



TECHNICAL SUPPORT TIMES

The **Technical Support Times** is an online newsletter highlighting EPA's field activities, research, and new documents on current topics. This issue is the third in a series of periodic publications from the Hazardous Substances Technical Liaison (HSTL) program and is available on the intranet at <http://intranet.epa.gov/ospintra/scienceportal/>.

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FOCUS ON: CONTAMINANT FINGERPRINTING FOR HAZARDOUS WASTE SITES

Human fingerprinting is used frequently during criminal investigations and for more routine purposes such as security clearances during certain job applications. Other analogous methods of identification are available besides literally examining a person's fingerprints. For example, DNA "fingerprinting" is a modern method that can be highly effective for identifying specific people, animals, and even plants based on genetic material. These methods often are used in court proceedings and referred to as forensic methods.

Analogous to human fingerprinting, contaminant fingerprinting identifies chemicals and other substances in the environment, as well as the sources of those materials.

Contaminant fingerprinting methods often are used for possible litigation (e.g., for identifying a polluter from the chemical characteristics of the pollution). Therefore, these methods are among the chief tools of environmental forensics investigations.¹ These same methods, however, can be used for purely scientific purposes, such as investigating contaminant fate and transport processes. This issue of *Technical Support Times* provides an overview of contaminant fingerprinting as well as two case studies. In this issue, "contaminant fingerprinting" will be limited to methods that are not routinely used in hazardous waste site investigations. Numerous methods exist for contaminant fingerprinting, all involving pattern recognition techniques (e.g., matching patterns resulting from chemical analyses with patterns known to be associated with a particular contaminant or waste material). A common approach

FINGERPRINTING
continued on page 2

Focus On: Contaminant Fingerprinting for Hazardous Waste Sites . . .1

Contaminant fingerprinting is among the chief tools used for environmental forensic investigations and it can be used to investigate contaminant fate and transport processes.

Science at Work2

There are two significant statistical methods used in contaminant source identification—FALCON and PVA.

Case Study Number 13

Dioxin-furan fingerprinting used at the Lower Roanoke River Site in North Carolina.

Case Study Number 23

Dioxin fingerprinting used at Diamond Alkali Superfund Site in Newark, New Jersey.

In the Laboratory4

The Office of Research and Development's National Exposure Research Laboratory has used fingerprinting and other analytical techniques to identify unknown contaminants at sites.

References6

OSP INTRANET

[HTTP://INTRANET.EPA.GOV/
OSPINTRA/](http://intranet.epa.gov/ospintra/)

OSP INTERNET

[HTTP://WWW.EPA.GOV/OSP](http://www.epa.gov/osp)

FINGERPRINTING *continued from page 1*

for pattern recognition involves making visual comparisons. The “eyeball” approach, however, can be highly subjective, just as two people looking at the same inkblot image for a Rorschach test may see different

objects. Chemical fingerprints can be “blurred” by sampling variability, analytical variability, contaminant fate and transport processes, and mixing of different waste materials at the hazardous waste sites. Therefore, more sophisticated approaches often are needed. ■

SCIENCE AT WORK

Statistical Methods

There are a number of multivariate statistical methods that can be used in contaminant source identification. These include Fingerprint Analysis of Leachate Contaminants (FALCON), which was used in the first case study described below, and Polytopic Vector Analysis (PVA), which was employed in the second case study.

There are significant differences between these two statistical methods. One difference that would be of interest to non-statisticians is that FALCON requires that the likely source of fingerprints be identified prior to statistical analysis of site analytical data, while PVA does not. The FALCON statistical analysis determines the extent to which each potential source fingerprint contributes to the observed site data. If there are likely to be unknown sources or sources whose fingerprints are poorly characterized, there can be difficulties using FALCON. On the other hand, PVA requires no prior identification of source fingerprints. PVA identifies source fingerprints solely by statistical analysis of site analytical data. Once PVA has identified fingerprints from site data, those fingerprints can be compared to known source fingerprints. In some cases, however, fingerprints will be identified that do not correspond to any known source fingerprint (analogous to finding fingerprints at a crime scene that are not on file with any law enforcement organization). The sources of those unknown fingerprints may still be discovered some time in the future.

