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May 15, 2013

Associate Director
Office of Science Quality and Integrity
U.S. Geological Survey
108 National Center
Reston, VA 20192

Via E-Mail (InfoQual@usgs.gov) and First Class Mail

Re: Request for Correction of Information Submitted Under U.S. Geological Survey Information Quality Guidelines

Publications: Coal Tar Sealants Largest Source of PAHs in Lakes [*http://water.usgs.gov/nawqa/home_maps/sealcoat.html*] and Related Press Release [http://www.usgs.gov/newsroom/article.asp?ID=2651]

Dear Sir or Madam:

On behalf of the Pavement Coatings Technology Council (PCTC), which represents numerous companies throughout the county that are part of the sealcoat industry, I write to submit a request for correction of information disseminated by the U.S. Geological Survey (USGS). This request is made pursuant to the USGS Information Quality Guidelines and the U.S. Department of the Interior and the Office of Management and Budget (67 F.R. 8452) in accordance with Section 515 of the Treasury and General Government Appropriations Act for Fiscal Year 2001 (Public Law 106-554).

INFORMATION REQUIRING CORRECTION - OVERVIEW

The National Water-Quality Assessment (NAWQA) Program has posted a page on the USGS website entitled *Coal Tar Sealant Largest Source of PAHs in Lakes*. The web page contains a map showing locations of 40 lakes from which sediment samples were collected. The web page also contains the following text:

> Coal-tar-based pavement sealant is the largest source of polycyclic aromatic hydrocarbons (PAHs) to 40 urban lakes studied by the U.S. Geological Survey. On average, coal-tar-based sealcoat accounted for one-half of PAHs in the lakes, while vehicle-related sources accounted for about one-quarter. Elevated concentrations are generally associated with those lakes with a large contribution of PAHs from sealcoat, in many cases at levels that can be harmful to aquatic life.

> Historical trends for a subset of studied lakes indicate that sealcoat use has been the primary cause of increases in PAHs since the 1960s.[1]

According to information presented on this web page, its content and conclusions are based on a paper entitled "Contribution of PAHS from Coal-Tar Pavement Sealcoat and Other Sources to 40 U.S. Lakes" (hereinafter the "40 Lakes Paper"). It first appeared in the journal *Science of the Total Environment* in 2010 and was authored by two USGS employees, Dr. Peter Van Metre and his wife, Dr. Barbara Mahler. The web page further reports that the 40 Lakes Paper can be accessed at the following USGS link:

http://tx.usgs.gov/coring/allthingssealcoat.html

While the name of the link makes it sound as though it contains "all things" related to seal coating - including all relevant research – a careful review of this USGS sponsored link discloses that it instead consists of little more than a collection of articles primarily written by the same two USGS scientists – Drs. Van Metre and Mahler. They rely heavily on the practice of self-citation and tend to repeat many of their observations and conclusions, sometimes in different journals and publications. The most disturbing fact, however, is that *peer reviewed* studies which challenge the findings and conclusions reached by Drs. Van Metre and Mahler in the 40 Lakes Paper, and in other similar papers published by them, have simply been ignored by the USGS as though they did not exist.[2] Such an approach reflects a deviation in sound scientific methodology as well as a clear breach of the USGS Information Quality Guidelines (hereinafter "USGS Guidelines") summarized below.

Additionally, the USGS web site has posted a press release with the same title, i.e. *Coal Tar Sealant Largest Source of PAHs in Lakes.* The press release, dated December 1, 2010, was issued coincident with the publication of the above mentioned paper with the express purpose of *promoting* the conclusions reached by Drs. Van Metre and Mahler.[3] Indeed, Dr. Van Metre boasts that their findings "represent a significant advance in our understanding of the sources of these contaminants in streams and lakes." It should come as no surprise that this sort of self-promotion represents yet another breach in the USGS Guidelines, especially when it comes at the expense of ignoring contrary scientific research, thereby misleading the public into thinking that there is a consensus on this issue within the scientific community when clearly there is not.

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[1] For convenience, a print out of the web page is attached hereto as Exhibit A.
[2] A summary of various peer reviewed articles, comments and presentations which have questioned the methodologies and findings of Drs. Van Metre and Mahler is attached hereto as Exhibit B.
[3] A copy of said press release is attached hereto as Exhibit C.

USGS GUIDELINES

The USGS Guidelines, which apply to the previously cited web page and press release, require that USGS data collection and research activities be "carried out in a consistent, objective, and replicable manner" aimed at ensuring the objectivity, utility, and integrity of information disseminated to the public. *See* USGS Guidelines, Section III; Office of Management and Budget ("OMB") Guidelines, 67 F.R. 8452 (February 22, 2002) (incorporated by reference in the USGS Guidelines). To be "objective," information published by the USGS must be presented in an "accurate, clear, complete, and unbiased manner." *Id.* at 8459. "Objectivity" also requires that original and supporting data be generated, and analytic results developed, using sound statistical and research methods. *Id.*

The USGS Manual also refers to "impartiality and non-advocacy" as terms that build upon the concepts of "objectivity" raised by the OMB. Specifically, § 502.4(5)(B)(3) of the USGS Manual emphasizes the importance of presenting facts and interpretations impartially for others to use for their own purposes:

> [USGS] information products present science based, peer reviewed facts and interpretations impartially. Information products do not advocate or appear to advocate a particular public policy.... The conclusions are based on the best available data interpreted with sound scientific reasoning that avoids speculation.

It goes without saying that a refusal to acknowledge or cite peer reviewed articles that take a position contrary to the USGS' own research is a form of advocacy that clearly lacks objectivity.

Another way to determine if any bias or advocacy exists within the USGS on the issue of coal tar sealants is for the USGS to produce all related data, correspondence and emails concerning its research regarding the 40 Lakes Paper and other similar articles. A FOIA request asking for such materials was sent off two years ago and, incredibly, still remains "open" today.[4] As will be demonstrated in greater detail below, the USGS has sought to minimize evidence of advocacy within its ranks by withholding, at least up to now, certain correspondence and email between the USGS staff and other individuals outside the agency who have made it their goal to ban coal tar sealants across the country. These efforts by the USGS to withhold certain documents are not only at odds with the above mentioned policies, but also contrary to the need for transparency that is emphasized throughout the USGS Guidelines. *See e.g.,* 67 F.R. 8453, 8459.

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[4] A copy of the DOI webpage that sets forth the status of the above mentioned FOIA request is attached hereto as Exhibit D.

EXAMPLES OF SPECIFIC GUIDELINE BREACHES

Drs. Van Metre and Mahler claim in their 40 Lakes Paper that contamination of urban lakes and streams by polycyclic aromatic hydrocarbons (hereinafter PAHs) is widespread in the U.S. and has been increasing over the last 40 years. This assertion is not particularly surprising since there is a consensus in the scientific community that PAHs have many potential sources, including vehicle emissions, tire particles, motor oil, crude oil, power plant emissions and industrial releases. Indeed, almost any type of combustion with organic matter will produce PAHs as a by-product, including natural sources such as forest fires and volcanoes down to something as basic as grilling on the backyard barbecue. Thus, one would expect PAHs to be ubiquitous in our environment and, in fact, they are.

Drs. Van Metre and Mahler use a source identification and apportionment method known as the Chemical Mass-Balance Model (hereinafter CMB) to link the PAHs associated with coal tar sealed parking lots to those found in urban lake sediments. Without the CMB modeling results, there is little basis for anyone to conclude that coal tar sealants are the "dominant" or "most substantial" source of PAH contamination in lake sediment. Thus, if the CMB modeling is in some way flawed, incomplete or inconclusive, then it necessarily follows that the findings published by Drs. Van Metre and Mahler in 40 Lakes Paper must be characterized in the same way. It also follows that the bold and unqualified assertions set forth within the challenged USGS web site and press release would need to be withdrawn or modified significantly to properly reflect the scientific uncertainty that exists.

Specifically, several articles and comments have been published in peer reviewed journals that call into question the precise source identification analysis offered by Drs. Van Metre and Mahler, not only in their 40 Lakes Paper, but in their earlier papers as well.[5] One of the most recent to do so was an article entitled "Forensic Assessment of Refined Tar-Based Sealers as a Source of Polycyclic Aromatic Hydrocarbons (PAHs) in Urban Sediments," published in the journal *Environmental Forensics* in 2012, attached hereto as Exhibit E. Additional scientific critiques have been provided by the PCTC in its White Paper 1301, entitled "Critical Review of USGS Conclusions Regarding Sources of PAHs in Lake Sediments," attached hereto as Exhibit F. The detailed scientific arguments set forth within these materials are incorporated by reference and will not be repeated here. That being said, several crucial themes are worth emphasizing.

First and foremost, even Drs. Van Metre and Mahler acknowledge in their 40 Lakes Paper that the alleged accuracy of the CMB model is dependent upon five crucial assumptions, such as chemical species not reacting with each other or the environment. It goes without saying

[5] See fn 3, supra, Exhibit B.

that if any of the five assumptions are incorrect, then the ultimate conclusions offered by Drs. Van Metre and Mahler are anything but certain. The attached PCTC White Paper explains in detail how all five assumptions are likely to be mistaken, some more than others. This is not surprising since the CMB model is an atmospheric source allocation model and generally is not used to evaluate sediment. Drs. Van Metre and Mahler have done little to demonstrate that their five CMB assumptions in the 40 Lakes Paper are sound. Thus, neither they nor the USGS can proclaim or even suggest that they have in fact proven that "coal tar based pavement sealant is the largest source of polycyclic aromatic hydrocarbons (PAHs) in 40 urban lakes studied by the US Geological Survey." At most, they have presented some data on a hypothesis that requires further testing and analysis.

Second, Drs. Van Metre and Mahler, along with other scientists, have used other types of chemical fingerprinting methods in the past to compare sealant PAHs with those found in sediment. These other methods relied upon the comparison of various PAH ratios. Details are provided in the attached materials referenced above. Suffice it to say that the USGS adaptation of the CMB model was shown to be inconsistent with all other PAH source apportionment methods, thereby generating further uncertainty regarding the accuracy of the CMB model as utilized by Drs. Van Metre and Mahler. Since reproduction of findings is crucial in order to demonstrate the validity of any hypothesis, these inconsistencies cannot be ignored.

Third, one of the most basic procedures available for establishing the validity of a hypothesis is to subject the data collected to the null hypothesis. In other words, have Drs. Van Metre and Mahler demonstrated that the same sediment results could not have occurred in the absence of coal tar sealants? Their answer is no. Quite simply, the null hypothesis was not tested by Drs. Van Metre and Mahler as part of their analysis in the 40 Lakes Paper, or in any other paper that they have published related to coal tar sealants. Thus, they have not eliminated, for example, atmospheric deposition of PAHs as a primary source of sediment contamination, as opposed to coal tar sealant run-off. Again, this issue is explored in detail in the attachments referenced above.

Fourth, other scientists at the USGS have conducted similar types of PAH research in the past and have outlined the steps necessary to go from a hypothesis to scientific proof. For example, in 2001-02, the USGS sought to determine the background levels and sources of PAHs in Chicago ambient surface soil.[6] In doing so, these USGS scientists went through great lengths to describe how sampling sites were randomly and statistically chosen. In the 40 Lake Paper, no such methodology was implemented. Indeed, only nine lakes were "selected" for the entire western portion of the United States, with merely three being in California, and all of them were

[6] See Kay, R., et. al., "Concentrations of Polynuclear Aromatic Hydrocarbons and Inorganic Constituents in Ambient Surface Soils, Chicago, Illinois: 2001-02," USGS and US Dept. of Interior, 2003, attached as Exhibit G.

located in the far southern part of the state. Just one lake was used to represent all of Oregon and two were somehow selected for Washington. Exactly how these six lakes were "statistically" chosen amongst the thousands of lakes that exist within these states is not described in the 40 Lakes Paper, nor was any effort made to identify what types of lakes were even to be included for consideration. For example, a natural lake can differ significantly from a man-made reservoir and a storm water detention pond in terms of age, size, depth, proximity to roads and function (i.e. recreation/fisheries versus designed trapping/filtering of urban run-off and contaminants). Incredibly, in concluding that "sealcoat has been the primary cause of increases in PAHs since the 1960s," Drs. Van Metre and Mahler relied on data from only 8 lakes, two of which were from the Western United States. No one can seriously suggest that this type of analysis is statistically sound. And if it is not, then the limitations of the 40 Lake Paper should have been made public and the need for additional research should have been emphasized, not hidden.

Finally, it must be noted that in the Chicago ambient soil study, the USGS scientists repeatedly subjected their data to a null hypothesis to determine what impact, if any, a variety of factors might have had on their sampling results, such as proximity to highways and industrial sites. As indicated above, this is what sound scientific reasoning requires. Ultimately, these USGS scientists concluded that the distribution of PAHs and benzo(a)pyrene in Chicago soil was "complex" and could not be attributed to any one factor. However, the USGS went on to conclude that the settling of atmospheric particulate matter "is an important source of PAH compounds in ambient Chicago soils." In other words, air emissions from sources such as automobile exhaust and power plants could not be ruled out. Drs. Van Metre and Mahler simply ignored the Chicago study, like they did with the peer reviewed articles that challenged their findings.

BIAS AND LACK OF TRANSPARENCY

A FOIA request related to coal tar sealant research was sent off to the USGS on April 15, 2011. As mentioned above, the request remains "open" more than two years later as the USGS reportedly struggles to decide which of the emails and correspondence marked for exclusion by Drs. Van Metre and Mahler actually need to be produced. These delays are disconcerting since one of the primary reasons for sending off the FOIA request was to assess fully the extent to which advocacy and bias may have slipped into and impacted the USGS research process.

It should be noted that a virtually identical FOIA request was sent to the Minnesota Pollution Control Agency ("MPCA"). This was done because it became apparent several years ago that Drs. Mahler and Van Metre had developed a relationship with a staff member of the MPCA who also shared their interest in banning coal tar sealants. By cross referencing some of emails that were exchanged between the MPCA staff member and the USGS scientists, it would be relatively simple to determine if Drs. Van Metre and Mahler, or their supervisors, were

withholding certain emails and documents from the ongoing USGS FOIA response. A USGS FOIA liaison confirmed in April of 2013 that many such materials were, in fact, being withheld at that time. It remains to be seen if the documents and emails will be voluntarily produced by the USGS in the future.

The MPCA emails seem to confirm that a small group of government researchers began to communicate with one another on the issue of coal tar sealants several years ago and quickly began to share behind closed doors a mutual disdain toward anyone who questioned their beliefs. Such conduct, in and of itself, should be a warning flag. Ultimately, one of the group members became such an extreme advocate that he started an anti-coal tar sealant blog. Other members of the group, which included Drs. Van Metre and Mahler, eventually agreed they should no longer send emails to the blogger at his government job website, but would continue to communicate with him through his private email account. Some of the MPCA emails that provide insights to these relationships can be found attached to correspondence that was sent to the USGA FOIA liaison on March 15, 2013.[7]

The extent to which this group dynamic has permeated and affected the research of Drs. Mahler and Van Metre is not presently known because, as mentioned above, the USGS has produced virtually no emails, correspondence or internal communications from the files of these two scientists. Once a small group of researchers has become personally and professionally vested in offering a new proposition to the scientific community and the public, the need for transparency becomes paramount since it is human nature to see what one wants to see and overlook the rest. Certainly, this precise argument has been directed toward researchers who are funded by industry. Science has recognized this human foible for over a century, which is why government scientists must not only produce all underlying data and methodologies that lead to their conclusions, but they should also produce those emails and correspondence that provide insights as to any biases they may possess, as difficult as that process may be personally. Unfortunately, this type of transparency seems to be in short supply when it comes to USGS research regarding coal tar sealants.

REQUESTED CORRECTIVE ACTION

Since the information promulgated on the web page titled *Coal Tar Sealant Largest Source of PAHs in Lakes* does not meet USGS or OMB guidelines for information quality, the USGS should remove the aforementioned web page from the NAWQA web site. Likewise, it is also important for the USGS to remove the related press release in its entirety. Any failure to do so will adversely affect those members of the PCTC who distribute or apply coal tar sealants

[7] A copy of the March 15, 2013 correspondence is attached hereto as Exhibit H. This correspondence also has attached as an exhibit a copy of the FOIA request that still remains "open" after two years.

since consumers and legislators who are being asked to consider the merits of proposed sealant bans are being misled by the unproven hypotheses and flawed "conclusions" offered by the USGS in these website publications.

If the USGS insists on posting and emphasizing for the public some of the findings set forth with the 40 Lakes Paper, then the USGS Guidelines and Manual mandate that it must be done in a way that accurately and objectively reflects the scientific debate that surrounds the issue of coal tar sealants and their hypothesized contribution to sediment contamination. Should the USGS or its scientists choose to go down this route, the undersigned respectfully requests that the PCTC be permitted to provide its input before anything is posted. Hopefully, this type of review will obviate any need for another DQA challenge. The posting of a new web page would also require the issuance of a new press release that properly describes the limited impact that the 40 Lakes Paper has had on this debate.

Finally, the USGS website "all things sealcoat,"[8] at the very least must include appropriate citations to those peer reviewed articles and related publications that have respectfully and scientifically challenged the findings of the USGS "coal tar sealant" articles authored by Drs. Van Metre and Mahler. [9] An alternative solution is to delete the website altogether so that the public does not mistakenly believe that it reflects an impartial and complete collection of all relevant scientific literature regarding coal tar sealcoating. Clearly, the USGS website has failed in that regard.

Sincerely,

Leonard S. Kurfirst

LSK:cs

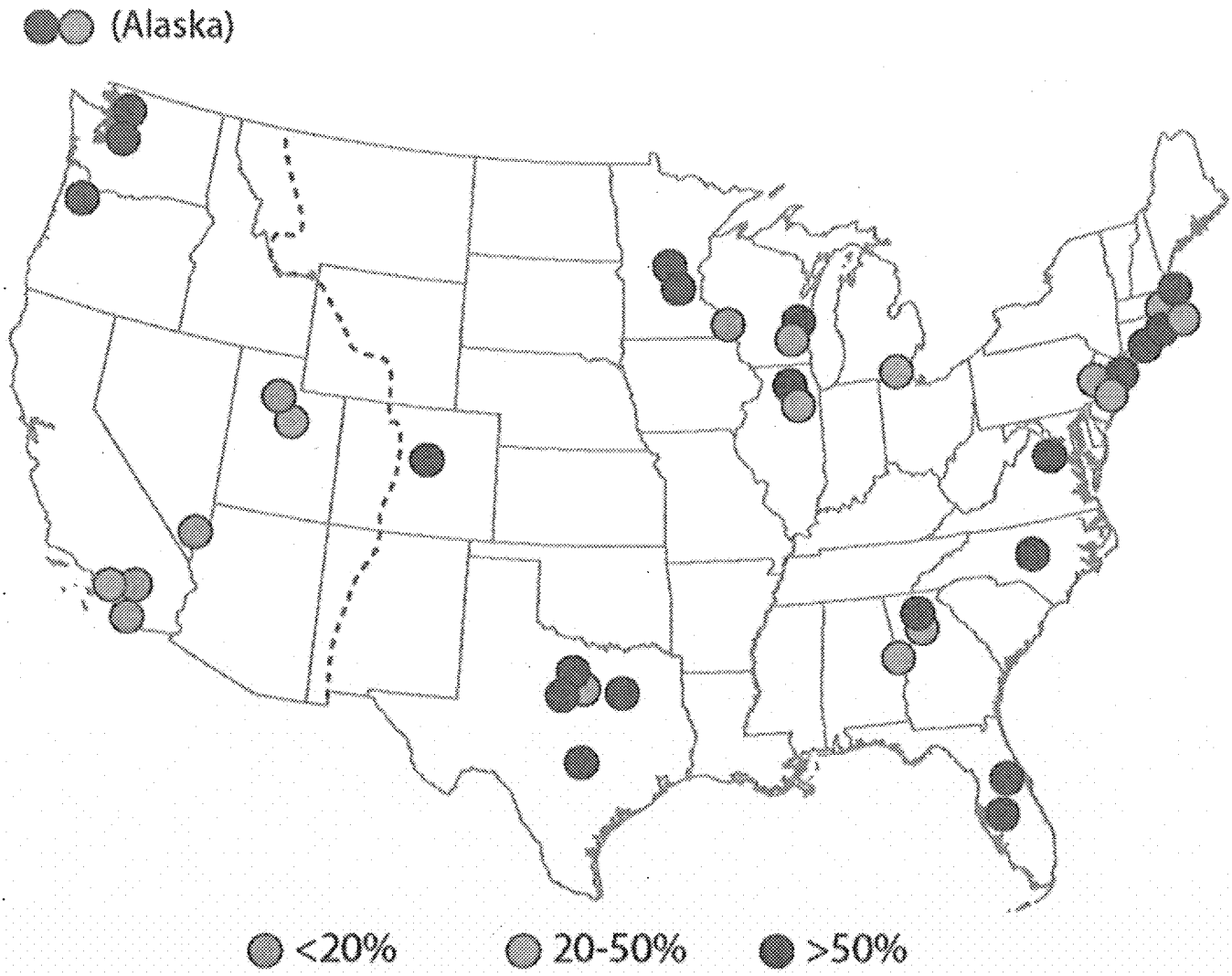
[8] http://tx.usgs.gov/coring/allthingssealcoat.html
[9] See Exhibit B.

Coal Tar Sealant Largest Source of PAHs in Lakes

Coal-tar-based pavement sealant is the largest source of polycyclic aromatic hydrocarbons (PAHs) to 40 urban lakes studied by the U.S. Geological Survey. On average, coal-tar-based sealcoat accounted for one-half of PAHs in the lakes, while vehicle-related sources accounted for about one-quarter. Elevated concentrations are generally associated with those lakes with a large contribution of PAHs from sealcoat, in many cases at levels that can be harmful aquatic life. Historical trends for a subset of studied lakes indicate that sealcoat use has been the primary cause of increases in PAHs since the 1960s.

The study, published in the journal Science of the Total Environment, along with other USGS findings on PAHs are accessible at http://tx.usgs.gov/coring/allthingssealcoat.html.

EXHIBIT A



Percentage of total PAH in recent sediment (post-1990) from coal-tar-based sealcoat

Accessibility FOIA Privacy Policies and Notices
U.S. Department of the Interior | U.S. Geological Survey
URL: http://water.usgs.gov/nawqa/home_maps/sealcoat.html
Page Contact Information: nawqa_whq@usgs.gov
Page Last Modified: Wednesday, 09-Jan-2013 12:09:50 EST

PAVEMENT COATINGS TECHNOLOGY COUNCIL

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PUBLICATIONS OF SCIENTIFIC STUDIES OF TAR-BASED SEALANTS IN THE ENVIRONMENT SPONSORED BY THE PAVEMENT COATINGS TECHNOLOGY COUNCIL

(REV. MAY 2013)

Publications in Refereed Journals:

O'Reilly, K., Pietari, J. and Boehm, P. (2012). A Forensic Assessment of Coal Tar Sealants as a Source of Polycyclic Aromatic Hydrocarbons in Urban Sediments. *Environmental Forensics,* 13:185-196.

O'Reilly, K., Pietari, J. and Boehm, P. (2011). Comment on "PAHs Underfoot: Contaminated Dust from Coal-Tar Sealcoated Pavement is Widespread in the U.S." *Environ. Sci. Technol.*, **2011**, *45* (7), pp 3185–3186

DeMott, R.P., Gauthier, T.D., Wiersema, J.M. and Crenson, G. (2010). PAHs in Austin Sediments after a Ban on Pavement Sealers. *Environmental Forensics*, 11:4, 372-382.

DeMott, R.P.; Gauthier,T.D. (2006) Comment on "Parking lot sealcoat: An unrecognized source of urban polycyclic aromatic hydrocarbons." *Environ. Sci. Technol.* **2006,** *40*(11), 3657-3658

Articles Published in Magazines for Professionals:

Pietari, J., O'Reilly, K. and Boehm, P. (2010). Polycyclic Aromatic Hydrocarbons in Stormwater and Urban Sediments: A Review. *Stormwater* Magazine. September 2010.

Publications and Presentations Submitted and in Preparation

O'Reilly, K., Pietari, J. and Boehm, P. (in preparation). Parsing Pyrogenic PAHs: Forensic Chemistry, Receptor Models, and Source Control Policy. Manuscript in preparation for submission to a refereed journal.

Pietari, J., O'Reilly, K. and Boehm, P. (2013) Parsing Pyrogenic PAHs—Urban Background or Refined Tar Products? Abstract accepted for presentation at the 29th Annual International Conference on Soils, Sediments, Water, and Energy, October 21-24, 2013, Amherst, MA.

O'Reilly, K., Pietari, J. and Boehm, P. (submitted 2013). Use of Receptor Models to Evaluate Sources of PAHs in Sediments. Abstract submitted for presentation at the 24th meeting of the International Symposium on Polycyclic Aromatic Compounds (ISPAC 2013) in Corvallis, Oregon USA September 8-12, 2013.

Magee, B. and Keating-Connolly, Janet (submitted 2013). Risk Assessment for Coal Tar-Based Pavement Sealants. Abstract submitted for presentation at the 24th meeting of the International Symposium on Polycyclic Aromatic Compounds (ISPAC 2013) in Corvallis, Oregon USA September 8-12, 2013.

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EXHIBIT B

PENGAD 800-631-6989

LeHuray, AP (submitted 2013). PAHs are Rare Causes of Impairment in US Clean Water Act Section 303(d) Reports. Abstract submitted for presentation at the 24th meeting of the International Symposium on Polycyclic Aromatic Compounds (ISPAC 2013) in Corvallis, Oregon USA September 8-12, 2013.

Presentations at Scientific Meetings:

O'Reilly K, Pietari J and Boehm P. (2012). Use of Alkyl Polycyclic Aromatic Hydrocarbon Data in Evaluating the Contribution of Pavement Sealers to Urban Sediments. Abstract of presentation at the 2012 annual meeting of the *Society of Environment Toxicology and Chemistry (SETAC).*

Feldpausch, A. and Schoof, R. (2012) Development of a residence-specific, health-based screening criterion for benzo(a)pyrene in indoor dust. Abstract of presentation at the 2012 annual meeting of the *International Society of Exposure Science.*

LeHuray, A.P. (2012). Bans of Pavement Sealers Have Demonstrably Absent Environmental Risk Reduction Benefits but Foreseeable and Knowable Economic Harms. Managing for a Healthy and Sustainable Chesapeake Bay: Human and Ecological Risk: *Joint Meeting of the National Capital Area Chapters of the Society of Environment Toxicology and Chemistry (SETAC) and the Society for Risk Analysis (SRA).* College Park, MD, April 23-24, 2012

O'Reilly, K., Pietari, J. and Boehm, P. (2011). Managing Risks: Will banning pavement sealers have the desired effect? Abstract and Poster Presented at the *32nd Annual Meeting of the Society of Environment Toxicology and Chemistry (SETAC)*, Boston, Nov. 2011.

DeMott, R.P. and Gauthier, T.D. (2011). Use of Mass Balance Bounding Estimates and Sensitivity Analysis to Prioritize PAH Inputs in Urban Systems. Abstract and Poster Presented at the *32nd Annual Meeting of the Society of Environment Toxicology and Chemistry (SETAC)*, Boston, Nov. 2011.

Pietari, J., O'Reilly, K. and Boehm, P. (2011). Environmental Forensics for PAH Source Management: Pavement Sealants and Sediments. Abstract and Poster Presentated at the *Sixth International Conference on Remediation of Contaminated Sediments*, New Orleans, LA Feb. 2011.

O'Reilly, K., Pietari, J. and Boehm, P. (2010). PAHs in Urban Sediments: Forensics Approaches for Assessing the Relative Contribution of Atmospheric Deposition. Abstract and Poster Presented at the *31st Annual Meeting of the Society of Environment Toxicology and Chemistry (SETAC),* Seattle, Nov. 2010.

Gauthier, T.D. and DeMott, R.P. (2008). Analysis of PAH Concentrations Detected in Austin Texas Stream Sediments Following a Ban on the Use of Coal Tar Sealers. Abstract of Presentation Made at the *29th Annual Meeting of the Society of Environmental Toxicology and Chemistry (SETAC),* Tampa, Nov. 2008.

U.S. Geological Survey

Coal Tar Sealant Largest Source of PAHs in Lakes

Released: 12/1/2010 2:59:13 PM

Contact Information:
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Peter Van Metre
Phone: (512) 927-3506

Coal-tar-based pavement sealant is the largest source of polycyclic aromatic hydrocarbons (PAHs) found in 40 urban lakes studied by the U.S. Geological Survey.

PAHs are an environmental health concern because several are probable human carcinogens, they are toxic to fish and other aquatic life, and their concentrations have been increasing in urban lakes in recent decades.

