Five developers of measurement technologies for dioxin and dioxin-like compounds participated in a field demonstration in Saginaw, Michigan, from April 26 to May 5, 2004. The demonstration was conducted in collaboration with the Michigan Department of Environmental Quality (MDEQ) and the U.S. Fish and Wildlife Services. The demonstration/quality assurance project plan for this study can be found on the SITE Web site.[1] The developers and technologies that participated were:

• AhRC PCR™ Kit, Hybrizyme Corporation

• Coplanar PCB Immunoassay Kit, Abraxis LLC

• DF-1 Dioxin/Furan and PCB TEQ Immunoassay Kits, CAPE Technologies L.L.C.

• CALUX® by Xenobiotic Detection Systems, Inc.

• Dioxin ELISA Kit, Wako Pure Chemical Industries, Ltd.

Each technology was operated by the developers at the demonstration site and utilized the necessary safety

precautions (e.g., fume hoods) to operate in a safe field environment. The purpose of the demonstration was to evaluate measurement technologies for dioxin and dioxin-like compounds in soil and sediment in order to provide: (1) potential users with a better understanding of each technology's performance and cost under well-defined field conditions and (2) developers with documented results that will assist them in improving their technologies and promoting its acceptance and use. To meet these objectives, samples were collected from a variety of dioxin-contaminated soil and sediment sampling locations around the country. The environmental samples were homogenized and characterized for dioxins, furans, polychlorinated biphenyls (PCBs), and a target list of 18 polynuclear aromatic hydrocarbons (PAHs) prior to selection for use in the demonstration. This provided a variety of environmentally derived dioxin-contaminated samples with concentrations over a large dynamic range (< 5 to > 10,000 picogram/gram [pg/g] toxicity equivalents [TEQ]) to be included in the demonstration. The sample design also included performance evaluation (PE) samples, which contained certified concentrations of dioxins, furans, and/or PCBs. Collectively, the demonstration samples covered a range of concentrations and chemical interferents to properly evaluate the technologies and ensured that the datasets produced were statistically sound.

In SITE demonstrations, the performance and cost of each technology are compared to those of conventional, off-site laboratory analytical methods, so the selection of a reference laboratory is a critical decision. For this demonstration, the selection was a performance-based process which included completion of a questionnaire, blind analysis of audit samples, and participation in on-site quality and technical systems audits. Criteria for final selection were based on the observations of the auditors, the performance on the audit samples, and cost. From this process, it was determined that Axys Analytical Services (Sidney, British Columbia, Canada) would best meet the needs of this demonstration, so Axys was selected as the reference laboratory for this demonstration. Seventeen dioxin/furan (D/F) congeners and 12 dioxin-like PCBs were determined for each of the 209 demonstration samples by the reference laboratory using EPA Methods 1613B and 1668A, respectively.[2-3]

The demonstration had both primary and secondary objectives. The primary objectives included determining the accuracy, precision, comparability to the reference method(s), estimated method detection limit, frequency of false positive/negative results, matrix effects, and cost. The secondary objectives included documentation of: skills and training required to properly operate the technology, health and safety aspects associated with operating the technology, portability of the technology, and sample throughput.

Results and Discussion

A separate innovative technology verification report (ITVR) was prepared for each technology and is posted on the SITE Web site (www.epa.gov/ORD/SITE). A brief description and summary performance statement are presented below for each technology. The performances of the technologies have not been compared to one another since it is the policy of the SITE Program to not judge or rank technologies.

The *Abraxis LLC Coplanar PCB ELISA Kit* is an immunoassay technology that reports the TEQ concentration of coplanar PCBs. The results indicated that the Abraxis kit could be an effective screening tool for sample concentrations above and below 50 pg/g TEQ_{PCB}.

The *CAPE Technologies DF1 Dioxin/Furan and PCB TEQ Immunoassay kits* are immunoassay techniques that report the TEQ concentration of D/Fs and PCBs, respectively, which can be summed to generate a total TEQ value. The results indicated that the CAPE Technologies kits could be an effective screening tool for determining sample results above and below 20 pg/g TEQ and even more effective as a screen for samples above and below 50 pg/g TEQ. The technology is most effective if characterization data is available from the site.

The *Hybrizyme Corporation AhRC PCR™ Kit* is a technology that reports the concentration of aryl hydrocarbon (Ah) receptor binding compounds in a sample, and the results are reported in Ah Receptor Binding Units (AhRBU). The results indicated that the Hybrizyme technology could be used as an effective tool to rank sample concentrations from low to high AhR activity within a particular environmental site.

The *Wako Pure Chemical Industries, Ltd. Dioxin ELISA Kit Wako (for environmental)* is an immunoassay technology that reports total D/F TEQ concentration in a sample. The results indicated that the Wako kit could be an effective screening tool for determining sample results above and below 20 pg/g $TEQ_{D/F}$, and even more effective as a screen for samples above and below 50 pg/g $TEQ_{D/F}$. Wako was the only developer to complete all of the sample

analyses on-site.

The *Xenobiotic Detection Systems, Inc., CALUX® by XDS* is an aryl hydrocarbon-receptor bioassay that individually reports the TEQ of D/Fs and PCBs in the sample, which can be summed to determine a total TEQ value. The results indicated that the XDS technology could be an effective tool to screen for samples above or below 1 pg/g TEQ for $TEQ_{D/F}$ and total TEQ, and that it could be effective for all three types of TEQ values to determine results above or below 50 pg/g TEQ.

Several important findings from this study should be noted.

· For all technologies, the cost and the time to complete the 209 demonstration analyses were considerably less than that of the reference laboratory which took 8 months and nearly $400,000 to complete.

· It is possible that AhR binding compounds were not all accounted for in the reference laboratory TEQ result and that the World Health Organization toxicity equivalency factors (TEFs) used to generate the reference laboratory TEQs may differ from the assay Ah-receptor binding affinity for certain analytes.

· Since the AhR binding technologies measure actual biological response, it is possible that these assays may give a better representation of the true toxicity of the sample from a risk assessment standpoint.

· TEQ results from immunoassay technologies may not directly correlate to HRMS TEQ in all cases because it is known that the congener responses and cross-reactivities to the kits are not identical to the World Heath Organization TEFs that are used to convert congener HRMS concentration values to TEQ.

· It is possible that correlation between the immunoassay TEQ results and HRMS TEQ results could be improved by first characterizing a site and calibrating the immunoassay results to HRMS results.

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