In both case studies, river sediments were contaminated by polychlorinated dibenzo-p-dioxins (commonly referred to as “dioxins” or “PCDDs”) and polychlorinated dibenzofurans (commonly called “furans” or “PCDFs”) from a number of sources. In these two cases, EPA regional personnel called on the Hazardous Substances Technical Liaisons (HSTLs), who coordinated technical assistance from EPA’s Office of Research and Development (ORD) and others. In the case studies, experts used statistical methods to identify dioxin/furan fingerprints from site-specific analytical data. Dioxin/furan fingerprints can be displayed graphically by plotting the relative abundances of the dioxin and furan congeners (see generic example below). By using statistical methods, the relative contributions of the sources to the environmental contamination were assessed.

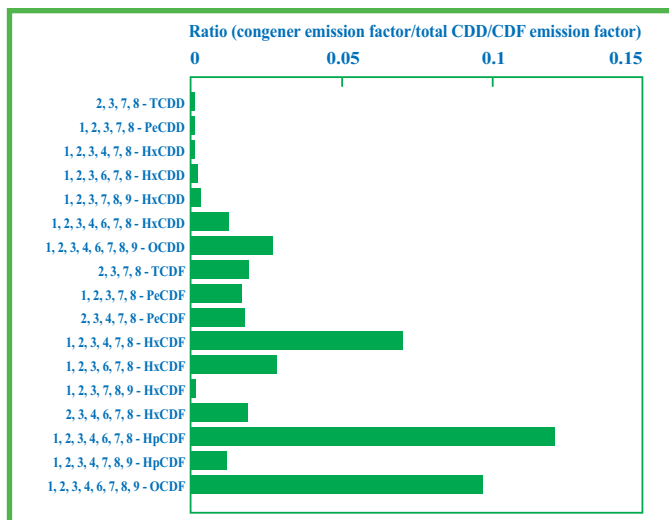


FIGURE 1. Example of Dioxin “Fingerprint” (i.e., Congener Profile) for Air Emissions from Hazardous Waste Incinerators

CASE STUDY NUMBER 1**Dioxin-Furan Fingerprinting—Lower Roanoke River Site, North Carolina**

The southeastern United States is heavily concentrated with facilities related to the wood, pulp, and/or paper industries. Many times these facilities are located within close proximity to one another. The Weyhauser Paper Plant and the Georgia Pacific Hardwood Saw Mill are large facilities located along the lower Roanoke River in North Carolina. The two facilities and the river are being investigated and remediated as a National Priority List concern.

Wastes from the facilities included dioxins and furans, along with numerous heavy metals, some pesticides, and other contaminants associated with the wood, pulp, and paper industry. Dioxins and furans have been found in high concentrations in the river sediments and the surrounding environment. Because the Lower Roanoke River Site encompasses a large area including soil, water, biota, and sediments and includes more than one source area, the concern for cross-contamination existed. Dioxins and furans also were found in sediments upstream of the two facilities, and there are Publicly Owned Treatment Works (POTW) discharges along the river from the City of Plymouth. To fully characterize the site, scientists needed to determine whether dioxins and furans from sources upstream of the Weyerhauser and Georgia Pacific facilities could be attributed to the facilities through another possible source pathway.

To address this concern, the Region 4 Project Manager requested, through coordination with the HSTL, that the

ORD National Exposure Research Laboratory, Environmental Sciences Division in Las Vegas, Nevada (NERL-ESD) attempt to fingerprint the dioxins and furans in the Lower Roanoke River to aid in determining liability and cleanup issues. The fingerprinting was accomplished using sampling and analysis of river, POTW, and onsite soil, water, sludge, and sediment samples performed as part of the site investigation; literature data on typical dioxin/furan congeners found in urban POTW discharges; and an evaluation of the individual dioxin/furan source fingerprints by NERL-ESD through its contractor Lockheed Martin.