Coal-tar-based pavement sealant is the black, shiny substance sprayed or painted on many parking lots, driveways, and playgrounds. USGS scientists evaluated the contribution of PAHs from many different sources to lakes in cities from Anchorage, Alaska, to Orlando, Fla. The full report can be found in the journal Science of the Total Environment (http://www.sciencedirect.com/science/journal/00489697).

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23 (#)

USGS scientists collected sediment cores from 40 lakes, analyzed the cores for PAHs, and determined the contribution of PAHs from many different sources using a chemical mass-balance model. On average, coal-tar-based sealcoat accounted for one-half of all PAHs in the lakes, while vehicle-related sources accounted for about one-quarter. Lakes with a large contribution of PAHs from sealcoat tended to have high PAH concentrations, in many cases at levels that can be harmful to aquatic life. Analysis of historical trends in PAH sources to a subset of the lakes indicates that sealcoat use since the 1960s is the primary cause of increases in PAH concentrations.

"These findings represent a significant advance in our understanding of the sources of these contaminants in streams and lakes," said USGS scientist Peter Van Metre. "Identifying where contaminants are coming from is the first step in designing effective management strategies."

Coal tar is made up of at least 50 percent PAHs. Pavement sealants that contain coal tar, therefore, have extremely high levels of PAHs compared to other PAH sources such as vehicle emissions, used motor oil, and tire particles. Small particles of sealcoat are worn off of the surface relatively rapidly, especially in areas of high traffic, and are transported from parking lots and driveways to streams and lakes by storm runoff. Manufacturers recommend resealing surfaces every three to five years. Runoff isn't the only path by which PAHs are leaving parking lots. A recent USGS study found that use of coal-tar-based sealcoat on parking lots was associated with elevated concentrations of PAHs in house dust.

Sealcoat products are widely used in the U.S., both commercially and by homeowners. The products are commonly applied to commercial parking lots (including strip malls, schools, churches and shopping centers), residential driveways, apartment complexes and playgrounds. The City of Austin, Texas estimates that before a ban on use of coal-tar-based sealcoat in 2006, about 600,000 gallons of sealcoat were applied every year in the city.

EXHIBIT
C
TENGAD 800-631-6989

Two kinds of sealcoat products are widely used: coal-tar-emulsion based and asphalt-emulsion based. Consumers can determine whether a product contains coal tar by reading the label or asking the company hired to do the pavement application. The coal-tar products have PAH levels about 1,000 times higher than the asphalt products. National use numbers are not available; however, previous research suggests that asphalt-based sealcoat is more commonly used on the West Coast and coal-tar based sealcoat is more commonly used in the Midwest, the South, and the East. The results of the lake study reflect this east-west difference. For example, sealcoat contributes over 80 percent of PAHs in Lake Anne, Va., and PAH concentrations there are about twenty times higher than in Decker Lake, Utah, even though the areas have similar population density and level of urban development. Furthermore, PAH levels in pavement dust from sealcoated parking lots in Va. are about 1,000 times higher than those from sealed parking lots in Utah.

To learn more, visit the USGS National Water Quality Assessment Program (http://water.usgs.gov/nawqa/) website on PAHs and sealcoat. (http://tx.usgs.gov/coring/allthingssealcoat.html)

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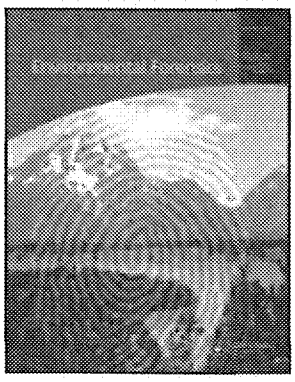

Environmental Forensics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uenf20

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Available online: 07 Jun 2012

To cite this article: Kirk O'Reilly, Jaana Pietari & Paul Boehm (2012): Forensic Assessment of Refined Tar-Based Sealers as a Source of Polycyclic Aromatic Hydrocarbons (PAHs) in Urban Sediments, Environmental Forensics, 13:2, 185-196

To link to this article: http://dx.doi.org/10.1080/15275922.2012.676598

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Environmental Forensics, 13:185–196, 2012
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ISSN: 1527-5922 print / 1527-5930 online
DOI: 10.1080/15275922.2012.676598

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Forensic Assessment of Refined Tar-Based Sealers as a Source of Polycyclic Aromatic Hydrocarbons (PAHs) in Urban Sediments

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Atmospheric deposition of particles and their subsequent transport by stormwater are a major source of polycyclic aromatic hydrocarbons (PAHs) in urban sediments. Recently, the results of forensic analysis have been used to promote a hypothesis that refined tar-based pavement sealers (RT-sealers) are another significant source. To evaluate this hypothesis, a suite of forensic methods was applied to a wider range of PAH data for this study. Sediments PAH profiles are no more similar to RT-sealers than they are to a number of other environmental inputs. While RT-sealers were not eliminated as a potential source in some locations, forensic methods did not differentiate their contribution from other sources of PAHs, indicating RT-sealers are not a unique or readily quantifiable source of PAHs to the urban environment.

Keywords: polycyclic aromatic hydrocarbons (PAHs), coal tar, refined tar, pavement sealers, sediments

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Polycyclic aromatic hydrocarbon compounds (PAHs) are ubiquitous in the environment and are commonly found in aquatic sediments (Stout et al., 2004; Rodenburg et al., 2010). Given the multitude of natural and anthropogenic sources that may contribute PAH compounds to sediments, identifying and characterizing PAH sources has been the subject of significant research. Efforts to evaluate contributions of various petrogenic (fossil fuel-derived) and pyrogenic (high temperature and combustion-derived) sources have consistently identified atmospheric deposition as a significant source of PAHs to soils, paved areas, and sediments in most urban environments (Hwang and Foster, 2006; Li et al., 2003; Lima et al., 2005; Simcik et al., 1996; Stein et al., 2006; Su et al., 2000; Van Metre et al., 2000; Yunker et al., 2002). Specifically, the higher molecular weight PAHs typical of combustion-derived particulate matter, consistent with motor exhaust, coal combustion products, or wood smoke, have been found to dominate PAH profiles in sediments that are impacted by "urban background" sources (Stout et al., 2004).

A number of studies have demonstrated a link between atmospheric sources and PAHs in sediments. Evaluation of PAH chemistry in sediment from lakes, creeks, and reservoirs from across the United States report temporal links between changes in PAH concentrations and increased automobile use and vehicle emissions (Simcik et al., 1996; Stein et al., 2006; Su et al., 2000; Van Metre et al., 2000; Dickhut et al., 2000). In the upper Midwest, the mass and chemistry of PAHs in lake sediment could be linked to specific atmospheric sources associated with activities such as steel production and motor vehicle use (Su et al., 2000, Simcik et al., 1999). Automotive emissions have been shown to be a major source of particulate PAHs in aquatic systems in the Los Angeles basin (Stein et al., 2006) and San Francisco Bay Area (Tsai et al., 2002). Yunker et al., (2002) demonstrated a link between sediment chemistry and atmospheric sources throughout a regional watershed.

Since 2005, several studies have hypothesized that refined tar-based pavement sealer (RT-sealer) is another potentially significant source of PAHs to urban sediment (Mahler et al. 2005; Van Metre et al., 2009; Yang et al., 2010; Van Metre and Mahler 2010; 2011; Watts et al., 2010). The hypothesis is based on observations of elevated concentrations of PAHs in particles and runoff associated with RT sealer-treated parking lots and comparison of PAH compositions in sediment and potential source samples. Mahler et al. (2005) presented data suggesting that mean PAH concentrations of particles (μg PAH per kg particle) associated with RT-sealed parking lots was up to 65 times as high as the concentration of particles associated with non-sealed lots. During artificial rainfall events, the mean yield (μg PAH/m^2) within sealed lots was up to 44 times that of the unsealed lots. Offsite flux during actual rain events was not measured, but PAH concentrations decreased with distance from the source (McClintock et al., 2005). In a study conducted by a different USGS research team (Selbig, 2009), the mean PAH concentration (μg/L) in actual runoff from a sealed lot was six times that of an unsealed lot, but less than 2.5 times the concentration of runoff from a local roadway. Maximum total PAH

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concentrations for runoff from the sealed lot, 96 μg/L, and roadway, 98μg/L, were similar.

Three PAH diagnostic ratios, fluoranthene (Fl)/pyrene (Py), benzo[a]pyrene (BaP)/benzo[e]pyrene (BeP), and indeno[1,2,3-cd]pyrene (IDP)/benzo[ghi]perylene (BGP), were used to indicate similarities and differences between parking lot and sediment sample chemistries (Mahler et al., 2005; Van Metre et al. 2009). While there were overlaps in the observed ratios for the sealed lot particles and sediments, other potential sources that often have similar ratios were not considered. As noted by DeMott and Gauthier (2006), ratios did not overlap between lots and sediments from the same urban area.

Van Metre et al. (2009) evaluated PAH concentrations and composition of parking lot samples and sediments from 10 urban watersheds. Higher particulate PAH concentrations measured in dust collected from sealed lots in the eastern United States compared to the west were attributed to a greater use of RT-sealers in the east. Independent data on the relative use of sealer types by region were not presented. A Fl/Py versus BaP/BeP double ratio plot was used to suggest similarities between eastern sediments and particles from RT–sealed lots.

In Van Metre and Mahler (2010), the United States Environmental Protection Agency (US EPA) chemical mass balance (CMB; Coulter, 2004) model was used to estimate the relative contribution of RT-sealers versus other PAH sources in the sediments of 40 urban lakes. The model inputs were the PAH profiles of five standardized source types including RT-sealers, vehicle emissions, and wood, oil, and coal combustion-related samples. Two significant problems exist with the RT-sealer inputs used in the model. First, the authors admit that they assumed the parking lots sampled were treated with RT-sealer, and secondly, the data were prescreened to select inputs that were the most statistically similar to the sediment data set. Coal- and vehicle emissions-related source types were not the results of individual samples, but the averages of data from the literature. It appears that the averages were calculated by summing the published average concentrations of subclasses of coal or vehicle emission sources and then dividing by the total number of published sources. Because this approach results in weighting the influence of each subclass by numbers of publication, and not by their environmental contribution, it is unclear that the calculated value represents any real source. The authors of this study have concerns about the results of this PAH apportionment exercise because it appears that model requirements of source sufficiency and stability were violated (Galarneau, 2008; US EPA, 2004). These critical assumptions for receptor models require that all potential significant sources have been considered, and that the chemistries of the identified sources are stable. The use of source chemistry at the point of emission instead of atmospheric deposition ignores the effect of chemical reactions that are known to occur in the atmosphere (Galarneau, 2008; Katsoyiannis et al., 2011; Ravindra et al., 2008). Atmospheric reactions such as photolytic decay, with half-lives as short as 1 or 2 hours, and processes including nonequilibrium gas/particle partitioning complicate the application of receptor models for PAH source apportionment (Gordon, 1988). Models such as the CMB do not identify sources, but only statistically fit mixtures of sources identified by the modeler to receptor chemistry, so they have been described as "biased by *a priori* assumptions as to the number and nature of the contributing sources" (Galarneau, 2008, p. 8146).

Because of uncertainties associated with the results of any one single method, it is important to develop multiple lines of evidence when using environmental forensics to characterize source contributions (Stout and Graan, 2010). This approach is especially true when potential sources have similar chemistries such as those consisting of largely weathered pyrogenic PAHs. The goal of this study is to evaluate the hypothesis concerning the role of RT-sealers as a source of PAHs in urban sediments by applying multiple methods and considering a wider range of environmental samples representing potential contributing inputs. Possible outcomes of such analyses are that the results either support the hypothesis that RT-sealers are a dominant source of sediment PAHs (Mahler et al., 2005), fail to support it, or disprove the hypothesis. Results that fail to support a hypothesis do not mean it is incorrect, only that other explanations can account for the observed effects.

Experimental Section

Environmental chemical forensic methods are based on comparing the chemistry of the medium of interest, in this case sediment, with the chemistries of potential sources (Li et al., 2003; Su et al., 2000; Burns et al., 1997). For sediments, the term *source* can have two meanings, one of which is the *processes that create the chemicals of interest*, such as coal combustion or vehicle emissions; the second describes the *particulate matter that transports chemicals from the broader environment to sediments*. Each has advantages and disadvantages in source allocation. While there may be a better understanding of the processes resulting in the emission sources, they can be site specific and do not account for changes that may occur between the source location and sediment. The opposite is true for environmental particles: Whereas all the processes resulting in the observed PAH chemistry may not be understood; they better represent results of both generation and fate. Because of uncertainties in primary source characteristics and the changes that occur as a result of reactions in the atmosphere (Gordon, 1988; Galarneau, 2008; Ravindra et al., 2008; Golomb et al., 2001), data on a range of environmental particulate materials were evaluated as potential sources of PAHs. These sources included fresh RT-sealer, particles from RT-sealed lots, atmospheric particles, coal combustion and traffic related emissions, road dirt, roof dust, urban soil, and highway runoff. PAH data for both sediments and sources were compiled from the literature. Asphalt-based sealers were not included in this study because they have not been suggested as a significant source of PAHs (Mahler et al., 2005). A list of the data sets used is shown in Table 1. Except for fresh sealer material and a coal tar standard, the data were derived from analysis of environmental

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Table 1. Data sources used in this evaluation

Material	Reference	n [a]	PAH16? [b]	Fl/Py[c] Min	Fl/Py[c] Max	ID/BgP[d] Min	ID/BgP[d] Max
Coal tar	1 NIST 1597a [e]	1	Y	1.36		1.10	
Refined tar-based pavement (RT) products	2 Mahler et al. (2005)	6	Y	1.26	1.30	0.77	0.81
RT-sealed lots	3 Mahler et al. (2004)	20	Y	1.24	1.66	0.82	1.48
	4 Selbig (2009)	15	Y	1.26	1.64	0.82	0.95
Air particles	5 NIST 1649b [e]	1	Y	1.25		0.77	
	6 Simcik et al. (1999)	2[f]	N	1.18	1.25	0.85	1.29
	7 Li et al. (2003)	6[g]	Y	0.58	2.52	0.25	1.18
Roofs	8 Van Metre and Mahler (2003)	6	N	1.18	1.27	NA	NA
	9 Selbig (2009)	8	Y	1.23	1.30	0.81	1.00
Roads	10 Van Metre and Mahler (2003)	3	N	1.18	1.38	NA	NA
	11 Selbig (2009)	11	Y	1.28	1.67	0.78	0.95
	12 Breault et al. (2005)	5	N	1.27	1.52	0.61	1.38
Soils	13 Wilson et al. (2006)	6	Y	1.12	1.34	1.06	1.57
	14 Polta et al. (2006)	4	Y	0.40	1.10	0.50	1.00
Sediments	15 Wilson et al. (2006)	12	Y	1.23	1.42	0.90	1.18
	16 Polta et al. (2006)	50	Y	0.00	1.42	0.19	3.00
	17 Van Metre et al. (2009)	8	Y	0.66	1.48	0.47	1.55
	18 Van Metre and Mahler. (2010)	40[h]	N	0.72	1.52	0.55	1.78

Note: NA = Not measured
[a] Number of samples
[b] Does data set include all 16 of the priority pollutant PAHs yes (y) or no (n)?
[c] Fluoranthene / pyrene ratio
[d] Indeno[1,2,3-cd]pyrene / benzo[ghi]perylene ratio
[e] National Institute of Standards and Technology (NIST), Gaithersburg, MD
[f] Both results are the mean of multiple samples from Figure 2 in Simcik et al. (1999).
[g] Each sample represents an average of multiple samples for both traffic and coal combustion–related emissions.
[h] Each sample presents an average of three samples.

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samples. While most of the studies analyzed particles, some such as Selbig (2009) analyzed unfiltered runoff, which would include both dissolved and particulate-associated constituents. Because organic carbon/water partitioning coefficients for the compounds used in the forensic analysis range from 10^4 to more than 10^6 (Hawthorne et al., 2007), the PAH profiles of the unfiltered samples were assumed to represent the particulate phase. Particulate bound PAHs have been shown to dominate over the dissolved phase compounds in environmental samples (Hwang and Foster, 2006).

The exact number and identity of PAH compounds analyzed differed among the studies evaluated, but typically most or all of PAHs of the 16 priority pollutant of the US EPA were included. Because of detection limit issues, fewer PAHs were reported in some cases. Individual sample data were typically available, but in some cases results were reported as the mean of a set of samples (Simcik et al., 1999; Li et al., 2003; Van Metre and Mahler, 2010). Where a concentration was listed as an estimated value or qualified with "J," it was included in the forensic analysis. To avoid skewing results based on detection limit issues, individual samples were excluded from the analysis if fewer than ten PAHs were detected. PAH diagnostic ratios were not calculated for samples where an analyte of interest was undetected. To standardize results of analysis among samples of different media and different contaminant levels, individual compound concentrations were converted to the relative fraction of the total PAHs, Ci, where the concentration of each compound, $[\mathrm{PAH}]i$, is divided by the sum of the individual PAH concentrations, as shown in Equation (1):

$$Ci = [\mathrm{PAH}]i / \Sigma\mathrm{PAH}x \quad (1)$$

Forensic Analysis

The data evaluation included diagnostic double ratio plots, (Boehm, 2006; Mahler et al., 2005) where the ratio of two PAHs was plotted on the x-axis and the ratio of a second pair of PAHs was plotted on the y-axis. Potential differences were identified by comparing the coordinates of samples to each other, to known sources, and to published values. Based on Mahler et al. (2005), the two PAH diagnostic ratios selected were the 4-ringed compounds Fl and Py and the 6-ringed IDP and BgP. Both ratios are commonly used in the PAH forensic literature to identify sediment sources (Stout et al., 2004; Yunker et al., 2002). While BaP/BeP has also been used to evaluate the influence of coal tars (Mahler et al., 2005; Van Metre et al., 2009), BeP data are available in fewer published studies because BeP is not one of the priority pollutant PAHs. When using double-ratio plots for source identification, it is critical to include an appropriate range of potential source materials to minimize the chance of misidentification (Yunker et al., 2002).

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Pearson correlations were used to evaluate the similarities between sediments and sources (Yang et al., 2010; Van Metre and Mahler, 2010). For each sample pair, the *Ci*-values of each compound in one sample were set as the x values, while the *Ci*-values of each compound of the paired sample were set as the corresponding y values. The average *Ci* result of each source type was used. The student *t* test was used to compare data sets consisting of the *r* values between each source and sediments from 40 urban lakes with the null hypothesis that the mean of the Pearson's correlation population for each source type was the same with 95% confidence level. The Pearson correlation *r* was determined using statistical algorithms in Microsoft Excel 2007 (Microsoft, Redmond, WA) Pro-UCL (EPA, Washington, DC) was used to conduct the *t* tests.

Principal component analysis (PCA) is a statistical technique commonly used to compare sediment samples and suspected source materials (Stout and Graan, 2010; Sofowote et al., 2008). The objective of PCA is to reduce the dimensionality of data sets with a number of interrelated variables by transforming the data into uncorrelated principal components that account for the observed variance (Johnson et al., 2007). By plotting the results of each sample against the primary and secondary factors, more and less similar samples are identified. PCA also allows for identification of the compounds that contribute to the observed differences between the samples. To allow inclusion of sediment data from Van Metre and Mahler (2010), 11 priority pollutant PAHs were used as the input. PCA was conducted using Systat 12 (Systat Software, Chicago, IL).

The receptor model Unmix 6.0 (Norris et al., 2007) was used to evaluate the sediment data presented in Van Metre and Mahler (2010). The inputs were either the 120 samples from 40 lakes (3 samples per lake) or the 122 samples from the extended analysis of eight of these lakes (12–19 samples per lake). Unmix solves a general mixture problem where the data are assumed to be a positive linear combination of an unknown number of sources of unknown composition. Using concentration data for a given selection of chemical species, the model estimates the number of sources, source compositions, and source contributions to each sample (Norris et al., 2007). Like the CMB, Unmix was developed to evaluate atmospheric sources for air pollution monitoring, but similar approaches have been used to evaluate sediment source data (Bzdusek et al., 2004). A critical difference between the two models is that the chemistry of potential sources is not an input to Unmix.

Results and Discussion

The results of forensic analysis depend on the chemistry of the samples considered, so it is important to understand the overall nature of the PAH chemistry. Evaluation of the PAH concentration histograms can suggest whether a sample contained PAHs from a petrogenic or pyrogenic source(s) and whether the sample had weathered. PAH histograms also provide qualitative information about similarities and differences between samples and sources. Challenges arise when potential sources are similar, as it possible to misattribute the contribution of these sources.

Figure 1 contains average compositional PAH histograms for a number of environmental inputs and urban sediments. The three sediments and the modeled RT-sealer contribution are from Van Metre and Mahler (2010). The similarity among the different source types stands out, especially in the patterns of the 4- to 6-ringed compounds. This pattern is consistent with PAHs originating from pyrogenic sources. The patterns for all these materials are well known in the sediment literature, and are consistent with what is typically called "urban background" (Stout et al., 2004, p. 2987). Similarities between RT-sealers and other environmental samples are not surprising, even if sealers are not the source, because this pattern represents the balance between the relative forces that generate and decay PAHs.

The histograms indicate that fresh refined tar-based sealers have a greater concentration of the lower molecular weight PAH compounds such as naphthalene, acenaphthene, fluorene, and anthracene than environmental samples from studies listed in Table 1. These four lower molecular weight PAHs are depleted relative to the fresh product in most samples, including dust collected at lots sealed with refined tar-based sealers. Differences in PAH compositional patterns of fresh product and samples from sealed lots can be explained by the weathering of the lighter compounds (Burns et al., 1997).

Double-ratio plots for 40 urban lakes, RT-sealed lots, and other environmental sample types are shown in Figure 2. Table 1 shows the range of diagnostic ratios for each sample type. A regional trend is observed in these lake sediments, with samples from the central United States more toward the upper right corner, samples from the west toward the lower left, and eastern samples between the two. Van Metre et al. (2009) suggested that such a trend could be explained by an unreferenced claim of lower use of RT-sealers in the west compared to the other two regions (Van Metre et al., 2009). Other regional differences, such as the concentration of coal-based electricity generation, might also account for the results. The apparent regional trend may be an experimental artifact. In another study, 50 samples collected from 10 ponds in a single metropolitan area (Polta et al., 2006) had a similar range of ratios as those from the three regions (Figure 3).

To more closely evaluate the double ratio results of the RT-sealer and other environmental samples, sediment data were removed from Figure 4. Samples from RT-sealed lots in Texas and Wisconsin grouped closely with material such as roof dust and highway runoff. While the possibility of the presence of some sealer in these materials cannot be eliminated, it seems unlikely for the roof dust, which is not in direct contact with tires that might have driven on sealed pavement. If just these two diagnostic ratios are considered, one could argue that there may be more similarity between the test plot samples with freshly applied sealer and the sediment samples from the central United States, but forensic evaluation requires the use of multiple methods and, as will be seen in the PCA result, unique chemical

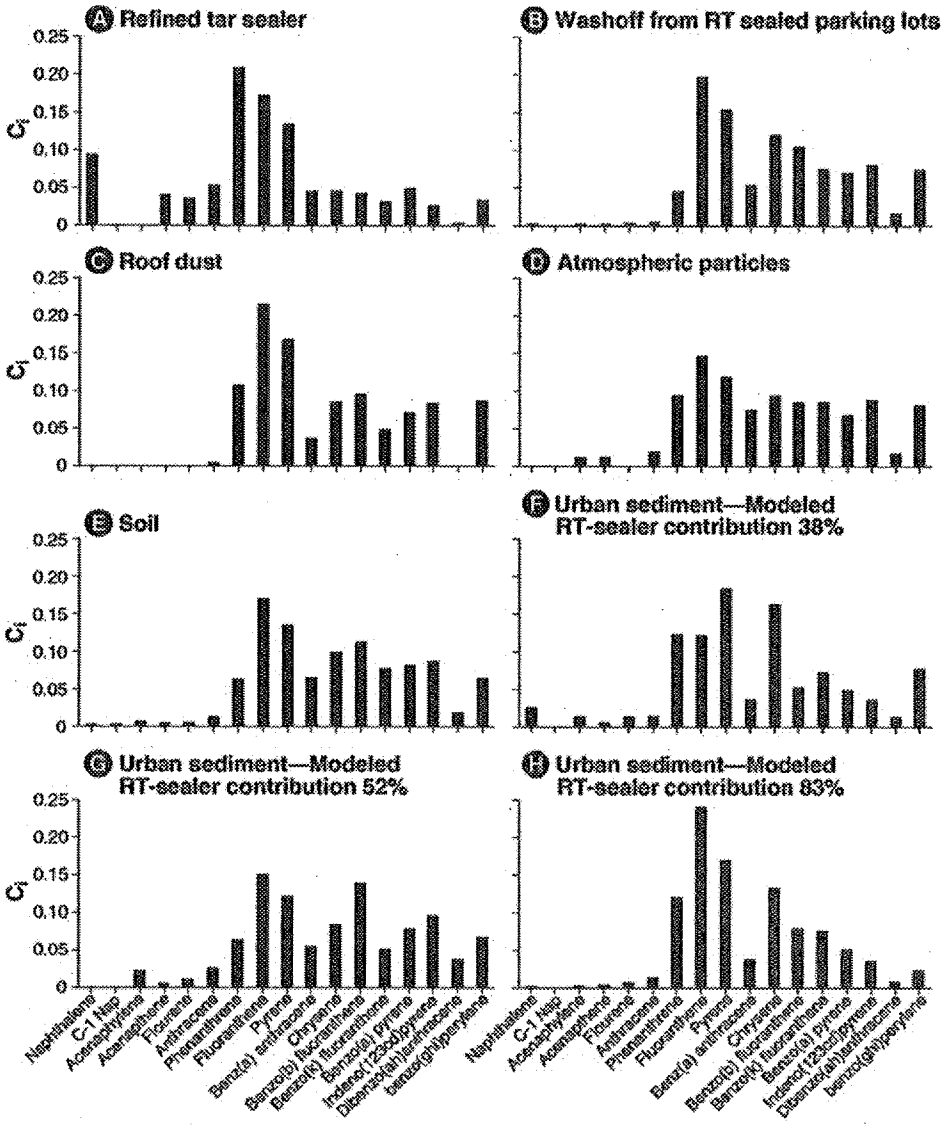

Figure 1. Polycyclic aromatic hydrocarbons (PAHs) concentration histograms for five environmental inputs and three urban sediments. The modeled refined tar-based pavement sealers (RT-sealers) contribution is from Van Metre and Mahler (2010).

similarity between sealers and sediment samples from the central United States is not supported.

In prior studies (Mahler et al., 2005; Van Metre et al., 2009), PAH ratio and double ratio analyses have been a primary forensic methods applied to evaluate the hypothesis concerning sealers. Because of uncertainties introduced by overlapping ranges for various sources, these types of ratio analyses are more useful for distinguishing between clearly different sources (such as petrogenic and pyrogenic) than for differentiating among similar ones such as a wide variety of pyrogenic sources of PAHs (Stout et al., 2004; Boehm, 2006). A number of combustion sources have been shown to have Fl/Py ratios consistent with the range for coal tar and RT-sealers reported by others and included in this paper (Costa and Sauer, 2005; Lima et al., 2005; Yunker et al. 2002). All appropriate potential sources must be included when evaluating the relative contribution of each to environmental sinks such as sediment. Yunker et al. (2002) considered more than 20 source classes and a variety of chemical ratios in an attempt to link combustion sources to sediment chemistry throughout a regional watershed, and argued that a limited assessment can result in misleading relationships between PAH sources and sinks. In another study, 18 potential source types were considered when evaluating the origin of PAHs in sediment samples (Burns et al., 1997).