Using the fingerprints derived from point sources at the site and POTWs, and from literature about POTW discharges, scientists determined that dioxins and furans found in the POTW discharges, which were typical of urban POTWs, were contributing to the upstream contamination of the river, and could be distinguished from the dioxins and furans characteristic of each paper mill facility. By using the FALCON statistical analysis, the relative contribution of each source fingerprint to the sediment contamination at each sampling location was calculated. Relative contribution information allowed the Project Manager to set dioxin/furan boundaries at the site and for the two different facilities, eliminating the need for additional sampling and reducing the liability of the facilities for the upstream contamination. The relative contribution information helped define these boundaries without additional litigation or investigative sampling. This information also eliminated the need for additional litigation and costly investigation and sampling by EPA in trying to determine if there was an additional pathway of concern. This case study and the FALCON method are described in greater detail in an EPA publication.² ■

CASE STUDY NUMBER 2**Dioxin Fingerprinting—Diamond Alkali Superfund Site, Newark, New Jersey**

The family of dioxins and furans includes 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), considered to be one of the most toxic organic chemicals. The Lower Passaic River Study Area of the Diamond Alkali Superfund Site is an urban waterway highly contaminated by many pollutants,

including dioxins. There are many sources of dioxins impacting this waterway, with each category of sources (e.g., combustion sources, sources, etc.) having a distinctive dioxin/furan fingerprint. The dioxin/furan congener contributing most to the risk is 2,3,7,8-TCDD. Because the mixture of dioxins/furans at any location in the sediments is likely to result from multiple sources, the individual source fingerprints are not apparent. Statistical techniques can be used, however, to mathematically

CASE STUDY
continued on page 4

ISSUE #3

CASE STUDY*continued from page 3*

un-mix the dioxin fingerprints. Contractors hired by parties who are potentially responsible for releases from the former Diamond Alkali Company factory used Polytropic Vector Analysis (PVA) to identify dioxin fingerprints from sediment sampling data collected in the Passaic River and vicinity. One fingerprint identified in relatively few samples was similar to the fingerprint expected from the manufacture of the herbicide 2,4,5-T, which was produced at the Diamond Alkali Superfund Site and used to make Agent Orange for the military during the Vietnam War era. A peer-reviewed paper presenting the results of this study suggested that the impact from the Diamond Alkali releases is relatively small compared to the impacts of other dioxin sources.

EPA Region 2 called on ORD for technical assistance in addressing this problem. The Region 2 HSTL met with statisticians at NERL-ESD. Although they provided useful references and insights into the issue, the statisticians did not have access to PVA software and were unable to determine the validity of the published findings. (ORD since has used PVA to fingerprint PCBs in Lake Hartwell sediments.³) The HSTL then discussed the issue with Dr. Peter Adriaens and Dr. Noemi Barabas, the University of Michigan, who had performed bioremediation research using Passaic River sediments, partially funded by ORD and EPA Region 2. With funding from a grant awarded by the National Science Foundation to perform statistical analyses using Passaic

River sediment data, University of Michigan researchers developed and applied a modified PVA program. The modified program allowed for fingerprints to contain both positive and negative components, as would result when a process (e.g., microbial dechlorination) reduces the concentration of one or more compounds, while increasing the concentration of one or more compounds (e.g., dechlorination product(s)). Traditional PVA only allows for positive fingerprint components. The HSTL coordinated Region 2 support for the University of Michigan's research, which included providing sediment sampling data and comments on draft manuscripts. After rigorous peer review, the University of Michigan research findings were published, and the HSTL's assistance was acknowledged in the publication.⁴

The findings of this study were significant. Contrary to the previous study, a fingerprint corresponding to the production of 2,4,5-T was identified in nearly all of the samples and was calculated to be the greatest source of 2,3,7,8-TCDD in Passaic River sediments. In addition, a fingerprint corresponding to microbial dechlorination of dioxins was identified, as were other dioxin fingerprints. The University of Michigan's research cast doubt on a previous site-related study that indicated releases from the Diamond Alkali Company activities were a relatively minor contributor to the dioxin contamination. These were the first findings based on field sampling data to yield strong evidence of naturally occurring in situ dioxin dechlorination in sediments. As a result, these findings have implications for dioxin fate and transport modeling and risk assessment at this site and other sites. ■

IN THE LABORATORY**Analyses for Nonstandard Analytes**

The standard analytical methods performed for routine hazardous waste site investigations do not provide complete chemical fingerprints. For example, in the two case studies described in this issue, the dioxin/furan fingerprints were based on analyses for the standard subset of dioxins and furans potentially present in the environment. These analyses address only 17 congeners, which are the most toxic.

More precise fingerprints could have been obtained, however, if non-routine analysis had been performed to measure other dioxin/furan congeners that may have been present in the environmental samples. Perhaps, other dioxin sources could have been identified with more complete fingerprints.

Non-routine analytical methods that can be useful for contaminant fingerprinting include methods for isotope analysis, methods to identify unknown contaminants, methods for DNA analysis, and methods for chiral analysis.

IN THE LABORATORY
continued on page 5

IN THE LABORATORY

continued from page 4

Isotope Analyses

Trichloroethylene (TCE), one of the most common contaminants at Superfund sites, is a single compound. Unlike the mixtures of dioxin and furan congeners discussed earlier, TCE cannot be fingerprinted using conventional analytical methods. In fact, it might surprise some environmental professionals to learn that not all TCE molecules are identical. The elements that make up TCE (carbon, chlorine, and hydrogen) exist in different varieties (called “isotopes”) having different atomic weights. As a result, TCE molecules can have different molecular weights. Carbon, for example, has two stable isotopes (Carbon 12 and Carbon 13), which do not decay, whereas, the isotope Carbon 14 decays with time. The ratio of stable carbon isotope concentrations for TCE at one site may be different than the ratio found at another site. This difference can result from the sources of raw materials used in the TCE manufacturing process. Therefore, the TCE produced at one chemical factory can differ from the TCE produced at another in regard to stable isotope ratios.

Additionally, stable isotope ratios can be affected by environmental fate and transport processes (e.g., biodegradation, bioaccumulation). As a result, analyses for stable isotopes can be used in investigating those processes. For example, EPA researchers are using compound-specific stable isotope analyses to measure naturally occurring biodegradation of methyl tertiary-butyl ether (MTBE) in groundwater.⁵

Contaminant fingerprinting using radioisotope data is complicated by the fact that radioisotope concentrations change with time due to radioactive decay. As radioisotopes decay with time, the concentrations of these isotopes (and their “daughter products”) will change. Because the radioisotope-specific decay rates are well-established, radioisotope concentration data sometimes can be used in computing the age of contaminants and/or contaminated materials. For example, concentrations of radioisotopes of cesium and lead were used in calculating the age of contaminated sediment deposition at the Wyckoff/Eagle Harbor (WA) Superfund Site.⁶ Using radioisotope data to understand the chronology of environmental contamination can be an important forensic tool for identifying the parties responsible for the contamination.

Methods to Identify Unknown Contaminants

Deciding what to do about a contaminant whose identity is unknown is problematic. Until the identity of the contaminant is established, the risk that it presents cannot be assessed accurately. In addition, the contaminant’s identity may provide evidence of the source of the contamination. Therefore, the use of special analytical methods to identify unknown or tentatively identified compounds may be warranted. One approach called Ion Composition Elucidation (ICE) was developed by the Environmental Chemistry Branch (ECB) at NERL-ESD.