The results of the CMB model (Van Metre and Mahler, 2010) and double ratio analyses are combined in Figure 5. If results of the CMB model were consistent with results of the double ratio method, one would expect there to be a relationship

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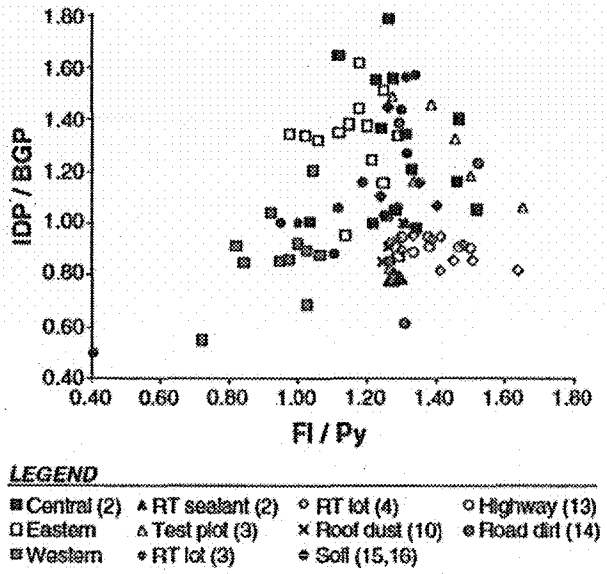

Figure 2. Polycyclic aromatic hydrocarbon (PAH) double-ratio plot comparing urban sediments with RT sealer, dust from sealed parking lots, atmospheric particles, roof dust, road runoff, and urban sediments. The sediments are classified by regions as identified in Van Metre and Mahler (2010). The numbers in parenthesis refer to the reference in Table 1.

between the PAH ratios and modeled fraction of sealer contribution. No relationship was noted as samples within each of four classes of percent RT-sealer contribution were calculated using the CMB model (≤25%, 26–50%, 51–75%, ≥76%) are spread across the range of PAH ratios. A similar lack of consistency has also been demonstrated between CMB results and the diagnostic PAH ratios Fl/Py versus BaP/BeP (O'Reilly et al., 2011).

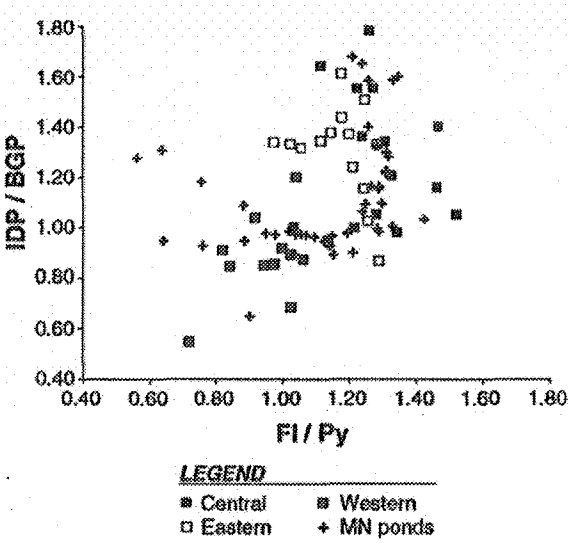

Figure 3. The range of polycyclic aromatic hydrocarbon (PAH) ratios for 10 ponds from one metropolitan area is similar to the range for samples taken across the country.

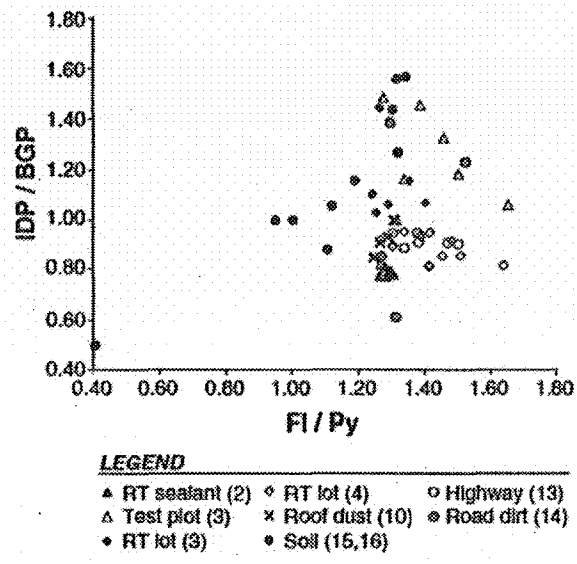

Figure 4. Double-ratio plot highlighting the similarities between environmental samples that may represent sources of polycyclic aromatic hydrocarbons (PAHs) to urban sediments. The numbers in parenthesis refer to the reference in Table 1.

Based on the selection of sources, it is not surprising that CMB results suggest that sealers are a major contributor to sediments. As noted by the authors, for most model runs they selected sealer sources for which they only assumed the presence of sealer, and of which the average Pearson coefficient (r) between source and the 40 lake sediments was greater than 0.95. The remaining sources had r of 0.83 (wood smoke), 0.67 (tunnel air), 0.55 (coal emissions), and 0.43 (fuel oil combustion). Sealer sources with average Pearson coefficients of 0.62, 0.55, and 0.38 were reported by the authors but the results of CMB modeling with these sources were not presented (Van Metre and Mahler, 2010). Using the compiled data set showed similar

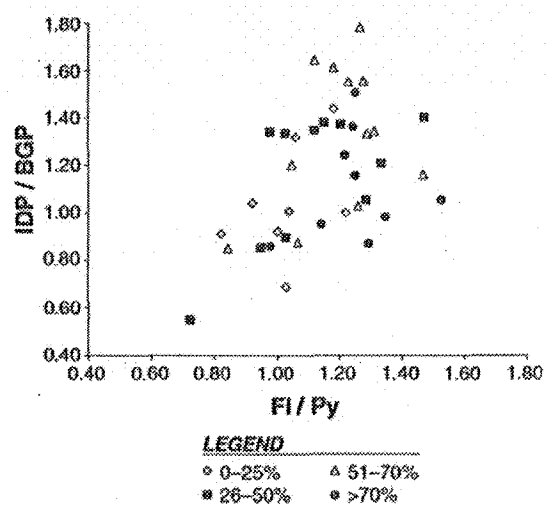

Figure 5. Comparison of double-ratio plot results to chemical mass balance (CMB) model output.

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Table 2. *t-test[a] results for comparison of Pearson coefficients for each lake sediment and source type.*

		Product ($n = 6$)	IL Air ($n = 2$)	WI Roof ($n = 8$)	WI Lots ($n = 7$)	WI Highway ($n = 11$)	Texas Soil ($n = 6$)	Texas Lots ($n = 8$)	Texas Test Plots ($n = 8$)
Reference # from Table 1	Average r (Range)	0.32 (−0.3–0.69)	0.78 (0.27–0.95)	0.76 (0.42–0.93)	0.75 (0.33–0.91)	0.89 (0.24–0.99)	0.82 (0.48–0.94)	0.88 (0.28–0.99)	0.77 (0.07–0.96)
2	Product ($n = 6$)		Different ($p = 0.000$)	Different ($p = 0.000$)	Different ($p = 0.000$)	Different ($p = 0.000$)	Different ($p = 0.000$)	Different ($p = 0.000$)	Different ($p = 0.000$)
6	IL Air ($n = 2$)			*Same* *($p = 0.618$)*	*Same* *($p = 0.533$)*	Different ($p = 0.026$)	Different ($p = 0.000$)	Different ($p = 0.000$)	*Same* *($p = 0.934$)*
9	WI Roof ($n = 8$)				*Same* *($p = 0.308$)*	Different ($p = 0.011$)	Different ($p = 0.000$)	Different ($p = 0.000$)	*Same* *($p = 0.644$)*
4	WI Lots ($n = 7$)					*Same* *($p = 0.188$)*	Different ($p = 0.002$)	Different ($p = 0.003$)	*Same* *($p = 0.678$)*
11	WI Highway ($n = 11$)						Different ($p = 0.023$)	Different ($p = 0.041$)	*Same* *($p = 0.115$)*
13	Texas Soil ($n = 6$)							*Same* *($p = 0.776$)*	Different ($p = 0.001$)
3	Texas Lots ($n = 8$)								Different ($p = 0.003$)
3	Texas Test Plots ($n = 8$)								

[a] The comparison of Pearson's coefficients of each source and sediment by source type was based on the null hypothesis that the means of populations of the Pearson's coefficients for each source type are the same.

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r values for soils from Fort Worth, TX (0.89), sealed lot dust from Austin, TX (0.88), and highway runoff from Madison, WI (0.82). The average r was also similar between sediments and sealed lot dust from Madison (0.75), sealer test plots in Austin (0.77), atmospheric particles from Chicago, IL (0.78), and roof dust from Madison (0.76). To further compare how these sources correlate with lake sediments, data sets consisting of the Pearson coefficient between each source and all 40 lakes were generated for the seven sources. Similarity between these data sets was evaluated using the student t test (Table 2). Consistent with the null hypothesis, no statistical difference was shown between the Pearson coefficients for each lake sediment and Austin sealed lots or Fort Worth soil, or between the sediments and Madison sealed lots, roof dust, highway runoff, and test plots in Austin. These results highlight the potential for biasing the outcome of receptor modeling by limiting the potential sources (Galarneau, 2008), and prescreening inputs to select specific source characteristics.

Whether using PAH ratios or more advanced receptor modeling such as the CMB, there are a number of challenges in linking PAHs in sediments to particular sources. A critical assumption in both modeling and forensic ratio analyses is that all potential significant sources have been considered, and that the chemistries of the identified sources are stable (Galarneau, 2008; Stout and Graan, 2010). To minimize these concerns, some investigators include ten or more well characterized sources even when applying receptor models to a single area (Boehm et al. 2001; Burns et al., 2006). Van Metre and Mahler (2010) focus on results from model runs where the inputs for RT-sealers were prescreened and only four other source types were used. As some of these other inputs were the geometric means of literature data compiled by another author, it is not possible to know how representative they are to actual source chemistries.

As described in a recent review (Galarneau, 2008) highlighting the potential pitfalls of PAH source apportionment, the use of source chemistry profiles based on samples collected near the point of emission fails to take into consideration changes caused by a variety of processes that affect the source material after environmental release, such as phase partitioning, differential settling, and photochemical-biodegradative reactions. Not only have these processes been shown to modify PAH profiles (Ravindra et al., 2008), they are of particular concern with PAHs because of differences in source characteristics, reactivity, and transport based on particulate size. Even within atmospheric studies, the use of emission chemistry in PAH source allocation may only be appropriate under limited conditions (Katsoyiannis et al., 2011). Because PAH profiles are known to change between emission and deposition in sediments, inclusion of decay rates should be considered when applying receptor models (Golomb et al., 2001; Xue et al., 2010).

A difference between multivariate methods, such as PCA or Unmix, and the CMB model is that pre-selection of a potential source is not required. The results of PCA using the entire sample set are presented in Figure 6. Sediment samples from Van Metre and Mahler (2010) are identified by the relative fraction of sealer contribution estimated by CMB. A first step in evaluating PCA is to review the factor-loading chart that indicates the influence of the individual compounds. As shown in Figure 7a, the less stable 3-ringed PAHs are in the upper left quadrant whereas the more stable 6-ringed compounds are toward the lower right.. The 4-ringed PAHs are spread perpendicular to the line between the 3- and 6-ringed compounds, with the 5-ringed group toward the right. This finding suggests that weathering

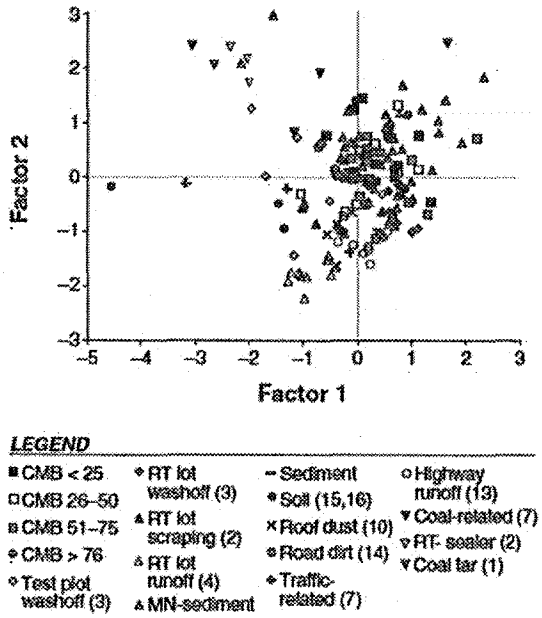

Figure 6. Principal component analysis of samples from refined tar-based pavement sealed (RT-sealed) parking lots, atmospheric particles, roof dust, road runoff, and urban sediments. The sediments are separated by results of the CMB model. Factors 1 and 2 explained 31 and 17% of variance, respectively. The numbers in parenthesis refer to the reference in Table 1.

will result in a trend from the upper left toward the lower right. Such a trend is seen with the known RT-sealer samples with the fresher materials toward the upper left and the more aged toward the lower right quadrant (Figure 7b). The use of weathered sealer samples and unweathered emission source samples as CMB inputs may have skewed the output toward a higher estimated sealer contribution.

To allow clearer comparison of the various environmental inputs, Figure 8 shows the same information as Figure 6 but with most sediment samples removed. Samples from the sealed lots, and many of those from roof dust, soil, and highway runoff are in the lower half near the center of the plot. While some sediment samples overlap with all these sample types, most sediment results are in the upper right quadrant. Looking at the

Table 3. Pearson coefficients between potential environmental sources and the source profiles determined by Unmix using the 40 and eight lakes sample sets from Van Metre and Mahler (2010). The highest coefficient with each Unmix source profile is bolded.

Source	40LS1	40LS2	8LS1	8LS2	8LS3
Coal-related	0.05	**0.86**	0.65	0.53	**0.91**
Traffic-related	0.52	0.69	0.70	0.70	0.76
Wood	0.34	0.80	0.68	0.62	0.86
Fuel oil	**0.78**	0.29	0.68	0.54	0.33
Texas lot dust	0.52	0.84	0.82	0.84	0.86
Highway	0.70	0.68	**0.86**	0.83	0.73
Roof dust	0.66	0.69	0.84	0.78	0.75
Soil	0.44	0.89	0.82	**0.89**	0.89
Coal tar sealant	0.37	0.79	0.76	0.59	0.86

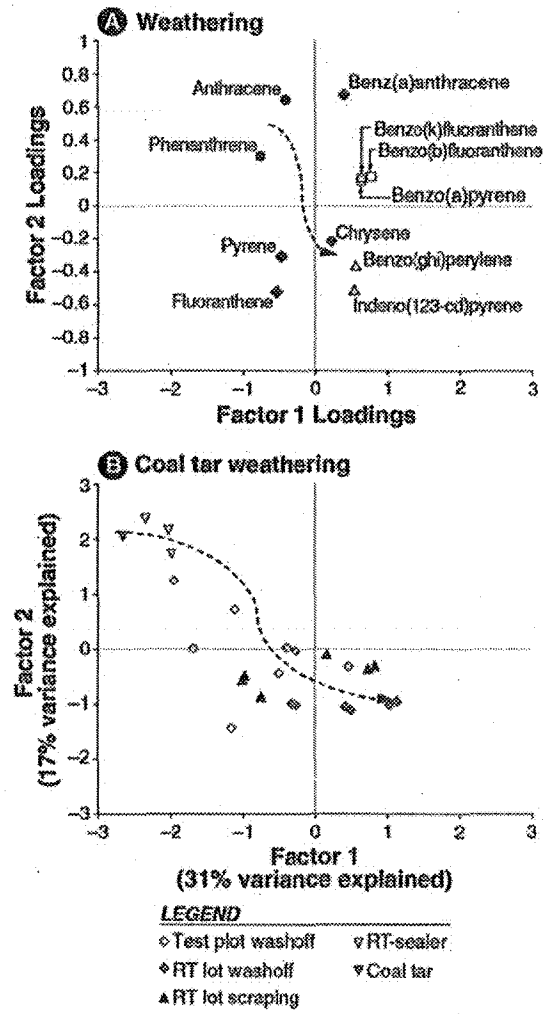

Figure 7. Illustration of impact of weathering of coal tar and refined tar-based pavement sealant (RT-sealant): (a) loadings for factors 1 and 2 for PCA shown in Figure 6; and (b) plot of factors 1 and 2 including only the coal tar and RT-sealant samples.

results from the 40 lake sediments, there might be a trend with samples having a lower modeled sealer contribution being more in the upper right quadrant, and samples with greater modeled contribution being in the lower right, but as with the double ratio plots, there is overlap among all four groups. The PCA results do not support the finding of a regional trend in sediment chemistry suggested by ratio analysis (Figure 9), or that sealers are a unique source of PAHs in sediments.

Unmix was unable to find a solution using 12 PAHs, but could find solutions if the three-ringed phenanthrene and anthracene were excluded. Two source profiles were identified for the 40 lakes sample set and three sources for the 8 lake samples (Figure 10). The two source profiles from the 40 lakes set are similar, with Source 1 having a greater fraction of IDP and BGP. The characteristics of Sources 1 and 2 of the 8 lake data results are even more similar, falling in between the chemistry of the 40 lakes Sources 1 and 2. The profile of the 8 lakes Source 3 is

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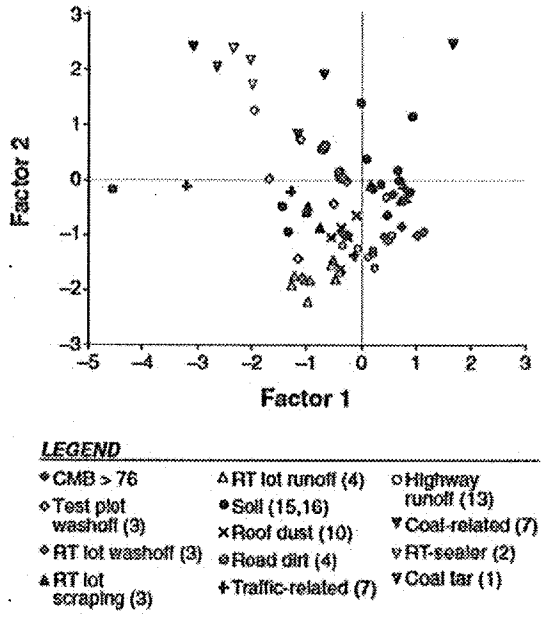

Figure 8. Principal component analysis from Figure 6 with most sediment sample points removed to allow comparison of the sources and other environmental samples. The numbers in parenthesis refer to the reference in Table 1.

weighted toward the lighter PAHs. Using these three sources profiles, the relationship between the predicted and measured concentrations exceeded 0.95 for all of the PAHs.

Since Unmix does not identify the sources, Pearson coefficients were used to compare the results to the potential sources (Table 3). For the 40 lakes data, Source 1 had the greatest similarity to the fuel oil combustion profile used as a input to the CMB (0.79), while Source 2 had the greatest similarity to the coal-related sources (0.86) and Austin lot dust (0.84). The three source profiles from the eight lakes run were most similar to

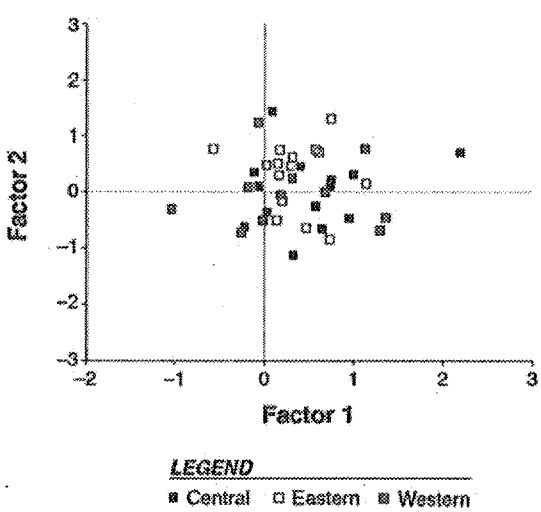

Figure 9. Principal component analysis results from Figure 6 highlighting the sediment results by regions identified by Van Metre and Mahler (2010).

highway runoff (Source 1, 0.86), soil (Source 2, 0.89), and coal–related sources (Source 3, 0.91). Pearson coefficients between the first two sources and Austin lot dust, highway runoff, roof dust, and soil were similar. If this evaluation had suggested that the PAH profiles identified by Unmix represented unique and independent sources, additional analysis that considered the confidence intervals of the output would be required for source identification (Norris et al., 2007; Pancras et al., 2011).

While Unmix characterized two or three source types, it is likely that there are more sources of PAHs in aquatic systems. What the results suggest is that the chemical profile of urban sediments is consistent with a mix of sources that differ in the fraction of lighter and heavier pyrogenic PAHs. These differences can be the result of both source-specific chemistry and the extent of weathering that occur between the source and deposition in sediment. Parsing out the relative contribution of these sources is challenging when using any of the forensic methods discussed.

Because of similarity in their PAH composition, multiple lines of environmental forensic data analyses are needed to examine possible linkages between sources and environmental samples, especially when investigating potential contributions of pyrogenic PAH sources to distal sediments (Boehm, 2006; Stout et al., 2001). Identification of a distinguishing factor among sources with otherwise similar pyrogenic PAH compositions may provide a sufficient basis for linking environmental samples to a source (Boehm et al., 1997). While the PAH histograms of fresh RT-sealer product suggest some potential distinguishing factors (i.e., greater relative amounts of the 2- and 3-ringed PAHs), this particular feature becomes less distinct as the sealer weathers and the lighter PAHs are lost. Because the variability within source type histograms and the source ratios themselves (Table 1) are similar to those between sources, no unique chemical indicator of RT-sealer is clearly identified within this limited set of 16 compounds used to link impacts to sediments. The evaluation of non-PAH source tracers may be required to accurately characterize the sources of PAHs. Such source-specific tracers may be present in RT-sealers, but no such data were found in the literature. In the case of other potential sources of PAHs, for example, in atmospheric source apportionment, hopanes and steranes indicate motor vehicle exhaust whereas levoglucosan and resin acids are indicative of biomass combustion (Fraser and Laskhmanan, 2000). Similarly, a number of markers have been identified that can assist in identifying coal combustion sources (Oros and Simoneit, 2000). If such differential signals are identified within otherwise similar chemical profiles, models such as CMB or Unmix may be sufficient to estimate the contribution of uniquely identifiable sources of PAHs (Burns et al., 1997).

Consistent with the approach of Van Metre and Mahler, data from numerous lakes were evaluated together. This is different from the typical application of forensic methods to a single watershed or water body (Li et al., 2003; Sofowote et al., 2008; Stout and Graan 2010; Su et al., 2000). Both the CMB and Unmix models were developed for use within a single source zone

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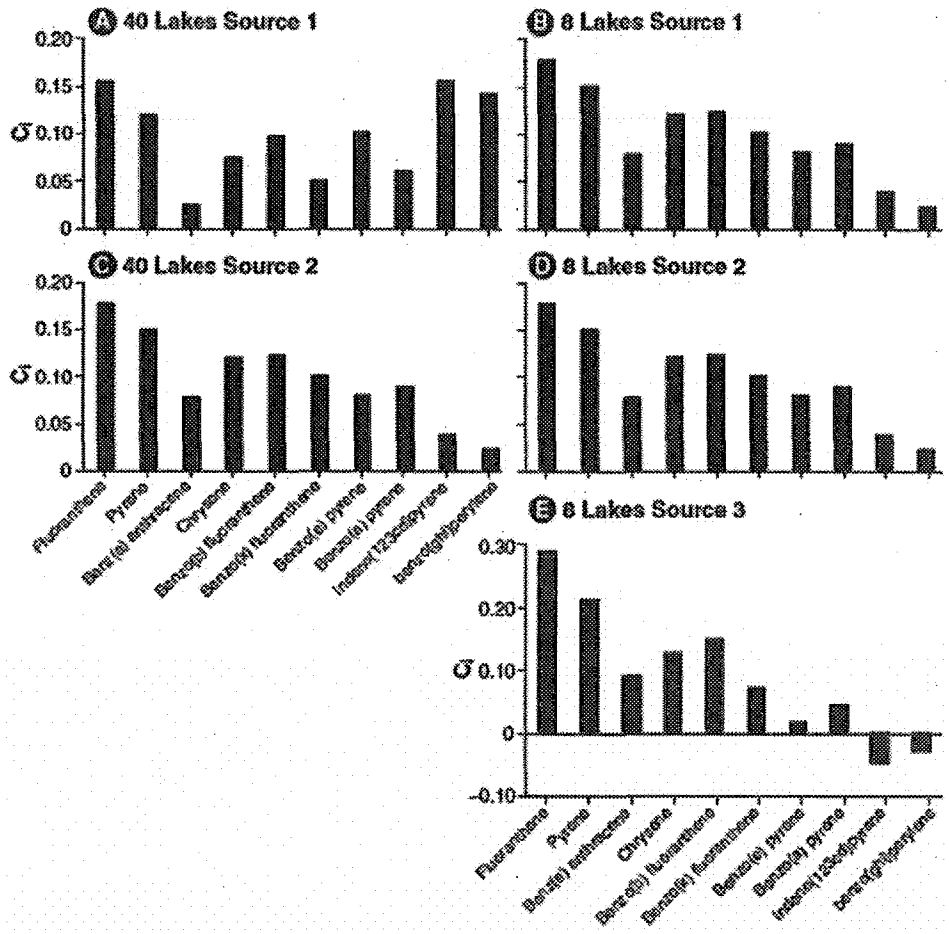

Figure 10. Source profiles determined by Unmix using the 40 and 8 lakes sample sets from Van Metre and Mahler (2010).

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(Coulter, 2004; Norris et al., 2007), and the results of methods such as ratio analysis are more meaningful when local differences in PAH profiles are considered (Stout et al., 2004). Given that the type and influence of sources is site specific and the variability in sediment chemistry indicated by the 40 lakes data set, the ability to accurately identify sources by applying forensic methods to a multisite data set is unproven. This is especially true when trying to evaluate the contribution of sources with similar PAH chemistry.

A hypothesis is a proposed explanation for observed phenomenon that is typically tested by attempting to demonstrate the null hypothesis. A hypothesis is supported if the phenomenon could occur only if the proposed explanation is correct, while the null hypothesis is appropriate if other explanations cannot be eliminated. The goal of this study was to evaluate the hypothesis that RT-sealers are a dominant (Mahler et al., 2005) or substantial (Van Metre et al., 2009) source of PAHs to urban sediments. The hypothesis would be supported if the PAH profile in the lakes studied could not be explained without inclusion of the sealants as a source. The results of this study indicate that while RT-sealer cannot be eliminated as a PAH source, sediment chemistry can be explained in the absence of any contribution from sealers. While Van Metre and Mahler's work has identified similarities between the PAH profiles of RT-sealer and urban sediments, such profiles are not unique, so the similarity does not prove that one is the source of the other.

Acknowledgment

This work was funded the Pavement Coatings Technology Council. The opinions are those of the authors.

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CRITICAL REVIEW OF USGS CONCLUSIONS REGARDING SOURCES OF PAHS IN LAKE SEDIMENTS

Executive Summary

Experts in environmental forensics have concluded in several peer reviewed articles that refined tar-based sealers (RTS) are not an identifiable source of polycyclic aromatic hydrocarbons (PAHs) in urban sediment. Although RTS have been banned in Austin, Texas and the state of Washington, no quantifiable environmental benefit has been shown to exist with respect to PAHs measured in sediment affected by the bans. Nevertheless, a small group of scientists, predominantly from governmental agencies, has advocated that RTS should be banned throughout the country. The Pavement Coatings Technology Council (PCTC) offers this White Paper as a detail analysis of the data and methods used by this small group of scientists to arrive at their conclusions.

The White Paper is premised upon scientific literature published by (a) government researchers, (b) PCTC - funded researchers, and (c) other researchers who have explored these issues "independently." Multiple environmental forensic methods are described within this literature and overall confirm that RTS are not a significant source of PAHs in the studied urban sediments. Indeed, comparison of results using different "fingerprinting" methods indicates that the dominant source of PAHs in urban sediments is likely atmospheric deposition, with little to no identifiable contribution from RTS.

All efforts have been made to include the most current studies and evidence available, including data and documents produced by the USGS in response to Freedom of Information Act (FOIA) request USGS-2011-00093, cited in this White Paper as Kurfirst (2011). Despite the pendency of this FOIA request for more than two years, the USGS response is not yet complete. Thus, it may be necessary to supplement this White Paper at a later date.

EXHIBIT
F
PENGAD 800-631-6989

Introduction

In a 2011 "Fact Sheet," the United States Geological Survey (USGS) published the following assertions regarding sources of polycyclic aromatic hydrocarbon compounds (PAHs) found in various lakes across the country (Mahler and Van Metre, 2011):

- Coal-tar-based sealcoat[1] is the largest source of PAH contamination in 40 urban lakes studied, accounting for one-half of all PAH inputs.
- Coal-tar-based sealcoat use is the primary cause of upward trends in PAHs, since the 1960s, in urban lake sediment.

These assertions are based on a body of work that has been generated, in large part, by two USGS scientists: Peter Van Metre and Barbara Mahler. The specific conclusion naming RTS as "the largest source of PAH contamination" is based on a paper by Van Metre and Mahler (2010) titled *Contribution of PAHs from Coal–Tar Pavement Sealcoat and Other Sources to 40 U.S. Lakes* (hereinafter the "40 Lakes Paper"). According to Van Metre and Mahler, the findings set forth in the 40 Lakes Paper are consistent with conclusions that they and other government researchers reached in previously published studies involving RTS.

This White Paper is organized into two main sections. The first section evaluates an initial set of PAH "fingerprinting" studies published between 2005 and 2009, including articles published by Van Metre and Mahler. These studies focus on a variety of strategies for source identification and apportionment of PAHs found in sediment. The second section analyzes in detail the 40 Lakes Paper in which Van Metre and Mahler contend that the chemical mass balance model (CMB) is the most reliable method for PAH source identification and apportionment and why their conclusions are flawed.

USGS Studies of PAHs in Sediments: 2005-2009

PAHs are ubiquitous – they occur naturally in fossil fuels and also are made when organic matter is burned (*e.g.* ATSDR, 1995). . Because PAHs are everywhere, an enormous amount of scientific research has been published worldwide covering just about every aspect of PAHs, including studies that attempt to identify and apportion sources of PAHs occurring in soils (*e.g.*, Kay *et al.* 2003; Mauro *et al.*, 2006) and sediments (*e.g.*, Stout *et al.* 2004 and the papers summarized in the Attachment to this White Paper).

PAH source identification – sometimes called "PAH forensics" – typically involves using graphical and statistical methods in an effort to identify source-

[1] RTS are characterized as "coal-tar-based sealcoat" or "CTS" by the USGS.

specific chemical characteristics – "fingerprints" – to distinguish sources. For example, Figure 1 contains a principle component analysis (PCA) plot of PAH data. The data (but not the statistical analysis) were published by the USGS team for sediments in Washington State (Lake Ballinger; Van Metre & Mahler, 2010) with samples from parking lots said to be treated with refined tar-based pavement. It is easy to see that there is no overlap of PAHs in Lake Ballinger sediments with PAH parking lot dust and parking lot scrapings data the USGS collected from lots that were said to be sealed.

Overlapping data can be an indication of a source-sink relationship between PAHs in samples. Likewise, the absence of an overlap, along with different trends in sample PCA plots can be an indication of the absence of a source-receptor relationship. It's not always straightforward – sometimes chemical data may overlap, but this doesn't necessarily mean that there is a source relationship. In cases of overlap, most scientists working in the field of environmental forensics suggest additional forensic analysis should be pursued. A requirement in source identification is consistency internally and among all the different forensic methods used (O'Reilly *et al.*, 2012). In cases such as the Lake Ballinger data in Figure 1, in which the data neither overlap nor display similar trends, the absence of a relationship is strongly suggested.

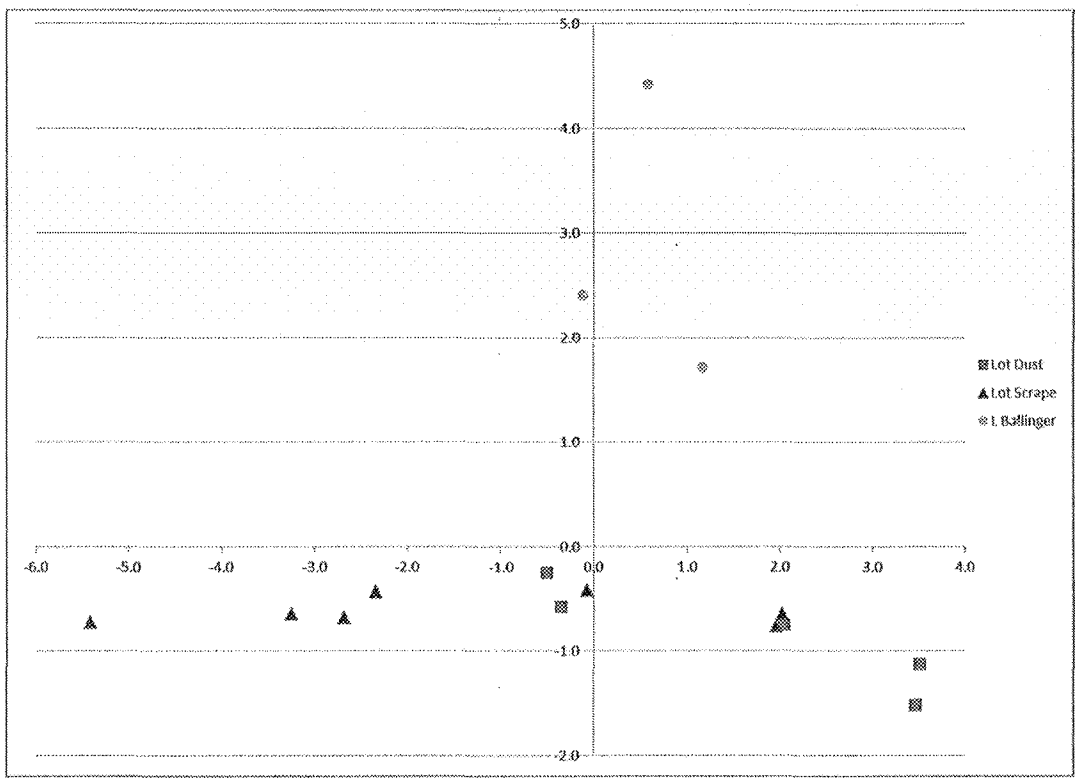


Figure 1. Principle Component Analysis (PCA) does not support the claim that RTS is a significant source of PAHs in the sediment of Lake Ballinger, located near Seattle, WA. The results are consistent with the WA Department of Ecology's conclusion that residential wood burning is the largest source of PAHs in sediments of Western Washington.

In their earliest publication about pavement sealers in Austin, TX, the USGS team used double ratio plots as the method of source identification (Mahler *et al.*, 2005). Inconsistencies, however, have been identified in the published data (DeMott & Gauthier, 2006; see Figure 2, below), and the source of the sediment data shown in the Mahler *et al.* (2005) figure remains unidentified to this day.

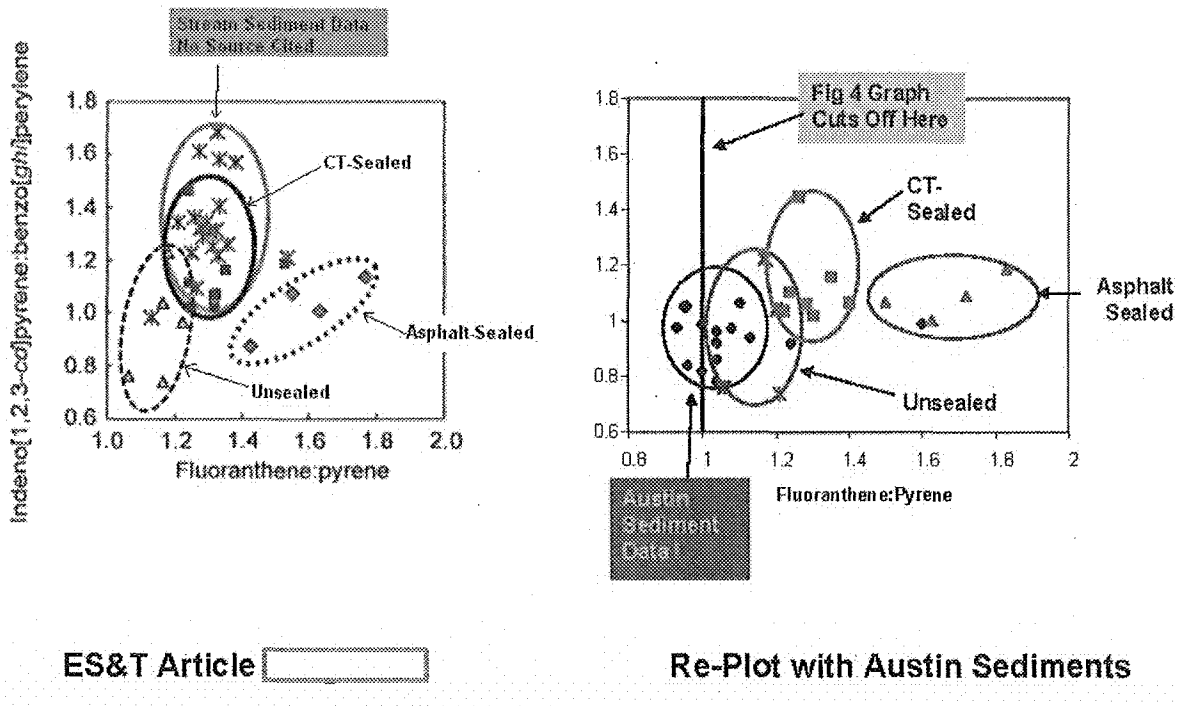


Figure 2. Comparison of double ratio plot from Mahler *et al.* (2005, on left) with graph of the same sealed parking lot data (DeMott & Gauthier, 2006, on right). The USGS states that the sediment data used in the graph on the left is not the data provided by the City of Austin and used in the graph on the right. The source of the USGS sediment data as well as the data themselves remain unidentified.

As is always the case when a science journal such as Environmental Science & Technology (ES&T) publishes a critical comment on a specific article, a response by the article's authors is also published. The DeMott & Gauthier (2006) comment, which critiqued Mahler *et.al.* (2005), focused on two main points:

> (1) With regard to the PAH ratio analysis, we could not identify the source of the values presented for stream sediment samples, and the values that we could identify from the City of Austin appear to contradict the interpretation developed by the authors [*i.e.,* Mahler *et al.* (2005)].

(2) With regard to the mass balance analysis, we could not identify the source for values from one watershed, the values presented for the other watersheds do not appear to match those from the cited sources, and the previously published values suggest the relative contribution of PAHs from parking lot sources is substantially less than the "majority" source suggested by the authors [*i.e.*, Mahler *et al.* (2005)].

Neither of these points was addressed by Mahler *et al.* (2006) in their response. Rather, the response addressed topics that are, at best, secondary issues raised in the DeMott & Gauthier comment. Topics raised in the response are as follows:

(1) A discussion of the use of specific PAH double-ratio plots, with highly debatable representations about the impact that concentrations may have had on ratios (debatable because ratios are not concentration dependent).

(2) Commentary that data used in the DeMott and Gauthier plot may not be comparable to the Mahler *et al.* (2005) data, but with no indication of what the source of the data in Mahler *et al.* was.

(3) A discussion of possible overestimation versus underestimation in mass balance calculations.

(4) A discussion of comparability of load calculations made for the Fort Worth and Austin, TX calculations.

(5) A correction of load calculations errors made in Mahler *et al.* (2005).

(6) An assertion that certain yield calculations support the conclusions of Mahler *et al.* (2005).

(7) An unreferenced statement that the sealing of parking lots is a fairly common practice, so sealants must be a "major contributor of PAHs to the urban watersheds studied."

Follow-up studies in Austin waterways confirm that RTS are not an identifiable source of PAHs in Austin when using either the double ratio plot of Mahler *et al.* (2005) (shown in Figure 2 above) or principle component analysis (shown in Figure 3, below; DeMott *et al.*, 2010; O'Reilly *et al.*, *in preparation*).

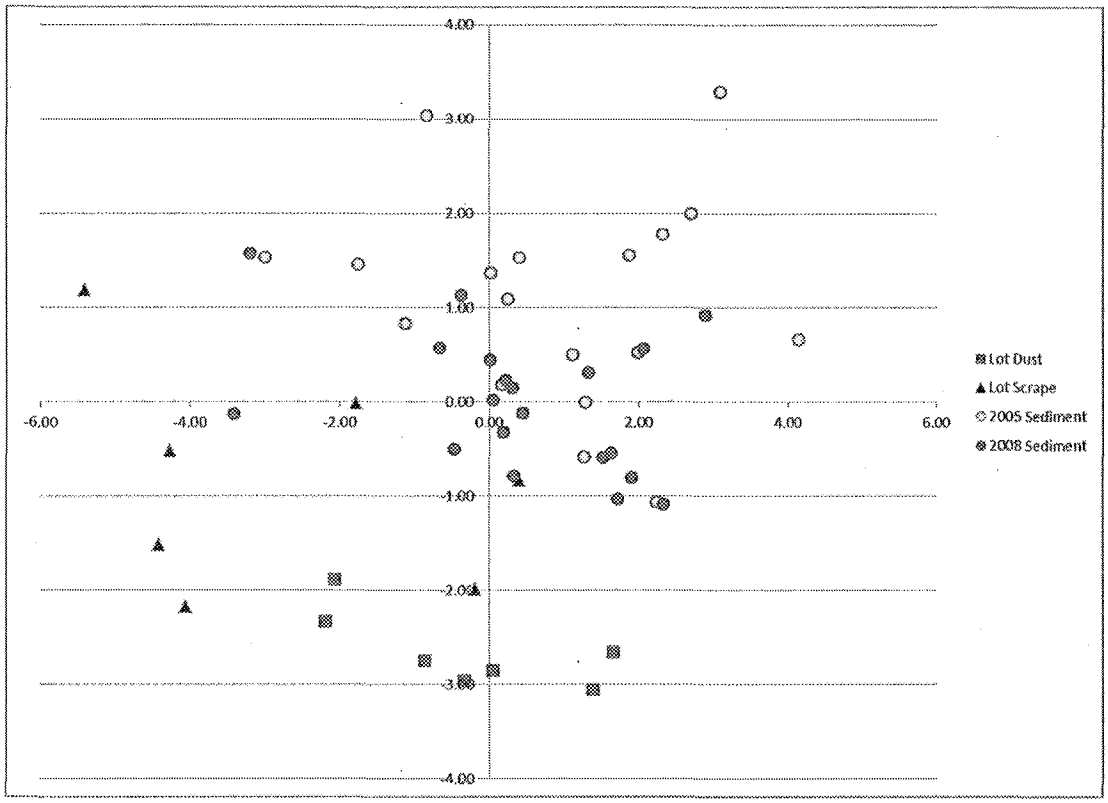


Figure 3. PCA evaluation comparing creek sediments in Austin, TX waterways to Austin parking lot dust and scrapings. PCA results combined with results of additional forensic methods do not support a claim that the lots are a significant source of PAHs. PAH data are from Mahler *et al.* (2005) and DeMott *et al.* (2010). Figure is from O'Reilly *et al.* (in preparation).

In a subsequent paper, Van Metre *et al.* (2009) again used a double ratio plot to display sediment data from 9 lakes and dust/scrapings data collected from parking lots and driveways in the vicinity of some of these lakes. This time, however, the plots and data were used to demonstrate a purported difference in ratios between samples collected in the Western U.S. versus samples collected in Central and Eastern U.S. As discussed in O'Reilly *et al.* (2012), the range of PAH ratios in samples collected from 10 ponds in the Minneapolis area is similar to the range of ratios in samples from nationwide locations presented in Van Metre *et al.* (2009), indicating that the apparent geographic differences in ratios is likely an artifact.

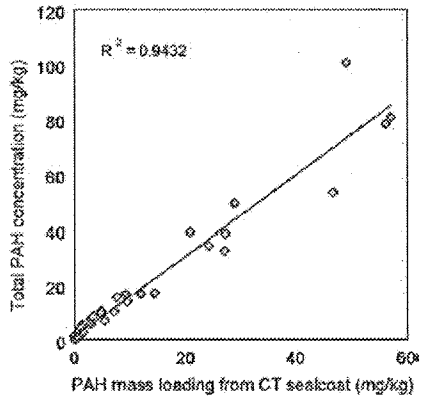
Instead of using one of the well-studied PAH fingerprinting methods to identify samples alleged to be influenced by RTS in the 9 lakes paper, the authors assert (not for the last time) that an elevated PAH concentration in a sample *must* indicate the "use of coal-tar-based sealcoat on this lot" (Mahler *et al.*, 2009, p. 21). This type of assumption and circular reasoning does not reflect sound scientific methodology. Indeed, the authors fail to mention that in a previous study of these lakes (Van Metre *et al.* 2000), they concluded that changes in PAH concentrations and chemical profiles were linked to increased automobile use within the respective watersheds.

USGS Studies of PAHs in Sediments: The 40 Lakes Study

In a 2010 study of 40 lakes across the country (Van Metre & Mahler, 2010; a/k/a the "40 Lakes Paper"), the USGS research team expanded its effort to determine the extent to which RTS contribute PAHs to urban sediments. O'Reilly *et al.* (2011) was a comment on the methods of PAH source identification and apportionment used by the USGS research team not only in the previously mentioned 9 Lakes study, but also in the 40 Lakes Paper. Van Metre and Mahler were given an opportunity to respond in the same journal at the same time (Van Metre and Mahler, 2011). The table below summarizes the comments and responses:

	COMMENT (O'Reilly *et al.*, 2011)	RESPONSE (Van Metre & Mahler, 2011)
1.	Results for individual samples are not consistent between papers on this topic by the same authors.	Stated that overall conclusions are consistent between the papers, apparently agreeing that individual results are inconsistent.
2.	To validate results of any single source apportionment method, run and compare multiple methods in one study to determine if results are consistent.	Without factual support, stated that different methods used with different data in separate studies to reach the same conclusion.
3.	Cited Stout & Graan (2010) as an example of a multi-forensic method investigation, and the types of expected results.	Did not address the point that Stout & Graan is an example of internal consistency within a multi-method forensic analysis, but did claim that Stout & Graan might have recognized the role of sealers if they had been considered.
4.	There is a poor correlation between the results of double ratio plot analysis and the CMB model used in the 40 lakes study. For example, only about 50% of the samples they modeled to be >75% sealer-derived PAHs have PAH ratios claimed to be diagnostic for sealer impacts.	Restated the data a different way and claim the restatement shows the original statement to be right.
5.	Cited Ahrens & Depree (2010) as an example of the expected relationship between PAH ratios and percent contribution	Dismissed Ahrens & Depree result as hypothetical and not expected for environmental samples. As Ahrens & Depree was a discussion of environmental

	COMMENT (O'Reilly *et al.*, 2011)	RESPONSE (Van Metre & Mahler, 2011)
		samples, the response seems to miss the point. The response did not address why there is no relationship between PAH ratios and percent concentration even for samples claimed to be almost all sealer.
6.	Explained concerns with application of the CMB model because of issues with source sufficiency and stability. Cited Galarneau (2008) as a paper that highlights the potential pitfalls of applying receptor modeling to PAHs.	Stated that the comment on "sufficiency and stability" was too vague to respond. Claimed it does not matter as Galarneau was focused on atmospheric modeling not sediment. Among other things, this response ignores that emissions were used as an alternative sources, and emissions are subject to atmospheric processes. Also ignores that the CMB was developed as an atmospheric source allocation model, and not as a sediment evaluation model.
7.	Combustion emissions were used as the CMB sources, but reactions that change PAH profiles were not taken into account.	Ignored the differences between fresh emission sources and post atmospheric reaction depositional particles
8.	Suggested application of multivariate methods such as PCA that do not require pre-identification of sources.	Stated that multivariate methods do require that sources be identified. Ignoring the difference between methods where sources are identified upfront and those that use the results of analysis to identify sources. Claimed that Watts et al (2010) use of PCA supported their conclusions. But, Watts only looked at samples taken from within a limited test area and considered sealers as the only source.
9	The null hypothesis was not tested, so atmospheric deposition as a primary source was not eliminated.	Restated claims from previous papers, in which the same authors concluded sealers were an important source of PAHs. Provided a circular argument referring to the figure below from Van Metre & Mahler (2010) in which sample concentration is a used to calculate both the X and Y axis:

	COMMENT (O'Reilly *et al.*, 2011)	RESPONSE (Van Metre & Mahler, 2011)
		

Ultimately, the conclusion offered by O'Reilly *et al.* (2011) in their Comment to the 9 Lakes Study and 40 Lakes Paper is worth repeating:

> In papers published in ES&T, PAH ratios were used to link PAHs associated with CT-sealed parking lots to urban sediments. Without this evidence, there is little basis for claims regarding the relative role of CT-sealants, and less for the use of such superlatives as the "dominant" source or "substantial" contribution. While the points raised in this commentary do not eliminate CT-sealants as a potential PAH contributor in some urban systems, we suggest that the authors apply and compare the results of multiple source characterization techniques including sample chemistry (PAH ratios and concentration histograms), receptor models, and multivariate methods.

Indeed, one of the primary flaws readily apparent in Van Metre and Mahler (2010), and in other USGS publications about RTS, is the temptation to confuse chemical similarity with causation. For many years, there has been a broad consensus that the PAH profile of urban soils and sediments is dominated by pyrogenic PAHs (*e.g.*, Boehm, 2006; Kay *et al.*, 2003; Mauro *et al.*, 2006; Stout *et al.*, 2004; Stout & Graan, 2010). Parsing the relative contributions of pyrogenic sources has numerous challenges which are routinely minimized in publications to date by the USGS-led research team. Quite simply, demonstrating that sealers are more similar to certain urban sediment PAH profiles than other sources of PAHs does not demonstrate that sealers are a "dominant" source.

In the 40 Lakes Paper, the USGS research team overstates the applicability of the chemical mass balance (CMB) model. The USGS research team adapted the CMB model (now version CMB 8.2) developed by the U.S. Environmental Protection Agency (EPA) to identify and apportion potential sources of atmospheric pollutants. The CMB model is designed to fit various summations of sources to the receptor profiles (Coulter, 2004). If one potential source has a similar profile to the receptor, whereas other sources have dissimilar profiles, the

model will indicate a higher contribution of the similar source. Like many source apportionment methods, CMB is ultimately a similarity indicator. Such similarity is not proof that a proposed source is an actual source. One reason for applying multiple forensic techniques to a source apportionment exercise is that demonstrating consistency among methods strengthens the weight-of-evidence that a proposed source is a probable source.

The CMB model was developed by EPA as an aid to identification of potential sources of air pollution in atmospheric studies, not for source apportionment of chemical components in sediments. The CMB model has been used in a number of published sediment evaluations, but conclusions reached based on CMB output are usually confirmed using other apportionment tools to validate that the input parameters used result in solutions consistent with the system under investigation.

Application of the CMB model requires use of appropriate source profiles as input. Published examples of using CMB to evaluate sediment are focused on individual watersheds (see Attachment for summary of examples). The USGS approach of using a single set of general source profiles for a nationwide sample set is not consistent with model assumptions. For example, in companion papers evaluating PAH sources in Chicago's Lake Calumet, Li *et al.* (2003) and Bzdusek *et al.* (2004) calculated different model outputs. Specifically, they calculated different fractional contribution scenarios from different potential PAH sources arrived at by using 9 different CMB and 2 different factor analysis model runs (Figure 4). Using different source profile inputs for different runs demonstrates how sensitive model outputs are to model inputs. For example, PAHs from "traffic" sources (identified on Figure 4 as traffic, tunnel air or diesel) results in modeled fractional contributions ranging from about 15% to over 60%, depending solely on the source input profile used.

In the 40 lakes paper, it is stated that "The CMB model was run more than 200 times using various combinations of source profiles, fitting parameters (PAHs), estimates of uncertainty, and combinations of lake-sediment samples." (p. 337) Out of the 200 runs, Van Metre and Mahler chose 4 that most closely matched the parameters chosen to represent a "good fit" for the 5 PAH sources chosen as source inputs, and then reported fractional contributions using an average of results of the 4 chosen source input models. It may be possible to evaluate the sensitivity of source profile inputs and graphically show results of the sensitivity analysis if data for all 200 model runs (or for that matter, even for the 4 chosen model runs) considered as source input models for the 40 Lakes Paper are made available in response to the FOIA request (Kurfirst, 2011). In the

meantime, the data on the sensitivity of calculated fractional contribution results on different source inputs in a local watershed, as developed by Li *et al.* (2003) and Bzdusek *et al.* (2004), and as illustrated in Figure 4, must serve as a sensitivity barometer for the 40 Lakes Paper.

As illustrated in Figure 4, use of the CMB model to estimate fractional contribution of different sources requires use of appropriate source profiles as input. Other researchers have published examples of using CMB to evaluate potential sources of PAHs in sediment – much as the Lake Calumet study discussed above – but these studies are focused on individual watersheds. The approach in the 40 Lakes Paper is to use a single set of general source profiles and apply them to a data set consisting of a small (but variable) number of samples collected at many locations nation-wide. Some of the studied lakes are dammed reservoirs which, like Town Lake (now called Lady Bird Lake) in Austin, Texas, has for at least a substantial part of its existence served as a cooling pond for an electric power plant.

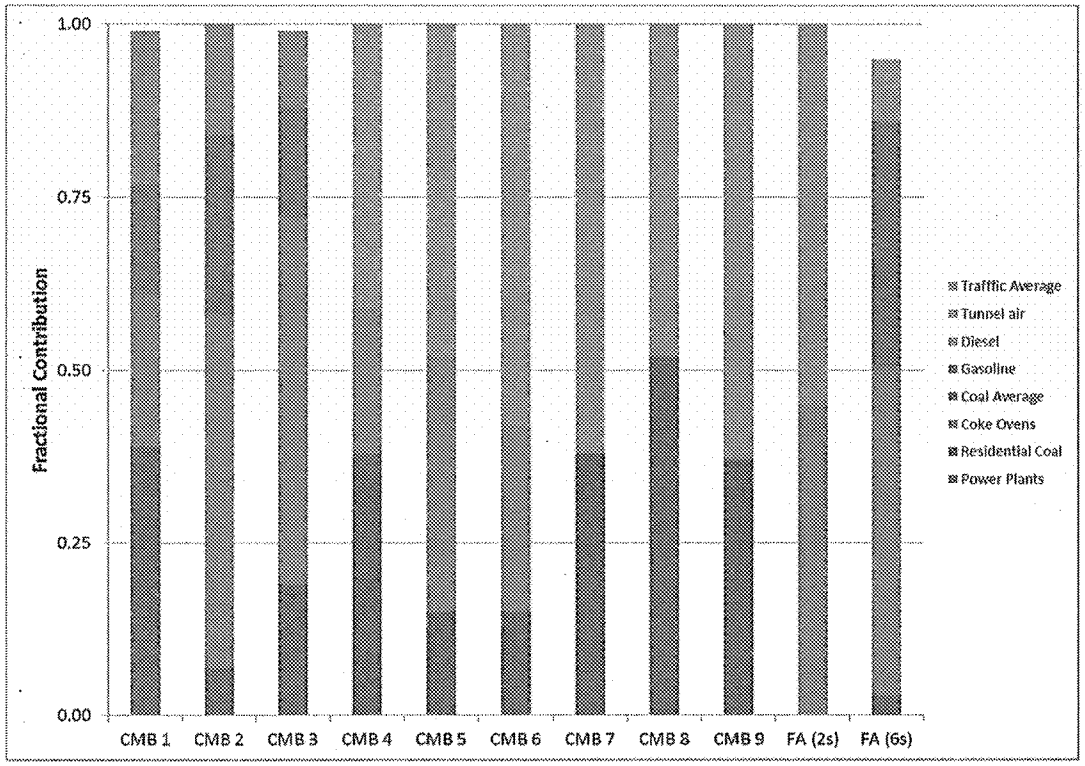


Figure 4. Fractional contribution of various PAH source types to sediment of Lake Calumet (Chicago, IL) based on nine CMB and two Factor Analysis model runs. Data from Li *et al.* (2003) and Bzdusek *et al.* (2004). Figure from O'Reilly *et al.* (in preparation).

The RTS research team's application of the CMB model does not account for the expected variability in both source profiles and location-specific variables,

which further casts doubt on the consistency of model application with model assumptions. Furthermore, the 40 Lakes Paper has no negative controls. The USGS research team has not demonstrated that sediments with and without RTS effects can be accurately distinguished.

By using results of analysis of emissions in the USGS adaptation of the CMB model, the methods used to generate source profiles ignore the large changes in PAH chemistry that have been demonstrated to occur as a result of atmospheric processes. In the 40 Lakes Paper, a point is made of explaining why using weathered samples to represent sealer source profiles is important, yet the authors did not apply the same reasoning to other source profiles.

The CMB model has five key assumptions that are applicable to identification of chemicals in sediments (Coulter, 2004). As detailed in the table below, all five assumptions are violated in the adaptation and application of the CMB model described in the 40 Lakes Paper.