ICE is a novel high-resolution mass spectrometric technique for identifying compounds found in extracts of environmental samples for which mass spectra are not found in mass spectral libraries. ECB frequently uses this technique to identify mystery compounds of interest to the EPA regions. As examples, several isomeric compounds found in a municipal well that serviced 50,000 people near two Superfund sites in Toms River, New Jersey, were identified for Region 2; sulfur-containing compounds most likely produced by anaerobic bacteria and chlorine-containing compounds resulting from pesticide manufacture at a Superfund site near Tampa, Florida, were identified for Region 4; and currently, halogenated phenols and other compounds are being identified by ECB for Region 1 in a subsurface drinking water source that rests above a plume of industrial wastes. ECB’s expertise is available to EPA regions for identifying organic pollutants that are difficult to identify by conventional means.

More information on ICE is available on the Web at <http://www.epa.gov/nerlesd1/chemistry/ice/default.htm>.

DNA Analyses

Similar to using DNA to “fingerprint” humans, DNA analyses can be used to identify microbial contaminants in the environment. This use was well-publicized in connection with the incidents involving the anthrax contamination of buildings, which apparently was spread through the U.S. mail. DNA fingerprinting also has been used to identify beneficial microbes, such as bacteria that have been isolated and shown to degrade chlorinated solvents. The presence of such bacteria in groundwater at Superfund sites was found to correlate with the extent of chlorinated solvent biodegradation.⁷ ■

IN THE LABORATORY

continued on page 6

IN THE LABORATORY

continued from page 5

Chiral Analytical Methods

Chiral chemistry has been called the “ultimate in pollutant speciation.” A chiral contaminant is one that can exist in forms (called “enantiomers”) that are identical except that their structures are non-superimposable mirror images (analogous to the structures of the right and left hands). Many pesticides and pharmaceutical chemicals are chiral (i.e., exist in mirror-image forms). The manufacturing processes for producing chiral chemicals can affect the relative proportions of the mirror-image forms. Chiral pharmaceuticals produced using biological processes (e.g., fermentation) and/or using biological materials (e.g., enzymes) may contain only one of the mirror-image forms or may contain unequal proportions of the forms. Chiral pesticides, however, usually are produced without using biological processes or biologically derived materials, so they generally contain equal amounts of the mirror-image forms. Therefore, chiral analytical methods (i.e., enantiomer-specific analytical methods) have the potential to fingerprint chiral contaminants and enhance the contaminant fingerprinting process.

In addition, one enantiomer may behave quite differently than its mirror-image counterpart when interacting with biota. For example, one enantiomer may be highly toxic, while its mirror-image counterpart can be virtually nontoxic. Biological processes (e.g., biodegradation, bioaccumulation) in the environment also can alter the proportions of mirror-image forms, while abiotic processes do not. Therefore, chiral analytical methods can be used to study interactions of chiral contaminants with biota.

ORD’s National Exposure Research Laboratory, Ecological Research Division in Athens, Georgia (NERL-ERD) has expertise in chiral analyses and chiral contaminants in the environment. For example, NERL-ERD has performed chiral analyses on sediments from Superfund sites, including Lake Hartwell, the Housatonic River, and the Hudson River.⁸ More information on chiral chemistry is available at <http://www.epa.gov/ATHENS/research/process/chiralchemistry.html>.

Limitations of Contaminant Fingerprinting

It should be noted that in spite of successes with contaminant fingerprinting techniques at many sites, there remain circumstances that may result in inconclusive results. For example, it may be impossible to distinguish between two very similar sources or there may be insufficient information to make accurate source identifications (e.g., lack of analytical data for historic contaminant sources that were never characterized and no longer exist). Although fingerprinting can provide valuable evidence to solve a forensic or scientific question, it should be recognized that other lines of evidence (e.g., eyewitness testimony, contaminant fate and transport findings) may need to be evaluated to successfully resolve most forensic or scientific questions. ■

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