	CMB Model Assumption	USGS Adaptation
1	The composition of each source emission is consistent over the period modeled and, as applied to a nation-wide data set in the 40 lakes paper, over the geographic area modeled.	- No site specific emission data were used, so no measure of consistency over time or space is available. - The source profiles used were averages of published data with no indication of how representative they are of actual sources that may impact each of the 40 lakes. - The types of emission sources used are known not to be consistent, changing with fuel and process conditions.
2	Chemical species do not react with each other or the environment	- PAHs have been shown to react quickly in the atmosphere so emission chemistry should not be expected to represent depositional chemistry. The USGS CMB application ignored this factor. - PAHs in RTS weather, and may weather differently in different climates, which would result in changes in the PAH profile. Some possible effects of weathering were accounted for in the 40 Lakes Paper. - The combination of ignoring atmospheric

	CMB Model Assumption	USGS Adaptation
		changes while considering weathering effects increases the likelihood of identifying RTS as sources.
3	All sources that contribute significantly to the receptors have been identified and their profile is known.	- The USGS application considered a limited set of sources assumed to be applicable nation-wide. - It is highly uncertain whether the source profiles used as inputs in the USGS application represent actual sources in each/any/all of the sample locations.
4	The composition of each source is linearly independent of other sources	- The adaption and application of the CMB model described in the 40 Lakes Paper indicate a positive relationship between the mass of PAHs sourced by RTS and the mass sourced by other sources (R^2=0.63). Samples with more sealer also had more other sources. - This positive relationship is the opposite of the result expected if sealers were actually a source.
5	Measurement uncertainties are random, uncorrelated, and normally distributed	- As noted in the 40 Lakes Paper, this assumption could not be met with most input source data so a generic uncertainty factor (UF) of 40% was applied. - This UF value was based on analytical uncertainty, ignoring the inherent variability in the chemical profiles of potential sources, as well as geospatial variability. - Profiles based on a limited set of published data are not expected to be random, uncorrelated, or normally distributed.

Based on explanations in the methods section of the 9 Lakes Study and 40 Lakes Paper, it appears that, with the sole exception of pavement, most source profile inputs are not the chemistry of individual samples or sources but averages of published data. It is not clear whether these mathematically generated source

profiles represent actual sources in the watersheds for which conclusions about the percentage contribution by sealers were reached by the USGS research team. In a study of PAHs in sediments in nine urban waterways across the US, Stout *et al.* (2004) found differences in PAH distributions between and even within different urban settings, thus concluding that "there is no single 'representative' urban background…PAH signature."

Averaging can make sense for duplicate samples of the same source, but averaging potential sources across wide geographic areas is not appropriate to represent what can be a very wide range of possible profiles for sources that may be similar in process but not in the many other parameters that influence PAH profiles. As demonstrated by the example shown in Figure 5, the profile for Source 1 is similar to the receptor but if it is averaged with Source 2, the resulting profile eliminates this relationship and results in a profile that doesn't look like either source. The proper approach is to run the model with each source profile as inputs (O'Reilly *et al.*, in preparation).

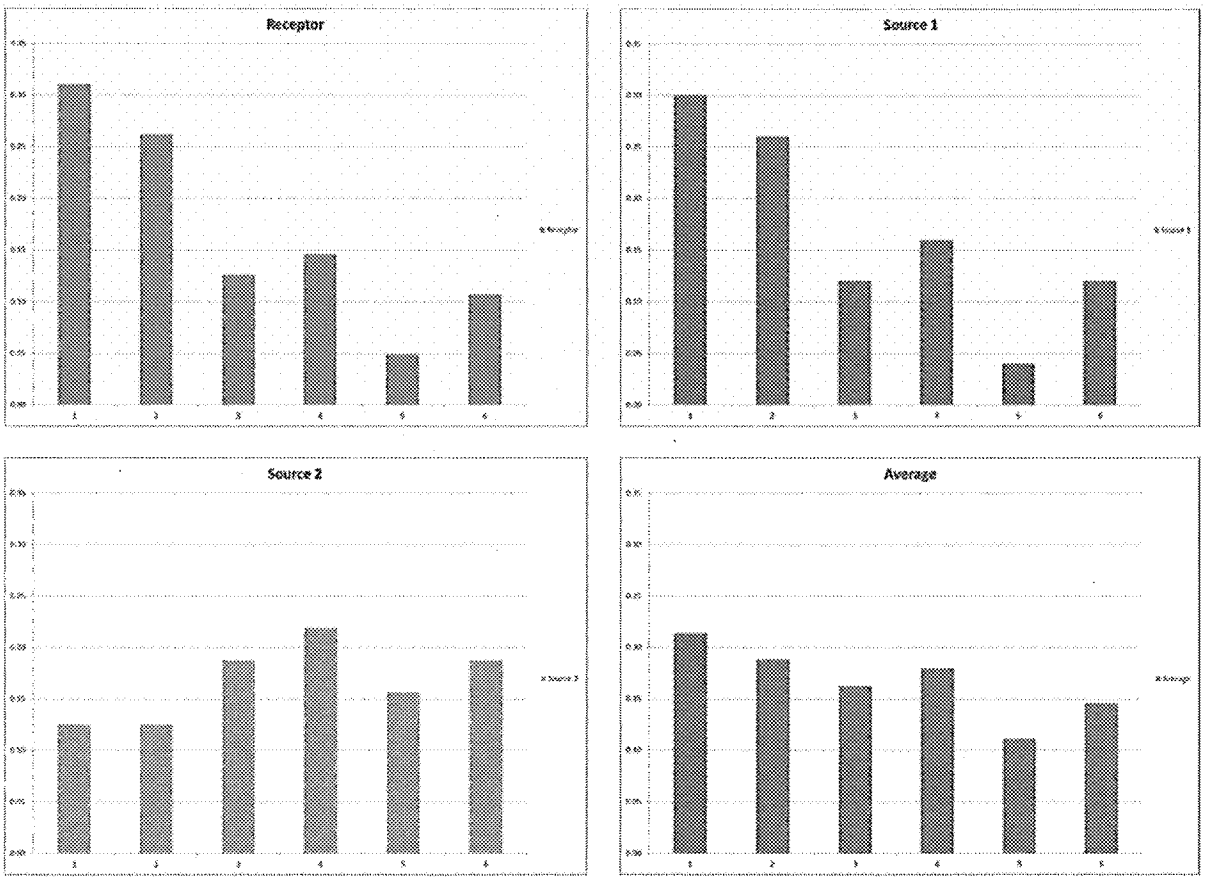


Figure 5. A hypothetical example of the effects of averaging PAH data. The profile for Source 1 is similar to the receptor but if it is averaged with Source 2, the resulting profile eliminates this relationship and results in a profile that doesn't look like either source. The proper approach is to run the model with each source profile as inputs. (O'Reilly *et al.*, in preparation).

Comparison of Results of USGS Adaptation of CMB Model with Other PAH Source Apportionment Methods

O'Reilly *et al.* (2012) applied multiple well studied and commonly used source apportionment methods to evaluate the same data that was generated by the USGS. This must be contrasted to Van Metre and Mahler using just one method – the previously discussed adaptation of the CMB model – to try to identify sources of PAHs. Methods used by O'Reilly *et al.* included:

- Diagnostic double ratio plots, in which the ratio of two PAHs is plotted on the x-axis and the ratio of a second pair of PAHs is plotted on the y-axis and potential differences are identified by comparing the coordinates of samples to each other, to known sources, and to published values;
- Pearson correlations to evaluate similarities between PAHs in sediments and potential PAH sources;
- Principal component analysis (PCA) to compare sediment samples and suspected source materials; and
- Another EPA receptor model, UNMIX 6.0, to evaluate specifically the same data evaluated by Van Metre and Mahler (2010) using EPA's receptor model CMB.

O'Reilly *et al.* (2012) also emphasized the significance of the null hypothesis, ignored by the USGS authors in their body of work:

> A hypothesis is a proposed explanation for observed phenomenon that is typically tested by attempting to demonstrate the null hypothesis. A hypothesis is supported if the phenomenon could occur only if the proposed explanation is correct, while the null hypothesis is appropriate if other explanations cannot be eliminated. The goal of this study was to evaluate the hypothesis that RT-sealers are a dominant (Mahler *et al.*, 2005) or substantial (Van Metre *et al.*, 2009) source of PAHs to urban sediments. The hypothesis would be supported if the PAH profile in the lakes studied could not be explained without inclusion of the sealants as a source. The results of this study indicate that while RT-sealer cannot be eliminated as a PAH source, sediment chemistry can be explained in the absence of any contribution from sealers. While VanMetre and Mahler's work has identified similarities between the PAH profiles of RT-sealer and urban sediments, such profiles are not unique, so the similarity does not prove that one is the source of the other.

In addition to results presented in O'Reilly *et al.* (2012), detailed forensic source apportionment investigation results have been presented at annual meetings of the Society of Environmental Toxicology and Chemistry (SETAC) and are the topic of papers in preparation. One set of results includes evaluations of PAHs in the lake sediments that are the topic of a web page in need of

correction. To use four of these lakes as examples, the table below summarizes the different conclusions reached by the USGS authors using only the USGS adaptation of CMB and by evaluation of the same data using multiple PAH source apportionment forensic methods.

Water Body	Percentage sealer, Multiple Forensic Methods	Percentage sealer, USGS Model
Lake Ballinger, WA	Little to None	~70%
Lake in the Hills, IL[2]	Little to None	~70%
Newbridge Pond, NY	Little to None	~65%
Town Lake, TX[3]	Little to None	~80%

The data in the above table is illustrated in Figures 5 and 6 below. Figure 5 contains results of PCA for the four lakes listed in the above table. The ranges of PAH values in none of the four lakes overlaps the range of PAH values in samples known to be directly derived from refined tar-based pavement sealer.

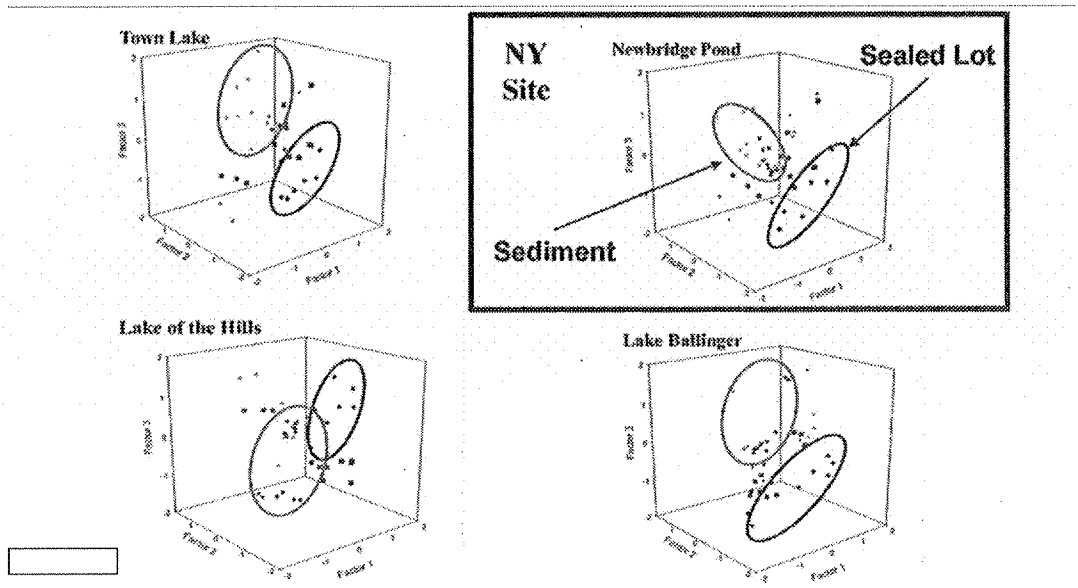


Figure 5. Three dimensional PCA plots of data from four lakes illustrating that none of the sediment data collected from the four lakes overlap data from RTS sealed lots. Data used are as reported in USGS publications. Rotating the Lake of the Hills plot reveals the absence of overlap. PCA analysis and plots courtesy of K. O'Reilly.

[2] Rotating the Lake in the Hills plot in 3 dimensions illustrates the absence of overlap between the fields.

[3] Town Lake, now known as Lady Bird Lake, is located in downtown Austin, TX, and is a reservoir that formerly served as a cooling pond for the Holly Street Power Plant, located on the lake shore.

Figure 6 (Figure 4 of the 40 Lakes Paper) shows the source percentages calculated for each lake considered in Van Metre and Mahler (2010), highlighting the four lakes listed in the table above. It is interesting to note how PAH mass loading in Lake Ballinger (West region) was reportedly greater than what was found to exist in Lake in the Hills and Town Lake (Central region), even though the USGS asserts that RTS generally have not been used west of the Rockies.

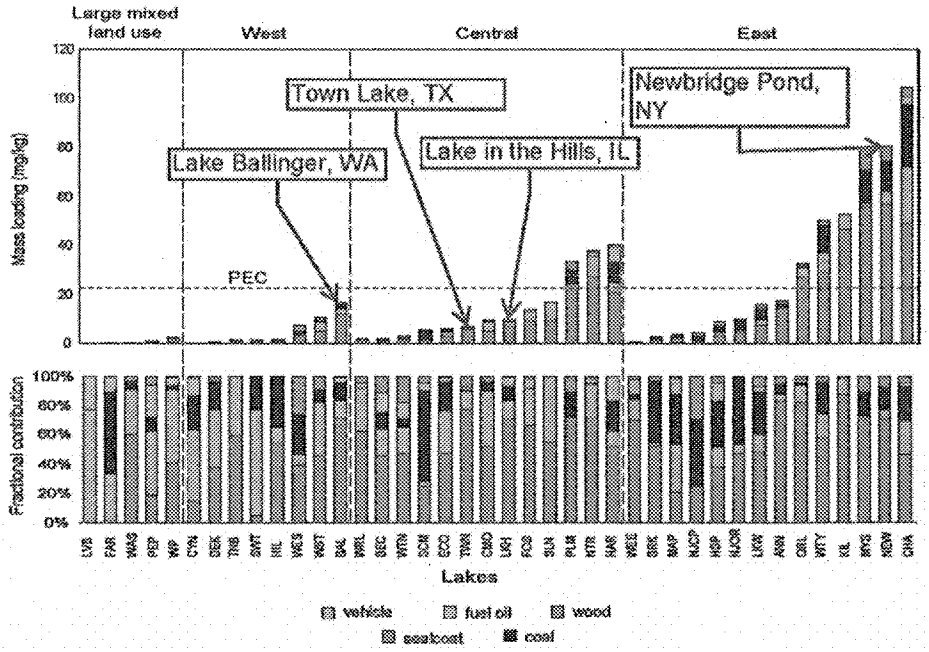


Fig. 4. PAH mass loading and fractional contribution from five source categories to ΣPAH (mean of four best CMB model runs). Lakes are grouped by region in order of increasing ΣPAH concentration. Horizontal dashed line indicates the probable effect concentration (PEC), the concentration of total PAH above which adverse effects to benthic biota are expected to occur (MacDonald et al., 2000).

Figure 6. Van Metre & Mahler (2010), with the four lakes discussed in the text and Figure 5 highlighted.

Conclusions

The data interpretation presented in the 40 Lakes Paper inherently lacks objectivity as no other possible solutions are considered, nor are conclusions presented in the context of the voluminous body of PAH source identification and apportionment literature that exists. All results in the 40 Lakes Paper are presented as though they demonstrate only the USGS hypothesis concerning RTS and no other conclusions are possible. Neither the null hypothesis nor any alternate hypotheses are considered. VanMetre and Mahler (2010) also ignore the uncertainty inherent in CMB results. Uncertainties should be quantified and discussed, and the sensitivity of outputs (fractional contributions) to different source profile inputs should be evaluated.

Other adaptations of the CMB model and similar approaches have been used in targeted evaluation of various individual watersheds. Attached to this White Paper is a summary of literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source. In all reviewed cases, sediment chemistry can be explained without including RTS as a source. Just as this does not prove that some sediments may be influenced by sealers, results of the USGS adaptation of CMB do not prove that sealers are a contributor to PAHs in sediments.

The USGS research team has used two methods to reach the conclusion that RTS is a "dominant" or "significant" source of PAHs in sediments in the United States: (1) the alleged similarity of between PAHs in double ratio plots of sample results of sealed pavement and unidentified sediment samples in Austin, TX (Mahler *et al.*, 2005) and (2) results of an adaptation of the CMB model. O'Reilly *et al.* (2011) pointed out that the two methods give inconsistent results, raising questions about whether reaching the same conclusion is warranted. O'Reilly *et al.* (2012 and in preparation) demonstrate that conclusions based on the CMB model as presented in the 40 Lakes Paper do not comport with conclusions reached evaluating the same data using other source identification and apportionment technique, including EPA's UNMIX receptor model. The USGS has not and, based on their data, cannot demonstrate a link between PAHs in RTS and PAHs in most urban sediments. Communications to the contrary posted on the USGS web sites constitute a dissemination of information that does not meet the USGS standards for data quality.

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CRITICAL REVIEW OF USGS CONCLUSIONS REGARDING SOURCES OF PAHS IN LAKE SEDIMENTS

ATTACHMENT

Literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source is summarized in the following table. These results are in conflict with the USGS's hypothesis that sealers are a widespread source of PAHs.

Citations for literature summarized in the table are as follows (numbers shown in first column of table).

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Summary of literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source. These results are in conflict with the USGS's hypothesis that sealers are a widespread source of PAHs.

Ref	Water Body	Source Characterization	Forensic Methods
1	Fox River (Green Bay, WI)	Coke oven emissions are in the range of 40 to 90% of total PAHs, and this fraction decreases from 1930 to 1990, except in core Fox River–A (FR-A).The overall highway dust (HWY) contribution is between 10 and 75%, and this fraction increases from 1930 to present, except in core FR-A. The wood burning (WB) contribution (i.e., wood burning or coal gasification) is less than 7% in cores FR-B, FR-C, and FR-D. In core FR-A, a maximum (ø23%) is found around 1960. The contribution of wood burning has changed from less than 6% in 1950 to between 3 and 10% in 1995.	CMB with inclusion of biodegradation.
2	Lake Michigan (Chicago, IL & Gary IN)	The relative abundances of individual PAH compounds from Lake Michigan sediments, PM-10 aerosol of Chicago, and a coke oven signature are statistically similar establishing a linkage between combustion sources in the south, atmospheric deposition, and sediment accumulation. Further support for this linkage is the historical PAH accumulation in lake sediments and historical coal use in Illinois over the same time period. The major source of PAHs to Lake Michigan sediments is coke and steel production found in the urban/industrial complex around Chicago, IL, and Gary, IN. These PAHs are deposited primarily in the southern basin after which they are redistributed throughout the lake as a result of in-lake integration processes (water and sediment transport).	The relative distributions of 27 PAHs were calculated to assess the source(s) of PAHs to Lake Michigan. Sources contributing to PAH accumulations in sediments are assessed using the relative concentrations of individual compounds and comparing them to the relative amounts from specific sources either in the form of compound ratios or on the distribution of an entire suite of PAHs.

Summary of literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source. These results are in conflict with the USGS's hypothesis that sealers are a widespread source of PAHs.

Ref	Water Body	Source Characterization	Forensic Methods
3	Chesapeake Bay	Most of the benz[a]anthracene, benzo- [a]pyrene, benzo[b]fluoranthene and their isomers in air, rain, and surface waters of Chesapeake Bay appear to be derived from automotive sources. Lesser, but still significant amounts (53%) of these PAHs in the sea surface microlayer near urban areas are motor vehiclederived, with 47% being coal-derived. In contrast, PAHs in surface sediments of Chesapeake Bay are predominantly coal-derived (86%) and at most 14% motor vehicle derived. Thus, carcinogenic PAHs input to the bay from motor vehicles are either degraded prior to deposition to the sediments or are diluted by previously deposited coal derived PAHs in the seabed.	PCA, Ratio analysis. Photooxydation in atomosphere considered.
4	Lake Calumet (Chicago, IL)	Overall, the average contribution from coke oven emissions calculated by different operations ranges from 21% to 53% of all sources, and that from traffic ranges from 27% to 63%. The pattern of source contributions shows spatial and temporal variations.	Chemical Mass Balance (CMB) Model 8.2
5	Lake Ontario (Hamilton Harbor, ONT)	Both methods predicted similar contributions from coal tar/coal combustion sources to the harbor (19 and 26%, respectively). One PCA factor was identified as contributions from vehicular emissions (61%); PMF was able to differentiate vehicular emissions into two factors, one attributed to gasoline emissions sources (28%) and the other to diesel emissions sources (24%). Overall, PMF afforded better source identification than PCA with MLR.	Principal component analyses (PCA) with multiple linear regression analysis (MLR) and positive matrix factorization (PMF).

Summary of literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source. These results are in conflict with the USGS's hypothesis that sealers are a widespread source of PAHs.

Ref	Water Body	Source Characterization	Forensic Methods
6	St. Lawrence River (from outflow of Lake Ontario to Massena, NY)	The sediment inventory of PAH is characterized by the dominance of 4 to 6 ring parent compounds, with the PAH ranging from 0.8 to 6700 mg/g. The high abundance of high molecular weight parent compounds, high parent/alkylated PAH ratios and 13C-enriched values recorded for individual PAH are consistent with a dominant combustion PAH source for the sediments upstream of the Massena area, but areas receiving higher petroleum contribution were also identified (e.g., Prescott-Ogdensburg, Cornwall). PAH contribution from aluminum smelting operations in the Massena area is pronounced in the southern bank of the St. Lawrence River, where sediment samples display the highest PAH and higher 13C values for three ring PAH than for sediments immediately upstream. Thus, sediments at the international segment of the St. Lawrence River show localized enrichments in petroleum-related and aluminum smelter contributions against the regional backdrop of combustion-dominated PAH sources in sediments.	Alkyl-PAH compound specific stable isotope analysis (C13).
7	Elizabeth River (near Chesapeake, VA)		Principal component analysis (PCA), with identification of source-specific isomer ratios and compound-specific carbon isotope ratio analysis (CSIA).

Summary of literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source. These results are in conflict with the USGS's hypothesis that sealers are a widespread source of PAHs.

Ref	Water Body	Source Characterization	Forensic Methods
8	Black River (North-central OH) and Ashtabula River (NE OH)	FA results for a three-source solution indicate traffic (58%), coke oven (26%), and wood burning/coal tar (16%) are the primary PAH sources to Black River sediments. The primary PAH sources to the Ashtabula River sediments are traffic (51%), coke oven (44%), and wood burning (5%).	Factor analysis (FA) model with nonnegative constraints.
9	Lake Michigan (Milwaukee Basin)	PAH apportionment results indicate the dominance of coke oven emissions from 1925–1976, and of highway inputs from 1983–1992 for most of the seven cores. This is consistent with results of carbon particle analysis from the same basin. Milwaukee and Port Washington appear to be primary contributors of point source inputs of PAHs from coke ovens and highway dust. Wood burning is a minor source (<13%).	Chemical Mass Balance (CMB) Model
10	Little Menomonee River (Milwaukee, WI)	"In total, creosote and urban background contributed 27 and 73% ((14%) of eight carcinogenic PAHs (CPAHs), respectively, in this part of the River. The concentrations of CPAHs derived from urban background were highest in surface sediments (0-6 in.; 20 (17 mg/kg), particularly near major roadway crossings, increased in the downstream direction, and (onaverage) exceeded the 15mg/kg regulatory cleanup threshold. Weathered creosote derived CPAHs were widespread at low concentrations (4.8 (8.1 mg/kg) although some discrete sediments, mostly at depths below 6 in., contained elevated CPAHs derived from creosote."	Principal component analysis (PCA), chemical fingerprinting, and positive matrix factorization (PMF).
11	Lake Michigan	Wood burning was identified as a third major source of PAHs in the area (20% of the total PAH flux). The other two sources petroleum (traffic), 45%, and coal (coke oven emissions), 35%, became more apparent, where the contributions are based on the sum of concentrations of 16 PAH compounds. A reduced mixing depth (1.0–1.5 cm) was found to be more appropriate than the originally estimated mixing depth (1.5–2.0 cm).	Factor analysis model with nonnegataive constraints.

Summary of literature demonstrating that PAHs present in urban system sediments can be explained even if sealers are not considered a source. These results are in conflict with the USGS's hypothesis that sealers are a widespread source of PAHs.

Ref	Water Body	Source Characterization	Forensic Methods
12	Lake Calumet (SE Chicago, IL)	FA results for a two-source solution indicate coke oven (45%) and traffic (55%) are the primary PAH sources to Lake Calumet sediments. A six-source FA solution indicates that coke oven (47%) and traffic (45%) related sources aremajor PAH sources and wood burning-coal residential (2.3%) is a minor PAH source. From the six-source solution, two coke oven profiles are observed, a standard coke oven profile (33%), and a degraded or second coke oven profile (14%) low in phenanthrene and pyrene. Observed traffic related sources include gasoline engine (36%) exhaust and traffic tunnel air (9.3%).	Factor analysis model with nonnegataive constraints.
13	Lake Anne, Lake Ballinger, Lake Fairfax, Lake Harriet, Newbridge Pond, Orange Reservoir, Lake Packanack, Palmer Lake, Town Lake, White Rock Lake (VA, WA, VA, MN, NJ, NJ, NJ, MN, TX, TX)	The assemblage ofPAH compounds in the cores indicates a general shift in PAH source over the last 40 years from uncombusted to combusted fossil fuels, coincident with increased concentrations and urbanization. Uncombusted sources (e.g., oil seeps, petroleum spills) contain predominantly two- and three-ringed compounds, whereas combustion (e.g., vehicle exhaust, domestic heating with coal, forest fires) results in predominantly four- and five-ringed species. The results of this study is that urban growth or sprawl outside the watershed may adversely affect water quality within the watershed.	PAH concentrations linked to time of sediment deposition, profiles, evaluation of local land use.

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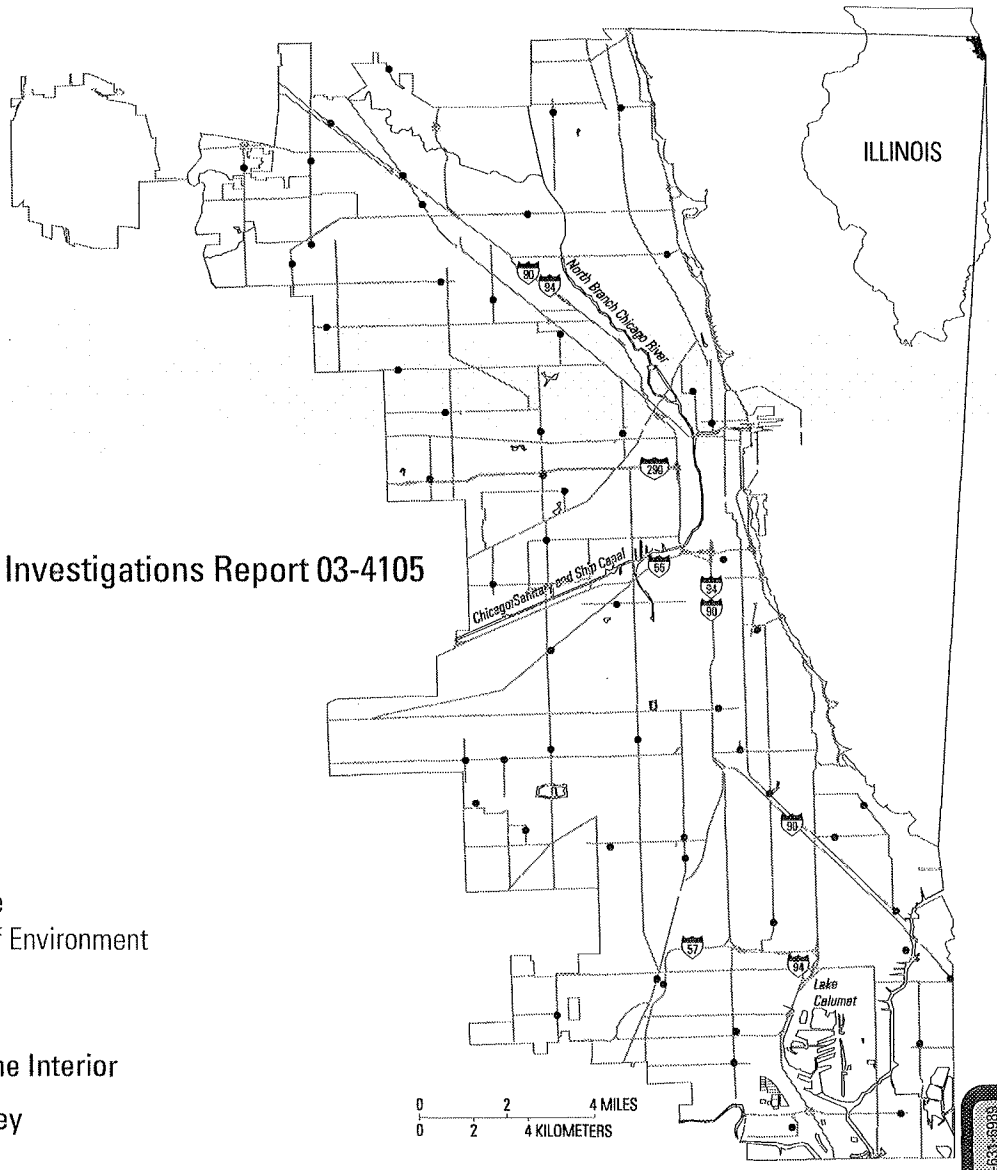
Concentrations of Polynuclear Aromatic Hydrocarbons and Inorganic Constituents in Ambient Surface Soils, Chicago, Illinois: 2001-02



Water-Resources Investigations Report 03-4105

In cooperation with the
Chicago Department of Environment

U.S. Department of the Interior
U.S. Geological Survey

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Concentrations of Polynuclear Aromatic Hydrocarbons and Inorganic Constituents in Ambient Surface Soils, Chicago, Illinois: 2001-02

By Robert T. Kay[1], Terri L. Arnold[1], William F. Cannon[1], David Graham[2], Eric Morton[3], and Raymond Bienert[3]

Water-Resources Investigations Report 03-4105

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CONVERSION FACTORS AND ABBREVIATED SOIL- AND AIR-QUALITY UNITS

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
	Area	
acre	0.4047	hectare
square foot (ft^2)	0.09290	square meter
square mile (mi^2)	2.590	square kilometer
	Mass	
ounce, avoirdupois (oz)	28.35	gram

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F = (1.8 \times °C) + 32$$

Abbreviated soil- and air-quality units: Chemical concentration is given in metric units. Chemical concentration is given in micrograms per kilogram (µg/Kg) and in micrograms per cubic meter ($\mu g/m^3$). Micrograms per kilogram is a unit expressing the concentration of chemical constituents as weight (micrograms) of the constituent per unit mass (kilogram) of soil. One milligram equals 1,000 micrograms. Micrograms per cubic meter is a unit expressing the concentration of chemical constituents as weight (micrograms) of the constituent per unit volume (cubic meter) of air.

Abbreviations:

µg/L micrograms per liter
mg/Kg milligrams per kilogram

Concentrations of Polynuclear Aromatic Hydrocarbons and Inorganic Constituents in Ambient Surface Soils, Chicago, Illinois: 2001-02

By Robert T. Kay, Terri L. Arnold, William F. Cannon, David Graham, Eric Morton, and Raymond Bienert

Abstract

Polynuclear aromatic hydrocarbon (PAH) compounds are ubiquitous in ambient surface soils in the city of Chicago, Illinois. PAH concentrations in samples collected in June 2001 and January 2002 were typically in the following order from highest to lowest: fluoranthene, pyrene, benzo(b)fluoranthene, phenanthrene, benzo(a)pyrene, chrysene, benzo(a)anthracene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, and anthracene. Naphthalene, acenaphthene, acenaphthylene, and fluorene were consistently at the lowest concentrations in each sample.

Concentrations of the PAH compounds showed variable correlation. Concentrations of PAH compounds with higher molecular weights typically show a higher degree of correlation with other PAH compounds of higher molecular weight, whereas PAH compounds with lower molecular weights tended to show a lower degree of correlation with all other PAH compounds. These differences indicate that high and low molecular-weight PAHs behave differently once released into the environment.

Concentrations of individual PAH compounds in soils typically varied by at least three orders of magnitude across the city and varied by more than an order of magnitude over a distance of about 1,000 feet. Concentrations of a given PAH in ambient surface soils are affected by a variety of site-specific factors, and may be affected by proximity to industrial areas. Concentrations of a given PAH in ambient surface soils did not appear to be affected by the organic carbon content of the soil, proximity to non-industrial land use, or proximity to a roadway.

The concentration of the different PAH compounds in ambient surface soils appears to be affected by the propensity for the PAH compound to be in the vapor or particulate phase in the atmosphere. Lower molecular-weight PAH compounds, which are primarily in the vapor phase in the atmosphere, were detected in lower concentrations in the surface soils. Higher molecular-weight PAH compounds, which are present primarily in the particulate phase in the atmosphere, tended to be in higher concentrations in the surface soils. The apparent effect of the PAH phase in the atmosphere on the concentration of a PAH in ambient surface soils indicates that atmospheric settling of particulate matter is an important source of the PAH compounds in ambient surface soils in Chicago.

The distribution of PAH compounds within the city was complex. Comparatively high concentrations were detected near Lake Michigan in the northern part of the city, in much of the western part of the city, and in isolated areas in the southern part of the city. Concentrations were lower in much of the northwestern, south-central, southwestern, and far southern parts of the city.

The arithmetic mean concentration of arsenic, mercury, calcium, magnesium, phosphorus, copper, molybdenum, zinc, and selenium was from 2 to 6 times higher in ambient surface soils in the city of Chicago than in soils from surrounding agricultural areas. The arithmetic mean concentration of lead in Chicago soils was about 20 times higher. Concentrations of calcium and magnesium above

those of surrounding agricultural areas appear to be related to the effects of dolomite bedrock on the chemical composition of the soil. Elevated concentrations of the remaining elements listed above indicate a potential anthropogenic source(s) of these elements in Chicago soils.

INTRODUCTION

Polynuclear aromatic hydrocarbon compounds (PAHs) are a family of fused ring hydrocarbon compounds derived primarily from the incomplete combustion of organic material including wood, coal, oil, gasoline, and garbage and from leaching from coal-tar products such as asphalt and roofing shingles. PAHs also are derived from natural sources such as forest fires and volcanic eruptions. However, the majority of PAHs released to the environment are derived from anthropogenic sources such as the operation of motor vehicles; burning coal, wood, or trash in a residential furnace; and industrial sources such as thermoelectric power generation and coking operations. There are more than 100 PAH compounds. However, the PAH compounds of interest for environmental investigations are acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene.

PAH compounds are released to the environment largely from emissions to the atmosphere. PAHs in the atmosphere typically are in the vapor phase or attached to particulate matter and are capable of being transported long distances from their sources before deposition on the land surface during precipitation and particle settling. Additionally, PAH compounds can be emplaced in surface soils by routine operations or leaks from storage tanks and during waste-disposal activities such as the historical use of coal ash and debris from the Great Chicago Fire as fill material. Surface-fill material is common in the Chicago area (Kay and others, 1997). PAH compounds enter surface water and sediment primarily in discharges from industrial and wastewater-treatment plants, and roadside runoff. Although PAHs do not easily dissolve in water, given the proper conditions PAHs in soils, sediments, and surface water are capable of degrading ground-water quality. Because of their physical properties and methods of production and dispersal, PAHs typically occur as a mixture of compounds in environmental media.

As in all urban areas, substantial quantities of PAH compounds have been generated within the city of Chicago (fig. 1) as a result of incineration of wood, coal, and trash; construction of roads and parking lots; operation of motor vehicles; coking operations associated with steel manufacturing; production of electricity at manufactured gas facilities; use of creosote for wood preservation; and a variety of other processes (Simcik and others, 1997). As a result of current (2003) and historical production and disposal practices, PAH compounds have been detected in a number of environmental media within the city of Chicago. PAH compounds have been detected in soils at a number of residential, commercial, industrial, and waste-disposal sites (Ecology and Environment, Inc., 1990; Harza Engineering, Inc., 1994; Ecology and Environment, Inc., 2001; U.S. Army Corp of Engineers, 2001). An investigation of ground-water quality in the southern part of the city detected PAH compounds (Duwelius and others, 1996) that may have been derived from fill materials and road runoff. PAH compounds also have been detected in surface water and streambed sediment in the Chicago area (HydroQual Inc., 1985; U.S. Army Corp of Engineers, 1986, 2001; Sullivan and others, 1998) and in lake-bottom sediments in Lake Michigan (Simcik and others, 1996). PAH compounds in streambed sediments are at least partially derived from erosion of surface soils.

Many PAH compounds are suspected carcinogens or mutagens, and are deemed hazardous substances by the U.S. Environmental Protection Agency (USEPA). Consequently, cleanup of residential, commercial, industrial, and waste-disposal sites, including Resource Conservation and Recovery Act (RCRA), Superfund, and Brownfield sites, in the city of Chicago requires remediation of soils containing concentrations of PAH compounds above what is prescribed in the Illinois Environmental Protection Agency's (IEPA) Tiered Approach to Cleanup Objectives (TACO) guidance (table 1). The TACO cleanup objectives vary with the intended future land use (industrial/commercial or residential) of the site, the route of exposure (ingestion, inhalation, and potential for migration

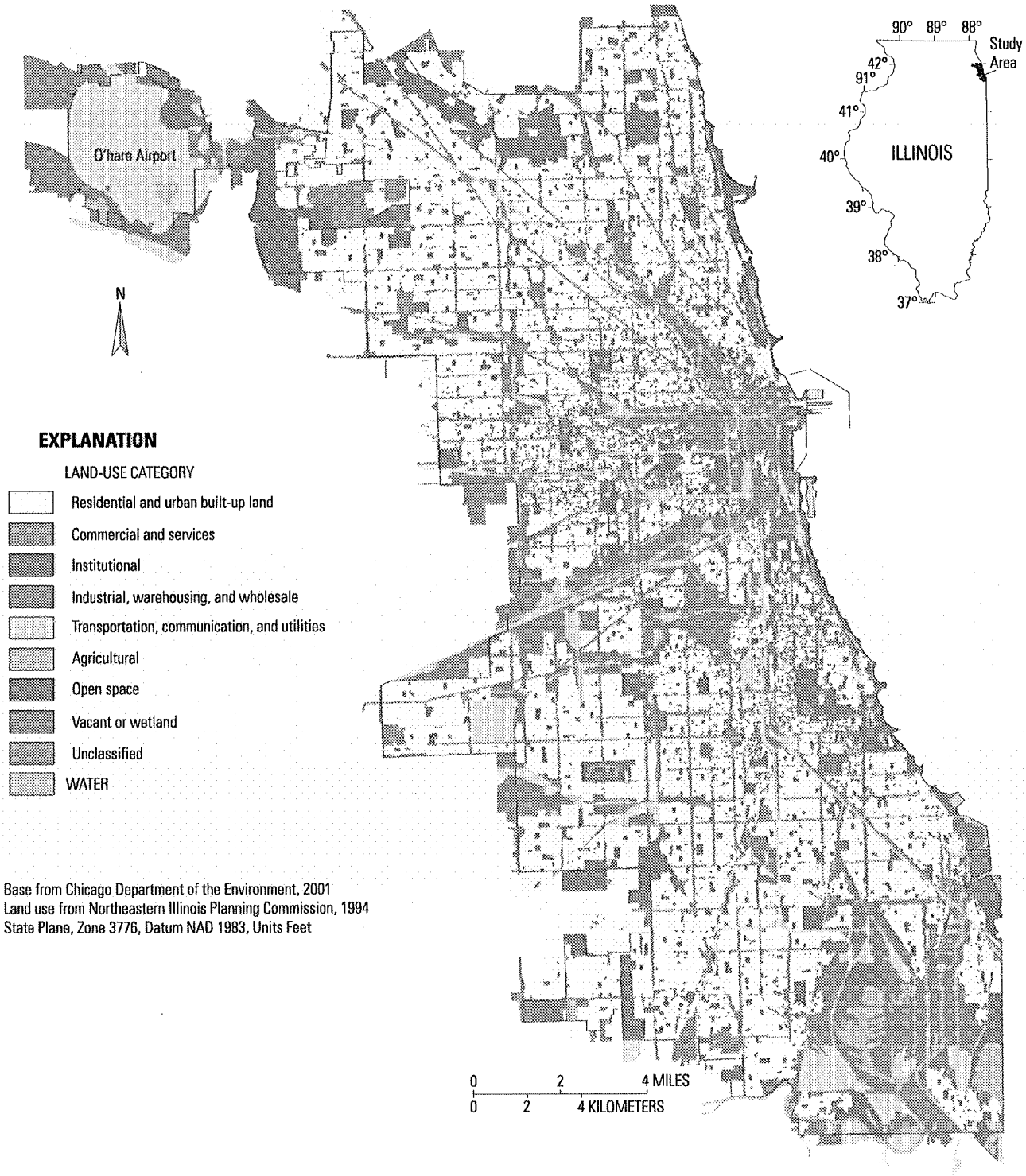

Figure 1. Land use within the city of Chicago, Illinois.

to ground water), and the type of activity leading to the exposure (resident or site-construction worker). Because the city of Chicago derives its water supply entirely from Lake Michigan and city ordinances prohibit the use of ground water wells for potable water use, TACO remedial objectives pertaining to potential for migration to ground water will not be discussed in this report.

The TACO cleanup objectives for a compound are based on assessment of the risk or hazard it poses to human health and the environment and do not automatically take its ambient concentration into account. The site-specific cleanup goals governed by the TACO guidance are intended to allow property remediation of hazardous compounds present as a result of historical operations, based on the site's future use, not to remove compounds present as a result of ambient (background) deposition. Therefore, the TACO guidance does allow for an interested party to calculate the background concentration of a compound in soil, which then can be used as the remediation objective.

Without an accurate determination of the ambient concentrations of PAH compounds in urban soils, it can be difficult to determine if concentrations of PAH compounds encountered in soils during site remediation are the result of contamination or ambient effects. Soil remediation may include excavation and disposal of contaminated soil to an appropriate waste-disposal facility or installation of an engineered barrier (clean soils, pavement, buildings) to prevent human contact. Often, excess soil removed during construction projects containing PAH compounds at concentrations similar to ambient concentrations but above site-remediation objectives must be disposed of in local landfills at additional cost. Therefore, the absence of values for the ambient concentrations of PAH compounds in surface soils in the city of Chicago may result in increased site-remediation costs associated with unnecessary soil excavation and disposal and installation and maintenance of unnecessary engineered barriers. Site-specific removal of soils containing ambient concentrations of PAH compounds also is unlikely to result in an improvement to human health and the environment. Development of a scientifically valid assessment of ambient concentrations of PAH compounds in surface soils and identification of the factors that affect PAH concentrations in surface soils has the potential to substantially help project managers and site investigators increase the effectiveness of remediation at waste-disposal sites in Chicago.

Potential receptors (with the exception of construction workers under some circumstances) are most likely to be exposed to PAHs through ingestion and direct contact with compounds in surficial soil, rather than to PAHs in soil at greater depths. As a consequence, it particularly is important to characterize surficial soils. For the purposes of conducting Tier 3 risk assessments under TACO, the IEPA requires that exposure point concentrations for soil ingestion be calculated based on analytical data for surface soil (typically 0 to 6 in. below ground surface) in addition to the requirement of evaluating the upper 3 ft of the soil.

The U.S. Geological Survey (USGS), in cooperation with the city of Chicago, Department of Environment, assessed the concentration of each of the regulated PAH compounds in ambient surface soils within the city. For the purposes of this report, ambient soils are those soils whose chemical composition is affected by ubiquitous natural and anthropogenic processes rather than the site-specific disposal of waste materials. This investigation did not include O'Hare Airport on the far northwestern part of the city. Samples were collected in June 2001 and January 2002 from areas near residential, commercial, and industrial land use. Based on discussions with IEPA personnel, analytical results from surficial soil samples, for the purposes of comparison, were considered applicable for all depths. This approach is consistent with the TACO guidelines, which recommend use of a single set of inorganic chemical background concentrations in surface soil for comparison to analytical results from site-specific soil samples collected at various depths (Illinois Pollution Control Board, 2002; Illinois Environmental Protection Agency, 1994).

In addition to PAH compounds, samples of surface soils were analyzed to characterize concentrations of a number of inorganic constituents, including metals and major elements. Analysis of the concentration of inorganic constituents was performed by the USGS as part of a program to chemically characterize surface soils in the United States.

Purpose and Scope

This report describes the results of an investigation that used stratified random sampling techniques and geographic information system (GIS) analysis to characterize the concentration of PAH compounds in ambient surface soils in the city of Chicago. In addition, a preliminary assessment is provided of the concentrations of inorganic constituents in these soils. This report presents the results of soil-quality sampling for PAHs and inorganic constituents at 57 randomly selected sites. It also presents statistical and GIS analysis of the soil PAH data. This report provides summary statistics of the concentrations of the PAH compounds, including the mean concentration of the individual PAH compounds. A summary of the concentrations of inorganic constituents is given. Potential sources of PAH compounds and inorganic constituents are identified, along with some of the factors that may affect the concentrations of these constituents in ambient soils.

Acknowledgments

The authors thank Commonwealth Edison for allowing access to their property for sample collection.

METHODS

This investigation required the selection of appropriate sampling sites, collection of representative samples, accurate measurement of concentrations of PAHs and inorganic constituents in the samples, and statistical analysis of PAH concentrations. Because sampling for inorganic constituents was designed to provide only a general assessment of the distribution and concentration of these compounds in Chicago and was not designed to meet regulatory needs, the inorganic data were not statistically analyzed.

Site Selection

A random site-selection computer program (Scott, 1990) was used with a GIS spatial data base to select 173 potential sampling sites in Chicago. Of these potential sampling sites, 60 were selected as primary sites and 113 were selected as alternate sites in the event that a primary site could not be sampled. For the purpose of site selection, the city of Chicago boundary was used as the boundary of the study area (fig. 1). Using the program, the study area was divided into 4,601 small square polygons (subareas), each of which was approximately 0.05 mi^2 (fig. 2a). These subareas later were aggregated to create equal-area cells from which sites were selected randomly. To create the cells from which the sites were selected, the subareas were accumulated into eight vertical strips (fig. 2b). The number of vertical strips was determined by taking the square root of the number of primary sites and rounding the result to the nearest whole number. The area of each vertical strip was approximately 30 mi^2. The number of cells created was equal to the number of primary sites (60), resulting in 60 equal-area cells (fig. 2c). Cells were created by aggregating each horizontal row of subareas within consecutive vertical strips, beginning in the lower left corner of the study area, until the desired area was obtained. The resulting cells had irregular shapes and were approximately 3.8 mi^2 in area.

A total of 374 properties owned by the city of Chicago and Commonwealth Edison (a local utility) were used as the population of potential sampling sites for this study (fig 3a). Properties owned by the city of Chicago including libraries, fire stations, and police stations and properties owned by Commonwealth Edison are located throughout the city. Point locations of these properties were combined into one layer using the GIS, with one point location representing each property. The density of the properties in the study area was about 0.5 of a point per square mile.

The modified GIS layer of properties owned by the city and Commonwealth Edison contained a total of 373 points (fig. 3b). These points were used as a fixed population of potential sites from which the site-selection program could choose randomly. From this fixed population of 373 points and the 60 equal-area cells, the site-selection program randomly selected 60 primary sites (one per cell), 58 secondary sites, and 55 tertiary sites (fig. 3c). The secondary and tertiary sites are alternate sites that could have been used if the primary site in a cell could not be

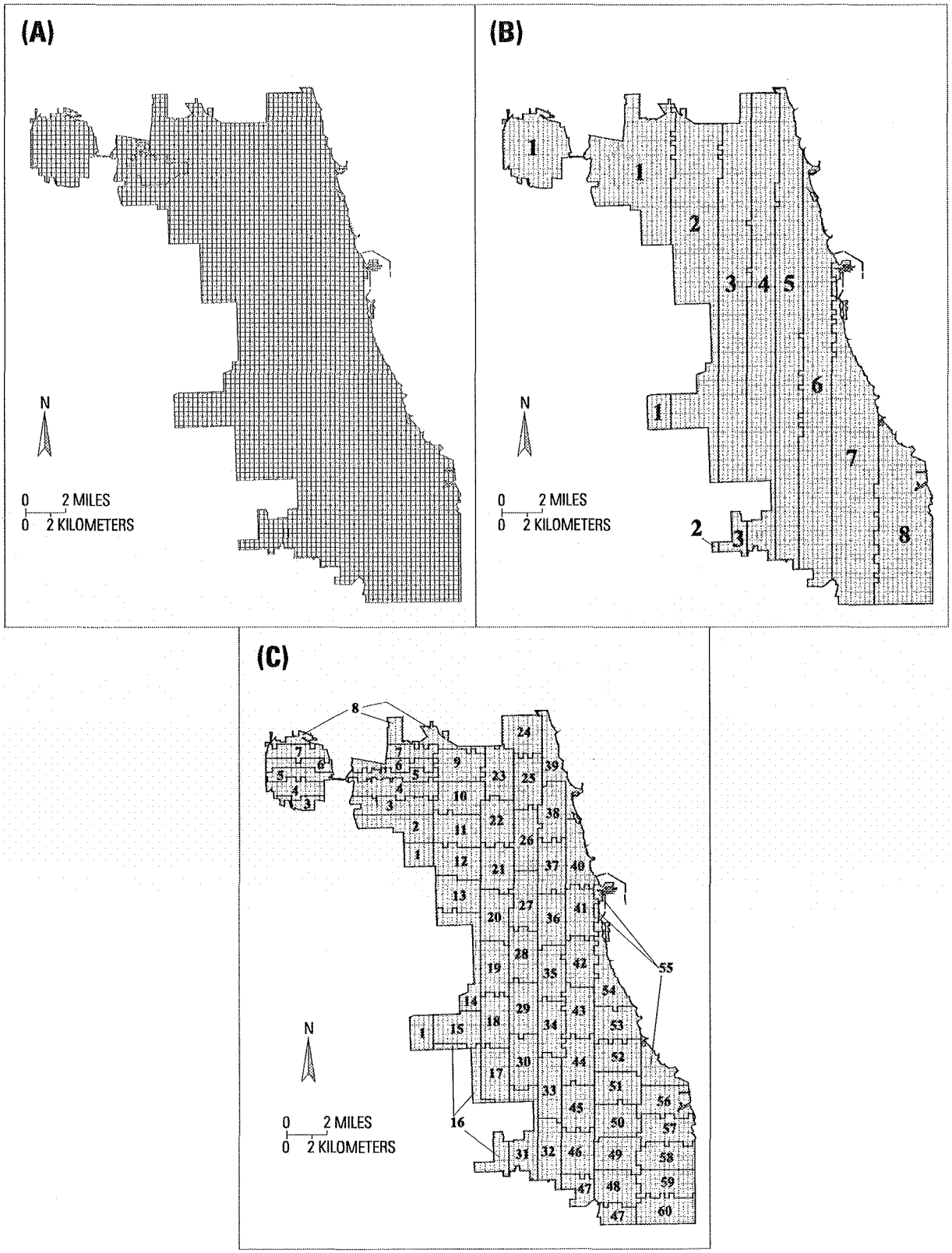

Figure 2. Locations of (A) subareas, (B) vertical strips, and (C) equal-area cells used for selection of random sample locations, Chicago, Illinois.

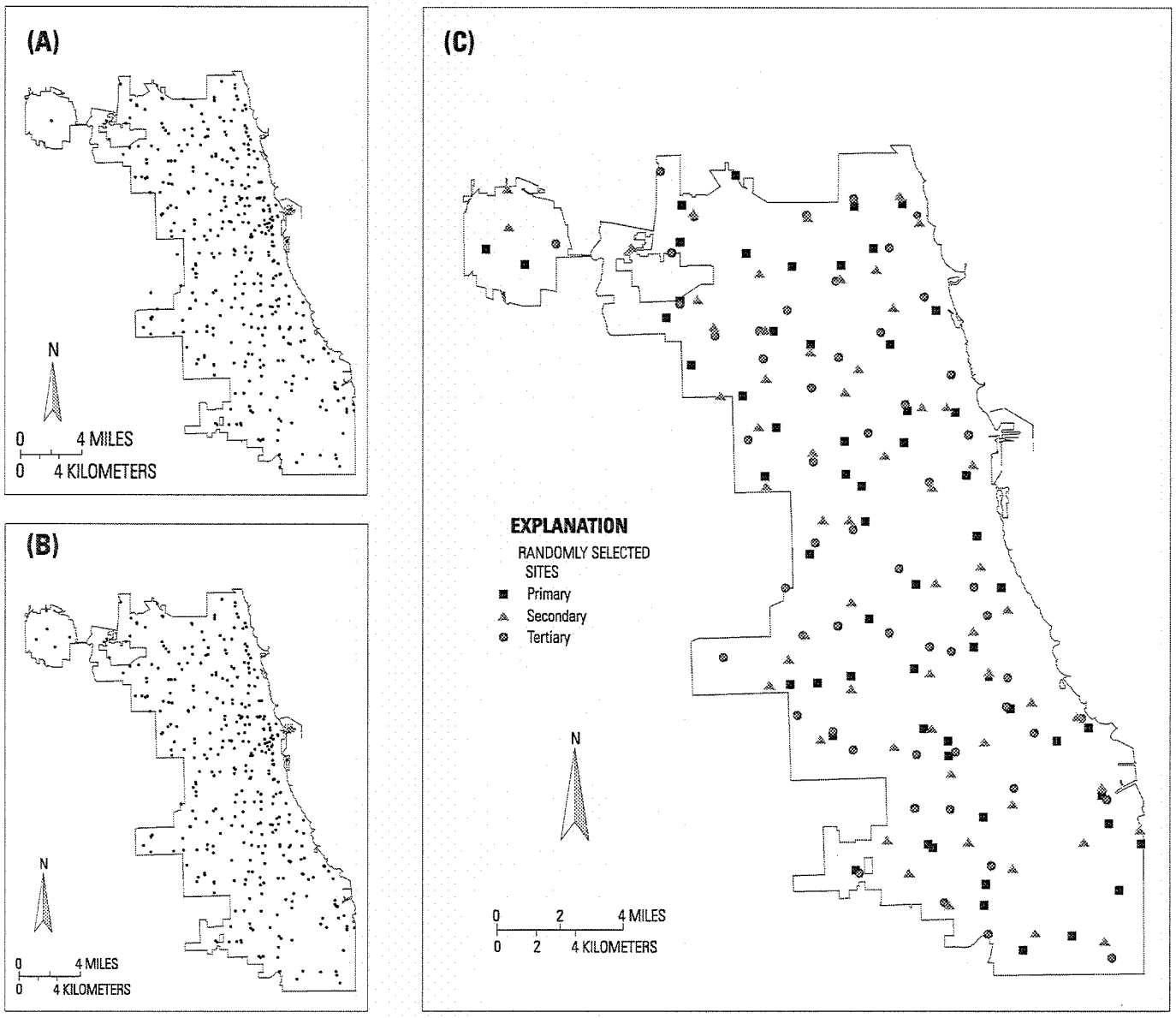

Figure 3. Locations of (A) properties owned by the city of Chicago and Commonwealth Edison, (B) final fixed population of potential sites used to randomly select sampling sites, and (C) randomly selected sampling sites, Chicago, Illinois.

sampled. Because of the distribution of potential sites, not every cell had enough points for the program to select two alternate sites from each cell.

Historical land use at each of the sample locations was evaluated by the Chicago Department of Environment (CDOE) to determine if PAH compounds derived from industrial activities or waste-disposal operations at the site might be present. Evaluation of historical land use consisted of reviewing available Sanborn Fire Insurance maps and aerial photographs. Within each cell, the primary location was the preferred sampling location unless it was deemed unsuitable based on the historical evaluation. For example, if the historical analysis indicated that land use at a particular location could have resulted in PAH contamination specific to the property, an alternative location within the cell was considered.

Following the historical review, the CDOE performed an inspection of the potential sampling sites. Sampling sites were rejected if there were indications of industrial sources of PAHs (electrical plants, steel mills, coke plants, gas stations, incinerators, and heating plants) at the site, if the property was paved entirely or contained structures so that soil samples could not be collected, or if stains or stressed vegetation were evident. If the site inspection indicated possible problems with the sampling site, the secondary or tertiary sampling locations were evaluated. Gravel areas that were not parking lots were considered for sampling if the gravel was less than 6 in. thick and could be scraped away to reveal soil.

Sample Collection and Analysis

Soil samples were collected at 57 sites (table 2). Samples collected from properties owned by the city of Chicago are denoted by a SS prefix. Samples collected from properties owned by Commonwealth Edison are denoted by a CE prefix. Samples were collected in accordance with the IEPA approved field sampling plan, which is included in the IEPA approved quality-assurance project plan (QAPP) (TetraTech EM, Inc., 2001) (table 2, fig. 4). Inorganic samples were collected and analyzed in accordance with standard USGS procedures (Arbogast, 1996).

Soil samples were collected from the upper 6 in. of the soil horizon (from 0 to 6 in. in an undisturbed soil horizon or from the upper 6 in. of a soil horizon where it may be covered by gravel) using a dedicated stainless-steel spoon or trowel. Samples were collected by personnel from Tetra Tech EM, Inc. and the CDOE. The soil type was characterized at the time of sample collection. Soil samples were placed in a disposable foil pan and homogenized by stirring the soil using the stainless-steel spoon or trowel. One 16-ounce and one 4-ounce sample jar were filled by spooning soil from the foil pan into the container. The latitude and longitude of the sample sites were determined with a global positioning system (GPS) unit (table 2).

Sampling activities were documented in the field. For each sample, all pertinent data including property address; cell number and whether primary, secondary, or tertiary property; sample number; date and time of sample collection; weather conditions; GPS coordinates; description of sample location; proximity to stained soil, stressed vegetation, asphalt, underground storage tanks, above-ground storage tanks, parking lots, or other distinguishing property characteristics, which could be a source of PAHs; soil characteristics; and sample depth were recorded. Samples were packaged, cooled to 4° C with ice, and shipped overnight to the laboratory for PAH analysis. Samples for inorganic analysis were stored at 4° C for as long as 7 days prior to shipment to the laboratory. Chain-of-custody procedures were followed for all samples collected for PAH analysis.

Soil samples were analyzed for PAHs in accordance with the approved QAPP (TetraTech EM, Inc., 2001). Soil samples used for PAH analysis were prepared according to SW-846 Method 3550 and analyzed by SW-846 Method 8270 SIM (U.S. Environmental Protection Agency, 1994a). All field and laboratory data were validated in accordance with accepted guidelines (U.S. Environmental Protection Agency, 1994b).

Analyses for inorganic constituents were performed using inductively coupled plasma-atomic emission spectrometry. Methods for handling and analysis of these samples are provided by Arbogast (1996). Samples were disaggregated and sieved to recover the minus 180 micrometer fraction for chemical analyses. Analyses were performed at Xral Laboratories in Toronto, Canada, using techniques developed by the USGS, and at USGS analytical laboratories in Lakewood, Colorado. Forty major, minor, and trace elements were determined by inductively coupled plasma-atomic emission

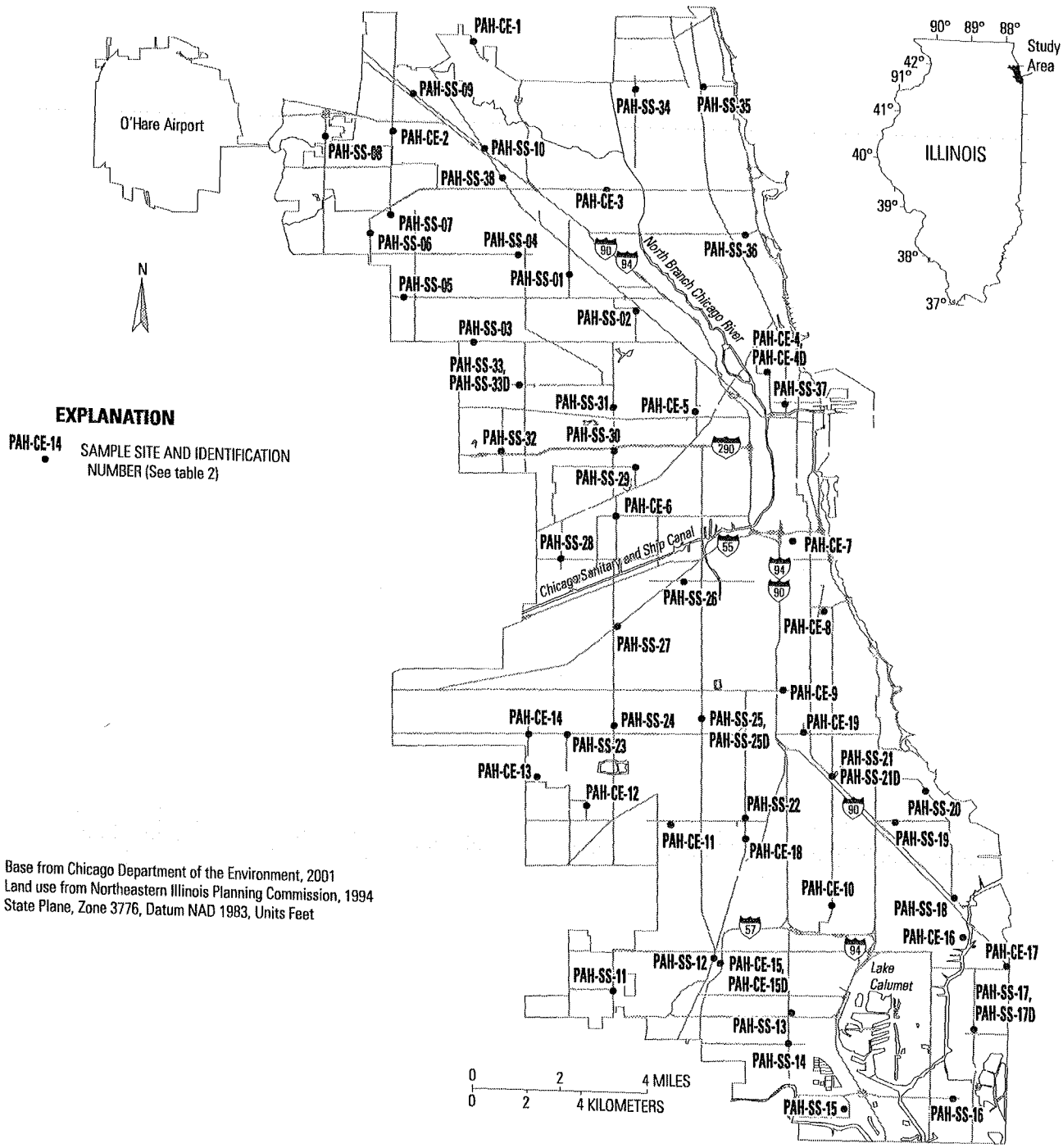

Figure 4. Locations of surface-soil sampling sites, Chicago, Illinois.

spectrometry (ICP-AES). The technique yields quantitative data for 28 elements (appendix 2); the remaining 12 have all or most analyses below the detection limit. In addition, total carbon was determined by an automated carbon analyzer and carbonate carbon was determined as carbon dioxide by coulometric titration. Organic carbon was calculated as the difference between total and carbonate carbon. Total sulfur was determined using an automated sulfur analyzer and mercury was determined by cold-vapor atomic absorption spectrometry. Arsenic and selenium were analyzed by hydride generation atomic absorption spectrometry.

Calibration of the inorganic samples was performed by standardizing with digested rock reference materials and a series of multi-element solution standards. Data were deemed acceptable if recovery for all was ±15 percent at five times the Lower Limit of Determination (LOD) and the calculated Relative Standard Deviation (RSD) of duplicate samples was no greater than 15 percent for all elements except mercury, arsenic, and selenium. For these elements, ±20 percent recovery and an RSD no greater than 20 percent was considered acceptable.

Field and internal laboratory quality controls were performed to determine the precision, accuracy, completeness, representativeness, and comparability of the data. To assist in this effort, one field duplicate sample was collected for every 10 investigative samples. One matrix spike/matrix spike duplicate PAH sample was collected for every 20 investigative samples. The laboratory prepared one PAH method blank sample for every 20 investigative samples. All data for both PAH and inorganic constituents were reviewed following quality-assurance/quality-control (QA/QC) procedures.

Statistical Analysis of Uncensored Polynuclear Aromatic Hydrocarbon Data

Benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene, indeno(1,2,3-cd)pyrene, phenanthrene, and pyrene were detected in each of the samples collected (table 3). As a consequence, the actual reported concentrations were used in the statistical analysis for these compounds (uncensored data). For sites where duplicate samples were collected, the average value was used for all analyses. Concentrations of all of the PAH compounds in sample PAH-CE-19 except acenaphthylene were substantially higher than in the remaining samples (table 3). Because sampling location PAH-CE-19 was considered a potential outlier, most of the preliminary statistical analyses were performed both with and without this data point.

The sample location of PAH-CE-19 is adjacent to a Commonwealth Edison transfer station with no obvious source of atmospheric discharge. The property was grass covered and vacant with remnants of a former building foundation. Historical property use was residential, based on Sanborn Fire Insurance maps. Land use in the surrounding area was predominately residential according to the Northeastern Illinois Planning Commission (1994) maps. No obvious sources of PAHs were identified during site reconnaissance or sample collection.

The uncensored PAH data were analyzed statistically using standard parametric techniques as follows: test for two independent samples from the same population; graphical exploratory techniques; calculation of basic descriptive statistics; test for lognormal distribution; test for outliers; re-test for two independent samples from the same population without the outlier; re-test for lognormal distribution without the outlier; re-calculation of basic descriptive statistics without the outlier; calculation of the 95th percentile of the population, 95-percent confidence interval for the mean, and the mean; simple linear regressions of PAH concentration with percent land use and PAH concentration with mean distance to land use. Estimates of the actual values of the mean, standard deviation, and the 95th percentile of the lognormal distribution were estimated using techniques recommended by Gilbert (1987).

Population Tests

City of Chicago properties were sampled in the summer of 2001 and Commonwealth Edison properties were sampled in the winter of 2002. Because all of the data were not collected at the same time or on the same set of properties, there potentially were two separate data populations (city of Chicago properties and Commonwealth Edison properties) for each of the PAHs. A two-sided Wilcoxon-Rank-Sum test in S-Plus (MathSoft, 2000)

was used to test if the one population contained larger or smaller values than the other. If the results of the test showed the populations likely were similar, then data from the city of Chicago and Commonwealth Edison properties could be combined into one dataset for further analysis. The null hypothesis was that the values in the two populations were similar and the alternate hypothesis was that the values from one population were larger or smaller than the other population. A 95-percent confidence interval (alpha of 0.05) was used for the Wilcoxon-Rank-Sum test. The Wilcoxon-Rank-Sum test was performed with and without sample PAH-CE-19.

Test for Lognormal Distribution

PAH concentrations were transformed in SAS (SAS Institute, Inc, 1999) by applying the natural logarithm (log transformation). The transformed data then were evaluated for lognormality using the Shapiro-Wilk test in SAS interactive data analysis with a significance level (alpha) of 0.1 as recommended by Helsel and Hirsch (1995) for normality tests. The Shapiro-Wilk test was performed with and without the data from sample PAH-CE-19.

Graphical Analysis

The raw uncensored data initially were investigated using graphical exploratory data techniques, including boxplots, histograms, and normal probability plots. Boxplots, histograms, and normal probability plots were graphed using Data Desk (Data Description, Inc., 1996). Natural-log transformed uncensored data also were explored using boxplots and normal probability plots graphed in Data Desk with and without the data from sample PAH-CE-19.

Descriptive Statistics

Standard descriptive statistics were calculated using interactive data analysis in SAS (SAS Institute, Inc, 1999). Descriptive statistics were calculated for raw and natural-log transformed data both with and without the data from sample PAH-CE-19. Calculated statistics (not all of which are presented in this report) include: mean, standard deviation, standard error, variance, number of observations, minimum, maximum, median, range of values, sum, corrected and uncorrected sum of squares, coefficient of variation, skewness, and kurtosis.

Outlier Test

A data point is classified as a mild outlier if the value is more than 1 step above the 75th percentile and classified as an extreme outlier if the value is more than 2 steps above the 75th percentile. A step is equal to 1.5 times the interquartile range (Helsel and Hirsch, 1995). To evaluate for an extreme outlier, the interquartile range and number of steps between the 75th percentile and the highest value were calculated. The interquartile range was calculated by subtracting the 25th percentile from the 75th percentile. The number of steps was calculated by subtracting the 75th percentile from the maximum value and dividing the result by 1.5 times the interquartile range. The outlier test was performed with the suspected outlier, PAH-CE-19, included.

To further determine if PAH-CE-19 is an outlier, the magnitude of the difference between the concentration of the PAH compound in this sample (the maximum value) and the next lowest value was examined using the number of standard deviations between them. The number of standard deviations between the maximum and next lowest value was calculated by subtracting the next lowest from the maximum value and dividing the result by the standard deviation.

95th Percentile, 95-Percent Confidence Interval For The Mean, and Geometric Mean

The 95th percentile and 95-percent confidence interval for the mean of the natural-log transformed data were calculated using interactive data analysis in SAS (SAS Institute, Inc, 1999). For natural-log transformed PAH concentrations, the geometric mean was calculated in Microsoft Excel (Microsoft Corporation, 2000) by taking the anti-log of the mean. The data from sample PAH-CE-19 were not included in these calculations.

Relation Between Polynuclear Aromatic Hydrocarbon Concentrations and Land Use

Various analyses were performed to determine if PAH concentrations in ambient surface soils were

affected by nearby land use. For the purposes of this discussion, land use also includes the distance between the sampling point and the middle of the nearest roadway.

The Northeastern Illinois Planning Commission's 1990 land-use summary (Northeastern Illinois Planning Commission, 1994) was used to identify the current land use for each sample location. Chicago's land-use code is broadly classified as urban, built-up land (85 percent), agricultural (less than 1 percent), open space (7 percent), vacant and wetland (6 percent), water (less than 2 percent), and unclassified (less than 1 percent). Urban, built-up land is further subdivided as residential (47 percent), commercial services (10 percent), institutional (6 percent), industrial (11 percent), transportation, communication, and utility (11 percent). Therefore, about 15 percent of the land composing the city of Chicago is considered undeveloped and the majority of the land use is for residential purposes.

Simple Linear Regression

The mean distance from each sampling point to each type of land use in the area of the sampling point was calculated (table 4). Land use was classified as residential, commercial, institutional, industrial/warehousing/wholesale (hereafter referred to as industrial), transportation/communications/ utilities (hereafter referred to as transportation), agriculture, open space, vacant/wetland (hereafter referred to as vacant), and water according to 1990 land-use spatial data obtained from the Northeastern Illinois Planning Commission (1994) (fig. 1). To calculate the mean distance to each land-use category from each sampling point, ArcInfo GIS (Environmental Systems Research Institute, 2001a) was used with four raster data layers representing soil-sampling point locations, sampling-point zones, distance, and land use in 1990 (Northeastern Illinois Planning Commission, 1994). Cell size of raster data layers was 30 ft^2. Each sampling-point location was enclosed by Thiessen (also called proximal) polygons using a Euclidean allocation function, which created sampling-point zones. The Thiessen polygons formed a zone around each sampling point such that any location inside the zone was closer to that zone's sampling point than any other sampling point. Zones ranged in area from 1 mi^2 to 10 mi^2. The distance layer was created by calculating the Euclidean distance outward in every direction from each sampling point to the edge of the zone. The distance layer then was combined spatially with the land-use and sampling-point-zone layers to calculate the mean distance to each land use in the zone from the sampling point. Simple linear regressions of mean distance to each land use with natural-log transformed PAH concentrations were calculated using Data Desk (Data Description, Inc., 1996). The suspected outlier, PAH-CE-19, was not included in the regressions.

Land use surrounding the sampling site also was examined. Buffers of 0.25, 0.5, and 1 mi radius around the sampling site were created using ArcInfo GIS (Environmental Systems Research Institute, 2001a). The buffers were overlaid spatially with the land use layer (Northeastern Illinois Planning Commission, 1994) and the percent of land-use category within 0.25, 0.5, and 1 mi of the sampling point was calculated (table 5). Simple linear regressions of percent land use within a 0.25, 0.5, and 1 mi radius of the sample with natural-log transformed PAH concentrations were performed for all uncensored PAHs using Data Desk (Data Description, Inc., 1996). The data from sample PAH-CE-19 were not included in the regressions.

The distance between the sample location and the nearest roadway was estimated by use of an on-screen digitizer. The location of the sampling point was determined by GPS measurement, and the location of the nearest roadway was determined visually from a GIS coverage. The distance between the point and the road then was calculated by use of ArcInfo. Correlation between the natural-log transformed concentration of the PAH and the natural-log of the distance from the roadway then were estimated by simple linear regression in Microsoft Excel (Microsoft Corporation, 2000). The data from sample PAH-CE-19 were not included in the regressions.

Unbalanced One-Way Analysis of Variance

A spatial overlay of sampling locations and land use (Northeastern Illinois Planning Commission, 1994) was performed in ArcInfo GIS (Environmental Systems Research Institute, 2001a) to identify the land use at the sampling point. Sample locations were grouped into seven land-use categories: residential; commercial and service; institutional; industrial,

warehousing, and wholesale; transportation, communication, and utilities; open space; and vacant and wetland (table 6). The Shapiro-Wilk test in S-Plus (MathSoft, 2000) was used to verify that the natural-log transformed PAH concentrations for those land uses with five or more samples (vacant and wetland; transportation, communication and utilities; commercial and service; industrial, warehousing, and wholesale; and residential) were normally distributed. To test if mean log-transformed PAH concentrations varied for different land uses, a one-way unbalanced analysis-of-variance (ANOVA) was performed for each uncensored PAH using S-Plus. The null hypothesis was that the mean natural-log transformed values statistically were the same for each land use. The alternate hypothesis was that at least one of the means differed with land use. An alpha value of 0.05 was used for the test. The data from sample PAH-CE-19 were not included in the ANOVA.

The distance between the sampling locations and the roadway were grouped into five categories: 10 ft or less (20 data points), 11 to 30 ft (15 data points), 31 to 50 ft (9 data points), 51 to 100 ft (6 data points), and greater than 100 ft (6 data points). The Shapiro-Wilk test in S-Plus was used to verify that the natural-log transformed PAH concentrations for distances were normally distributed. To test if mean log-transformed PAH concentrations varied with distance from the roadway, a one-way unbalanced ANOVA was performed for each uncensored PAH using S-Plus. The null hypothesis was that the mean natural-log transformed values statistically were the same for each distance category. The alternate hypothesis was that at least one of the means differed with distance. An alpha value of 0.05 was used for the test. The data from sample PAH-CE-19 were not included in the ANOVA.

Geospatial Analyses of Benzo(a)pyrene Concentrations

ArcMap Geostatistical Analyst, (Environmental Systems Research Institute, 2001b) was used to spatially evaluate variations in benzo(a)pyrene concentrations with land use and location. Benzo(a)pyrene was used because it typically is the compound of greatest concern. To obtain the spatial distribution of benzo(a)pyrene concentrations, the natural-log transformed data was kriged using geospatial statistics in the GIS. Kriging is a geostatistical method used to statistically predict values at unsampled location based on the theory that points closer together are more similar than those farther apart. Kriging compares the values at pairs of sampling points (called bins) and considers the distance the points are from each other. The distribution of the bins were fit visually to a spherical spatial model using a semivariogram. A semivariogram graphs the variance in values with the distance that separates each pair of points.

Statistical Analysis of Censored Polynuclear Aromatic Hydrocarbon Data

Concentrations of naphthalene, acenaphthylene, acenaphthene, fluorene, and anthracene were below the detection limit in some of the samples (appendix 1) (table 3). Each of these compounds had multiple detection limits (the data are censored at multiple levels). Because concentrations for all of the samples are not known, assumptions about the presence of a normal or lognormal data distribution cannot be verified for the censored PAH compounds, which is a requirement for the use of parametric analytical techniques. As a consequence, the censored data were analyzed using nonparametric techniques described in Helsel and Hirsch (1995), Helsel and Cohn (1988), and Cohn (1988). Censored data were analyzed statistically as follows: test for two independent samples from the same population, graphical exploratory techniques, calculation of limited descriptive statistics, graphical analysis of lognormal distribution, test for outliers, and calculation of the 95th percentile and geometric mean. As was the case for the uncensored data, results of duplicate samples were averaged.

Graphical Analysis

Boxplots of raw and natural-log transformed censored data were made using Data Desk (Data Description, Inc., 1996). For construction of the boxplots, the censored values were used to create the portions of the box below the median. However, during visual analysis of the boxes, the highest censoring level of each PAH was considered and the parts of the box below that highest censored value were ignored. Boxplots were drawn with and without the data from sample PAH-CE-19.

Normal probability plots also were utilized during exploratory graphical analysis. Plotting positions for normal probability plots were calculated using a C program (Dave Lorenz, U.S. Geological Survey, written commun., 2002), which utilizes the methods outlined in Helsel and Cohn (1988). The program input is a specifically formatted ASCII file of the natural-log transformed data above and below the detection limit. The plotting positions output from the C program then were used in Data Desk (Data Description, Inc., 1996) to graph a scatterplot of the plotting positions with the natural-log transformed PAH concentrations. A regression line then was drawn for the scatterplot. Boxplots and normal probability plots were drawn with and without the data from sample PAH-CE-19.

Descriptive Statistics

Limited descriptive statistics for raw and natural-log transformed censored PAHs were calculated and estimated using robust methods described in Helsel and Hirsch (1995). Calculated statistics include: number of observations, number of censored values, range of censored values, maximum, median, 25th, 75th, and 95th percentile of the distribution, and geometric mean. The mean and standard deviations were estimated using robust log-probability regression based on plotting points for data censored at multiple levels using the methods outlined by Helsel and Cohn (1988) and Cohn (1988) and the C program (Dave Lorenz, U.S. Geological Survey, written commun, 2002). Another C program (Dave Lorenz, U.S. Geological Survey, written commun., 2002) that calculates an adjusted maximum-likelihood estimator following methods outlined by Helsel and Cohn (1988) and Cohn (1988) was used to estimate the median and quartiles. Descriptive statistics were performed with and without the data from sample PAH-CE-19.

Outlier Test

Outlier testing for the uncensored data set was performed using most of the same procedures as for the censored data. However, the 25th, 50th, and 75th percentiles for the censored data were estimated using a C program, which calculates an adjusted maximum-likelihood estimator following methods outlined by Helsel and Cohn (1988) and Cohn (1988). Estimates of the standard deviation were calculated by log-probability regression using a C program, which follows the methods outlined in Helsel and Cohn (1988), Cohn (1988), and Helsel and Hirsch (1995).

Relation between Polynuclear Aromatic Hydrocarbon Concentrations and Land Use

Because of the high number of non-detects for some of the censored PAH compounds, simple linear regression of PAH concentrations with land use could not be performed for these constituents. The natural-log transformed concentrations of individual censored PAH compounds were compared for samples grouped by land-use category using multiple-population parametric and nonparametric statistical tests in a manner similar to the analysis of the uncensored data. Censored analytes were not analyzed with regard to distance from the roadway. Censored data in the distribution testing and multiple-population tests were treated by replacing each censored datum with its estimated value calculated using robust log-probability regression, following Helsel (1990), Helsel and Cohn (1988), and Akritas and others (1994).

Correlation of Polynuclear Aromatic Hydrocarbon and Inorganic Concentrations

Pearson product-moment correlations (r values) were obtained from the natural-log transformed concentration of each of the PAH pairs as well as each of the PAHs and total organic carbon using Microsoft Excel. PAH samples below the detection limit were assigned a concentration value of 1.39 μg/Kg, the natural log of 4 μg/Kg, which is 1 μg/Kg lower than the lowest detection limit for any PAH. Correlations involving the PAHs were performed with and without the data from site PAH-CE-19. Pearson product-moment correlations also were obtained for every pair of inorganic constituents detected in more than 75 percent of the samples. Inorganic constituents below the detection limit were assigned a concentration value

of two-thirds the detection limit. Results from site PAH-CE-19 were used for correlation of the inorganic constituents.

ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBON DATA

The results of soil-quality sampling indicate that 11 or more of the 16 PAH compounds were detected in each of the 57 soil samples collected (samples and duplicates are counted as one sample) (appendix 1). Of the 57 samples collected, 35 contained detectable concentrations of every PAH compound analyzed (table 3). Of the 22 samples in which 1 or more PAH compounds were not detected, naphthalene was the most frequent non-detect, followed by acenaphthylene, fluorene and acenaphthene, and anthracene.

Fluoranthene was the PAH detected at the highest concentration of all the PAH compounds in every sample except samples PAH-SS-10 and PAH-SS-11. The concentration of benzo(g,h,i)perylene was highest in sample PAH-SS-10 and second highest in sample PAH-SS-11. The concentration of indeno(1,2,3-cd)pyrene was highest in sample PAH-SS-11 and second highest concentration in sample PAH-SS-10. Pyrene was present at the second highest concentration of any PAH compound in 37 of the samples. Samples PAH-SS-10 and PAH-SS-11 were the only samples where the ratio of fluoranthene to pyrene was less than one. Because the fluoranthene/pyrene ratio is an indicator of the temperature at which the PAHs were generated (McCarthy and others, 2000), the low value of this ratio in samples PAH-SS-10 and PAH-SS-11 may indicate that the PAHs at these locations were derived from a different source, or combination of sources, than most of the remainder of the city. However, there are no obvious anomalies in location, land use, or the soil descriptions at these sites to indicate differences in the source(s).

After fluoranthene and pyrene, PAH concentrations in a given sample, from highest to lowest, were roughly in the following order: benzo(b)fluoranthene, benzo(a)pyrene, phenanthrene, chrysene, benzo(a)anthracene, indeno(1,2,3-cd)pyrene, benzo(k)fluoranthene, benzo(g,h,i)perylene, anthracene, and dibenzo(a,h)anthracene. Naphthalene, acenaphthene, acenaphthylene, and fluorene consistently were present at the lowest concentrations in each sample (appendix 1).

Boxplots and histograms of the concentrations of the individual PAH compounds showed that the majority of the samples were in the lower end of the concentration range, with a smaller number of samples in the higher end of the range, including a number of potential outliers (figs. 5a and 5b). This left-skewed distribution indicated that the PAH concentrations in these samples did not exhibit a normal distribution. Boxplots and histograms of the natural-log transformed concentration data typically displayed a more symmetrical distribution, indicating that the PAH compounds may exhibit a lognormal distribution (figs. 6a and 6b). One remaining potential outlier (sample PAH-CE-19) was identified for each of the PAH compounds, except acenaphthylene, from the boxplots of the natural-log transformed data.

Analysis of the natural-log transformed concentration data for the uncensored PAH compounds indicated that the null hypothesis of a lognormal distribution could be accepted (p-value was greater than alpha level of 0.1) if the data from sample location PAH-CE-19 were excluded from the analysis (table 7). If the data from site PAH-CE-19 were included in the analysis, the hypothesis of a lognormal distribution was rejected (p-value was less than or equal to alpha level of 0.1) for pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene. Normal probability plots of natural-log transformed censored PAH data without sample PAH-CE-19 were similar visually to those of the natural-log transformed uncensored PAH data without this sample (figs. 7a and 7b). Based on the visual comparison, the censored natural-log transformed PAH data also had a normal, or nearly normal distribution.

Maximum-likelihood estimation and log-probability regression on the natural-log transformed concentration data for the censored PAH compounds were used to calculate the mean, standard deviation, 25th percentile, median, and 75th percentile of the distribution for these compounds (table 8). Estimates of the values of these parameters varied with the method, but agreed within a factor of four in all cases, and typically agreed within a factor of two.

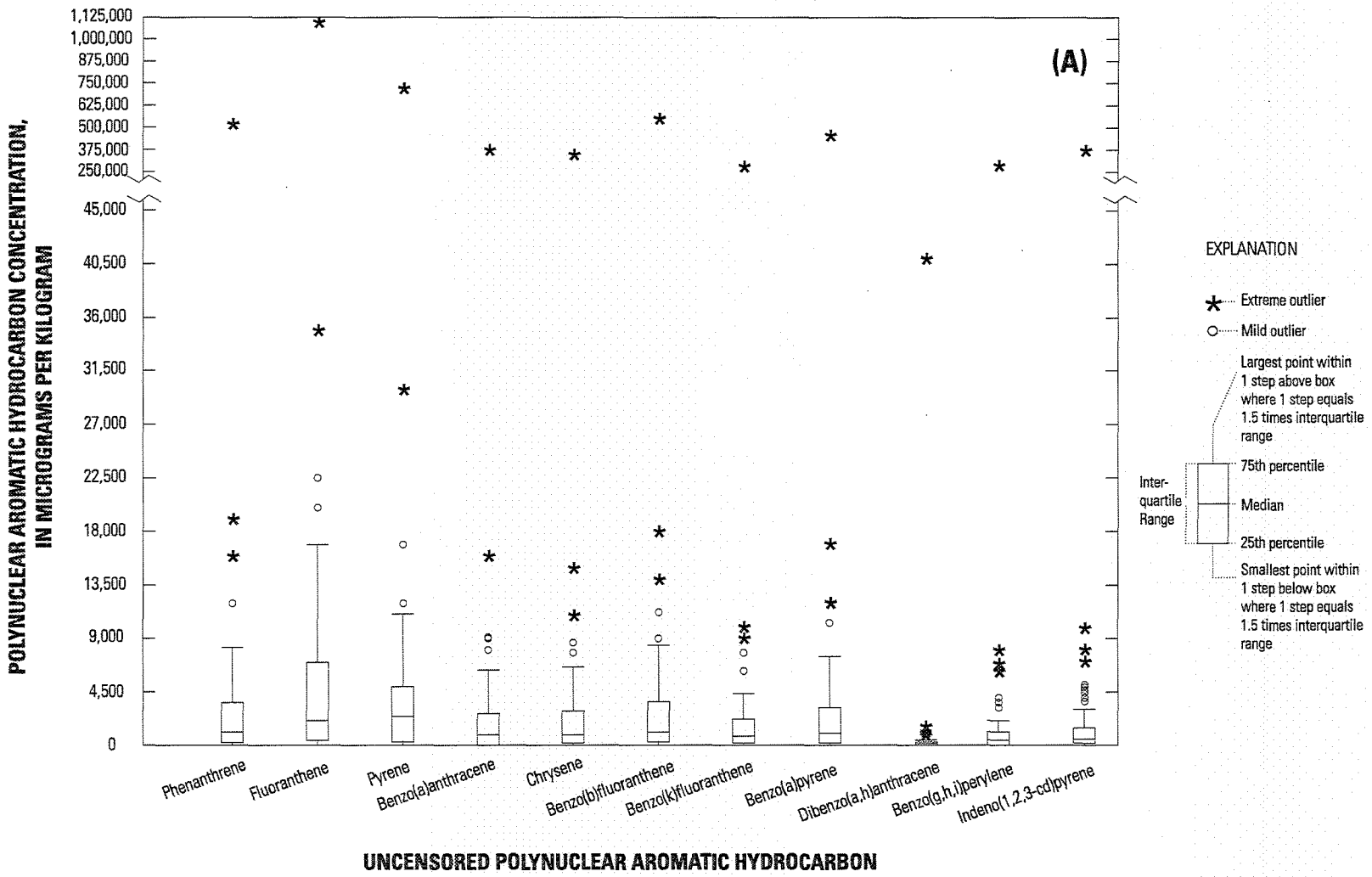

Figure 5. Boxplots of (A) uncensored and (B) censored polynuclear aromatic hydrocarbon concentrations in ambient surface soils, Chicago, Illinois.

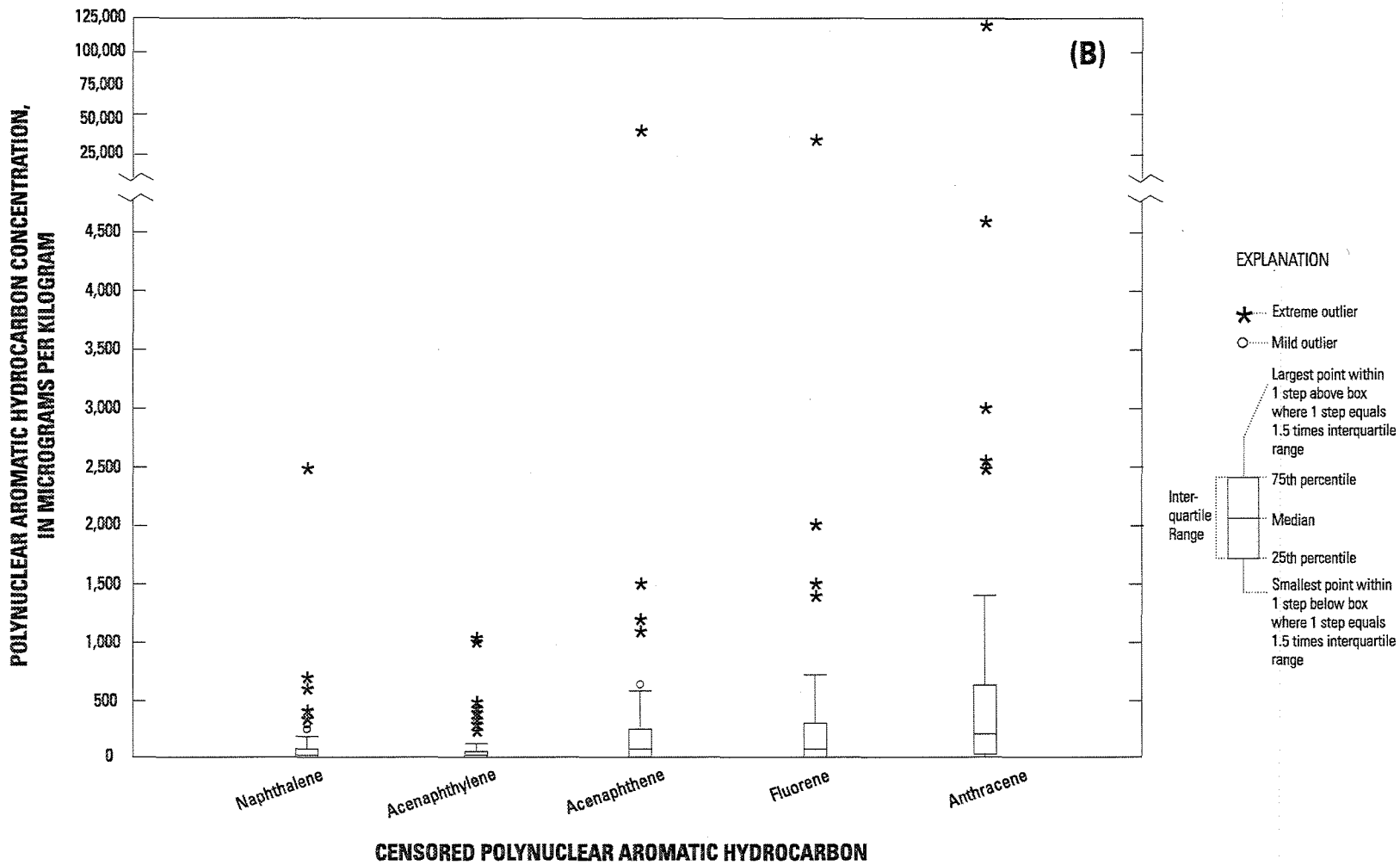

Figure 5. Boxplots of (A) uncensored and (B) censored polynuclear aromatic hydrocarbon concentrations in ambient surface soils, Chicago, Illinois—Continued.

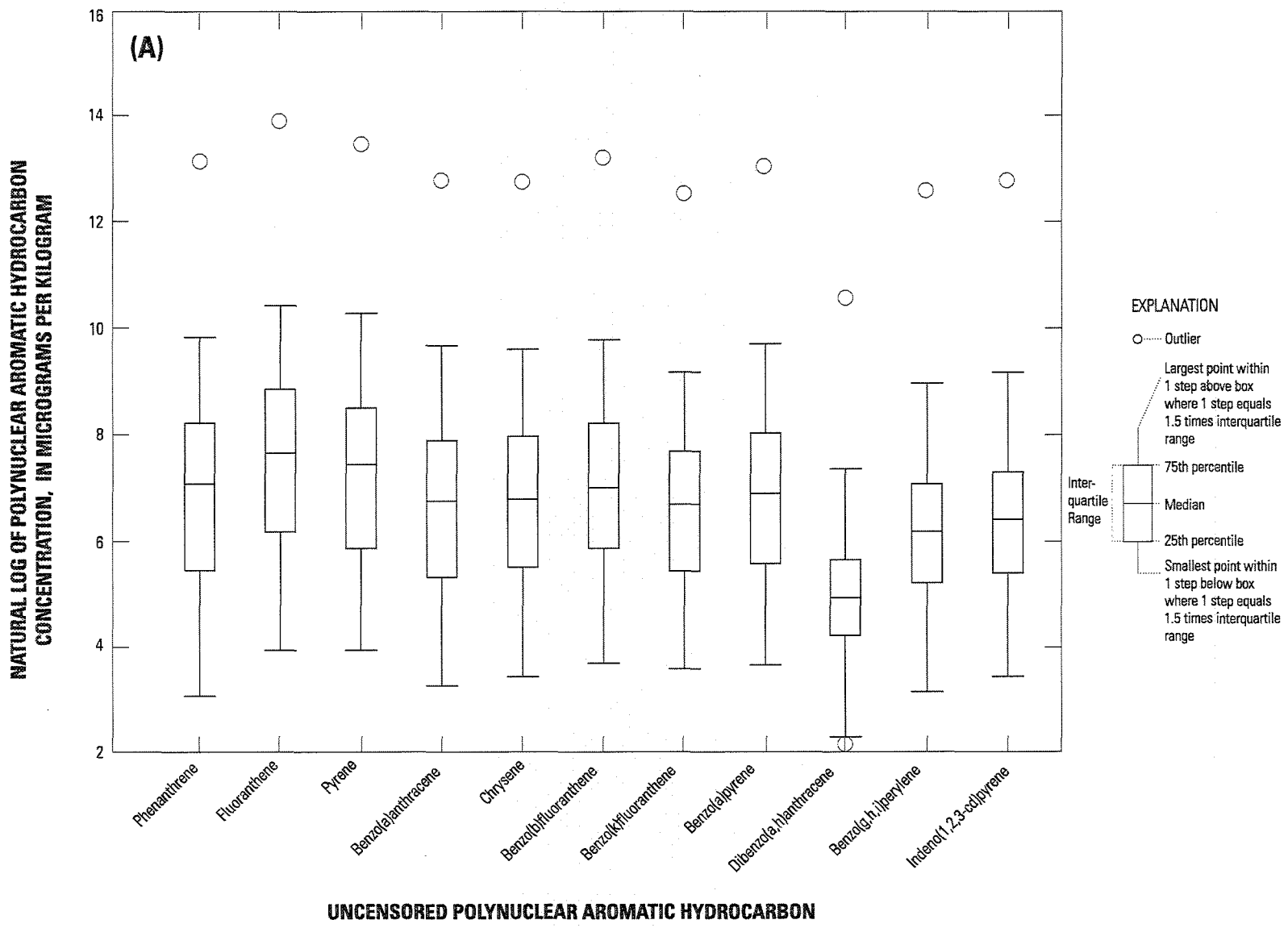

Figure 6. Boxplots of natural-log transformed (A) uncensored and (B) censored polynuclear aromatic hydrocarbon concentrations in ambient surface soils, Chicago, Illinois.

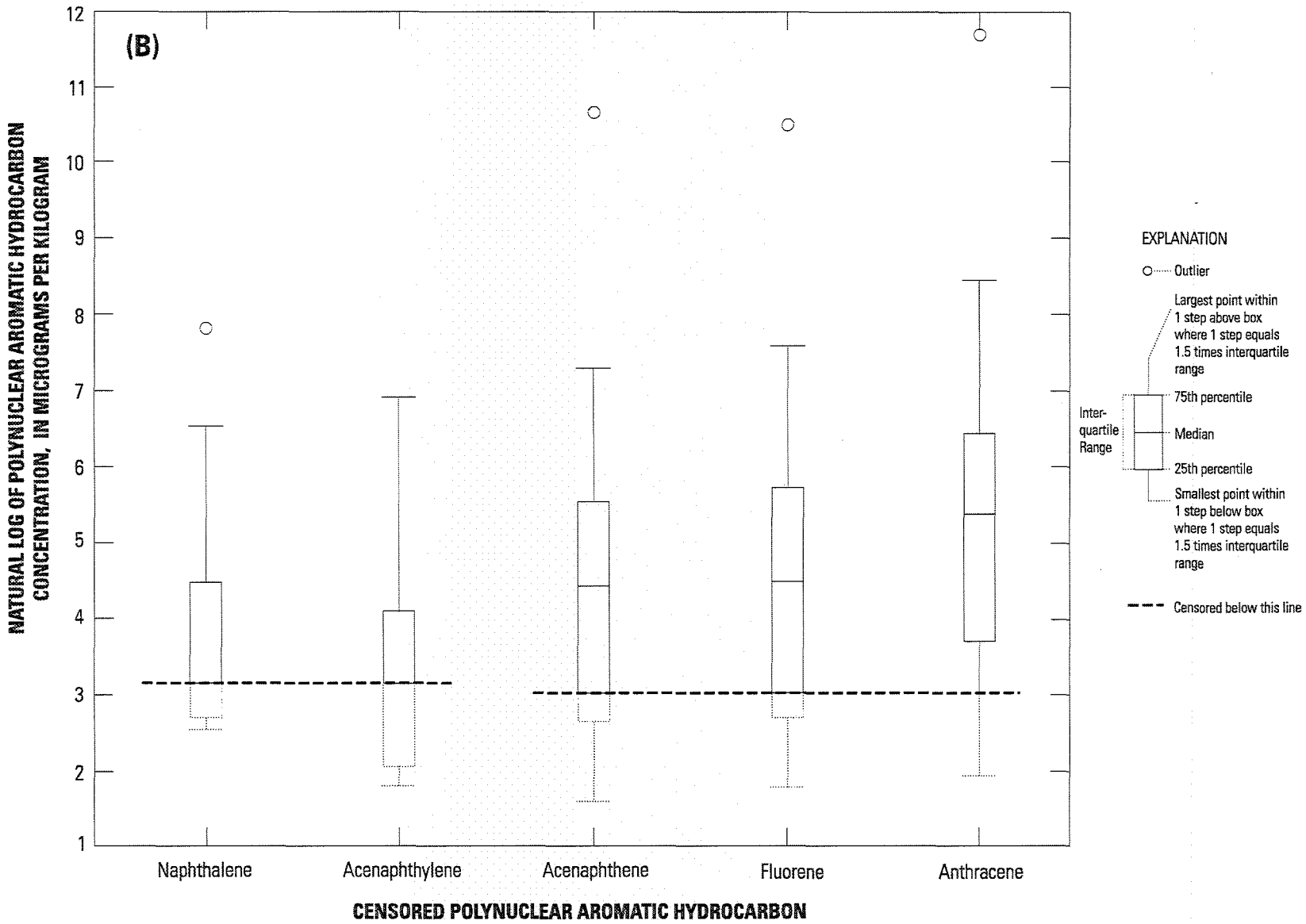

Figure 6. Boxplots of natural-log transformed (A) uncensored and (B) censored polynuclear aromatic hydrocarbon concentrations in ambient surface soils, Chicago, Illinois—Continued.

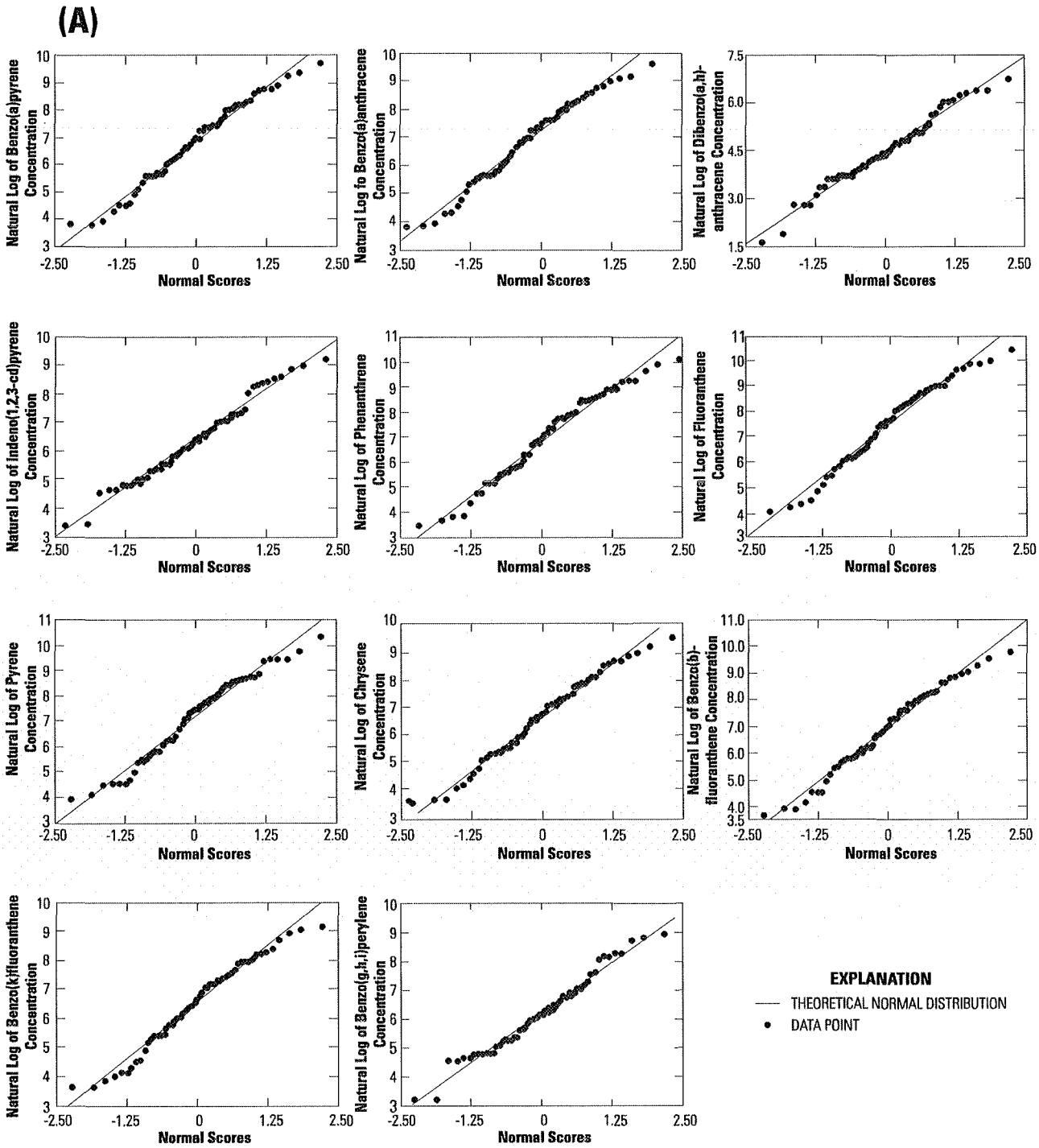

Figure 7. Normal probability plots of natural-log transformed (A) uncensored and (B) censored polynuclear aromatic hydrocarbon concentrations in ambient surface soils, Chicago, Illinois.

(B)

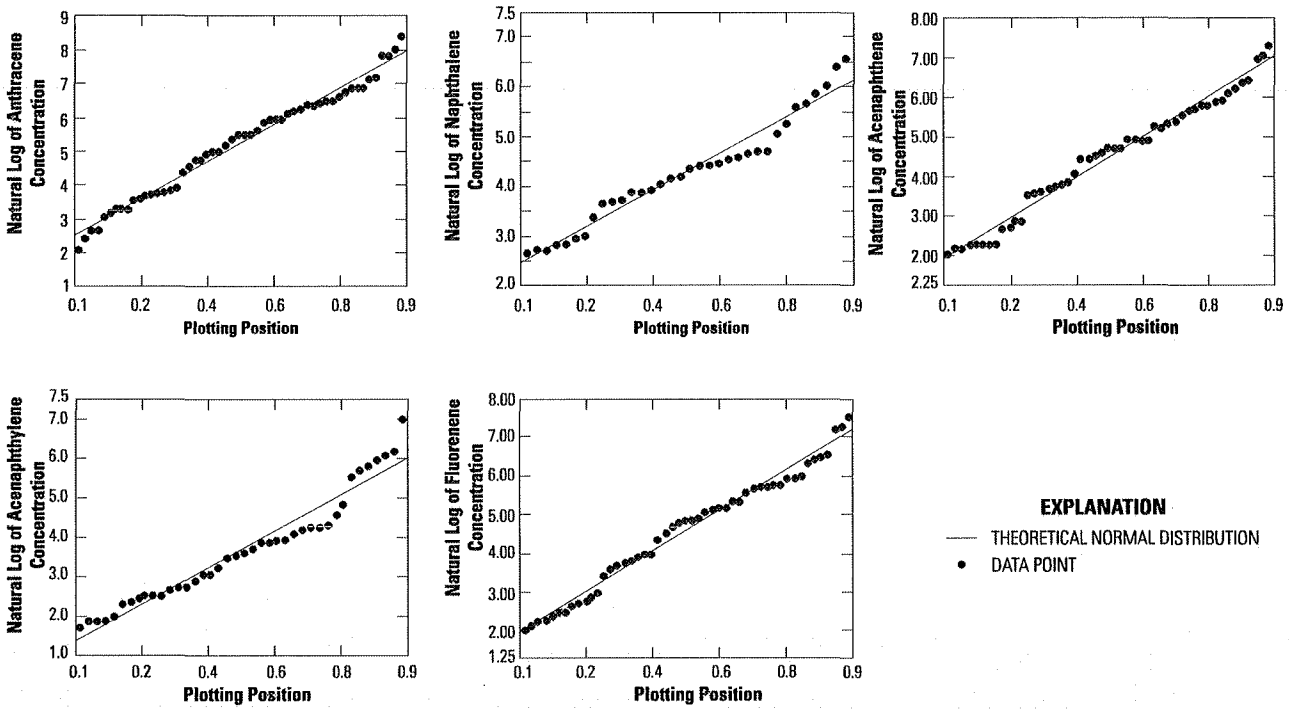

Figure 7. Normal probability plots of natural-log transformed (A) uncensored and (B) censored polynuclear aromatic hydrocarbon concentrations in ambient surface soils, Chicago, Illinois—Continued.

Estimates of mean and standard deviation were obtained by use of the log-probability regression, and estimates of percentiles were obtained by use of the maximum-likelihood regression (Helsel and Hirsch, 1995).

Outlier testing indicates that with the exception of acenaphthylene, concentrations of all of the PAHs in the sample from site PAH-CE-19 were five or more standard deviations greater than the next highest concentration, indicating that the PAH data from sample PAH-CE-19 are a statistical outlier (Helsel and Hirsch, 1995) (table 9). Therefore, the results from site PAH-CE-19 were omitted from all statistical analyses of the PAH compounds, including kriging of the benzo(a)pyrene distribution. As a consequence, the distribution of the uncensored PAH compounds in the surface soils could be considered lognormal, and reliably described by parametric statistical analyses (table 10).

The two-sided Wilcoxon-Rank-Sum test resulted in a p-value greater than the alpha value of 0.05, indicating that the null hypothesis, that the data from the city of Chicago and Commonwealth Edison properties represented a similar population, was acceptable (table 11). As a consequence, combination of all of the data (excluding the outlier sample from site PAH-CE-19) into one dataset for analysis was acceptable.

The Pearson product moment correlation coefficients for the natural-log transformed concentrations of the PAH compounds were 0.70 or greater (table 12), indicating a high degree of correlation. Naphthalene and acenaphthylene, the PAH compounds with the lowest molecular weights (table 13), were the only PAHs that did not show a correlation coefficient of 0.90 or higher with at least one other PAH. Naphthalene, the PAH compound with the lowest molecular weight (table 13), was the only PAH that did not show a correlation coefficient of 0.80 or higher with at least one other PAH.

The Pearson product moment correlation coefficients showed a low degree of positive correlation between the natural-log transformed concentrations of PAHs and the natural-log

transformed concentration of total organic carbon, with the value of the correlation coefficient typically about 0.50 (table 12). This positive correlation may indicate that the PAH compounds attach to organic matter in the soil. However, the low value of the correlation coefficient indicated that the organic carbon content of the soil does not have a substantial limiting effect on PAH concentrations.

As would be expected of PAH compounds that tend to show a high degree of correlation, the concentrations of the various PAH compounds in soils tended to show similar patterns (appendix 1). Samples with high concentrations of one compound tended to have high concentrations of all compounds. Samples with low concentrations of one compound tended to have low concentrations of all compounds.

The distribution of PAH compounds at concentrations below the detection limit showed similar patterns. In all samples in which anthracene was not detected, acenaphthylene, fluorene, acenaphthene, and naphthalene also were not detected. In all samples in which fluorene and acenaphthene were not detected, acenaphthylene and naphthalene also were not detected. Sampling locations in which fluorene and acenaphthene were not detected are identical. In all samples in which acenaphthylene was not detected, naphthalene also was not detected.

Although this interpretation is complicated by differences in the detection limit among compounds, the frequency of detection tended to increase as the molecular weight of the compound increased (fig. 8). Naphthalene, the compound with the lowest frequency of detection, also has the lowest molecular weight of any PAH (128 grams per mole). Acenaphthylene (molecular weight 154 grams per mole) had the second lowest frequency of detection. Acenaphthene, fluorene, and anthracene, all with molecular weights below 180 grams per mole, also did not have a 100-percent detection frequency. Every PAH with a molecular weight of 202 grams per mole or higher, and phenanthrene with a molecular weight of 178 grams per mole, were detected in every sample analyzed.

Comparison of the PAH concentration and frequency of detection in ambient soils with PAH concentrations in the atmosphere over Chicago obtained from June through December 2000 show large differences. Naphthalene, the PAH detected least frequently and at among the lowest concentrations in soil samples, was the PAH detected at the highest concentrations in ambient air, by at least a factor of four (Illinois Environmental Protection Agency, 2002) (table 14). Fluoranthene and pyrene, the predominant PAH compounds in Chicago soils, were detected at the fourth and fifth highest concentrations, respectively, of the PAHs in the atmosphere. These results are consistent with air samples affected by various PAH sources within Chicago (Khalili and others, 1995), which typically show naphthalene present in the highest concentrations and substantially lower concentrations of fluoranthene and pyrene in air (table 14). These sampling efforts did not distinguish between concentrations of PAHs in the vapor and in the particulate phase.

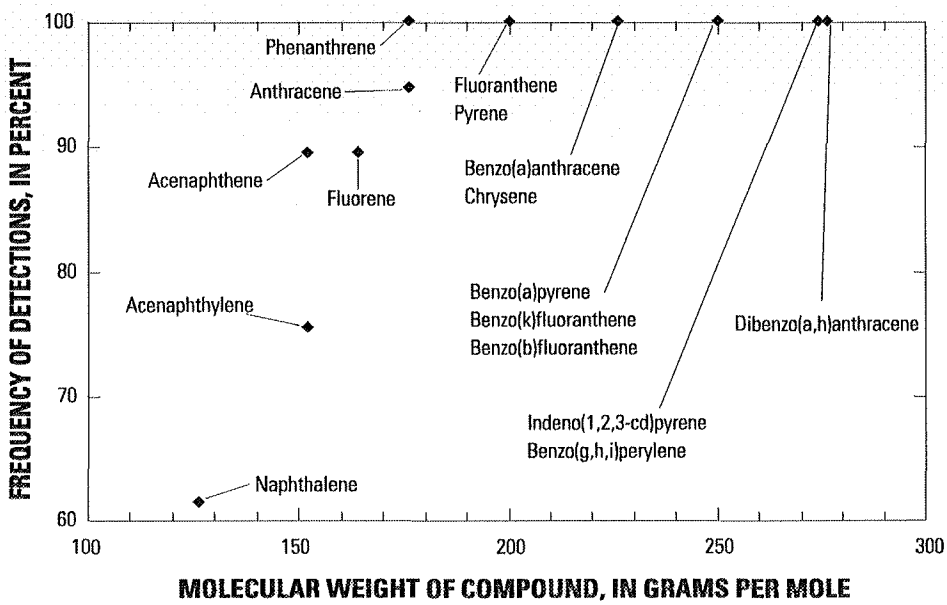

Figure 8. Frequency of detections of polynuclear aromatic hydrocarbons in ambient surface soils, Chicago, Illinois, plotted against molecular weight of compound.

The comparatively low correlation coefficient for the PAHs with low molecular weight, the frequency of detection of the PAH compounds in the soils, and the lack of correlation between the concentration of PAH compound in the atmosphere and in the ambient soils indicate that the concentration of PAH compounds in surface soils in the city of Chicago was affected by the physical properties of the compound. There are two aspects to this relation. First, the stability of a PAH compound in the soil environment increases with its molecular weight because of a decrease in its solubility in water and potential for volatilization and an increase in the potential to partition onto organic carbon and clay minerals (table 13). As a consequence, the tendency of a PAH to attach to particulate matter, and to stay attached to particulate matter, increases with increasing molecular weight. Second, the molecular weight of the PAH compound affects its phase in the atmosphere, through which the PAHs must travel from their sources to the ambient soil.

Although affected by temperature and particle size (Baek and others, 1991), PAHs with molecular weights equal to or less than that of phenanthrene (178 grams per mole) with a higher Henry's Law constant (table 13) partition primarily to the gas phase in the atmosphere. As the molecular weight of the PAH increases, partitioning to the gas phase decreases and partitioning to the particulate phase increases (Dickhut and Gustafson, 1995; Yaffe and others, 2001). PAHs with a molecular weight of more than about 247 grams per mole are primarily bound to particulate matter in the atmosphere. In comparison to the particulate-bound PAHs with higher molecular weights, the gas-phase PAHs with low molecular weights tend to remain in the atmosphere because they are less efficiently scavenged from the atmosphere by precipitation or particle settling. Higher molecular weight PAHs, therefore, are transported preferentially to the land surface where they can be incorporated into soils. The apparent effect of the phase of the PAH in the atmosphere on the presence of a PAH in ambient surface soils indicates that atmospheric settling of particulate matter is an important source of the PAH compounds in Chicago soils.

Concentrations of individual PAH compounds in ambient surface soils typically vary by at least three orders of magnitude across the city if the outlier sample is excluded (table 3). Data from sites PAH-SS-12 and PAH-CE-15 and 15D (fig. 4) indicate that individual PAH concentrations can vary by more than an order of magnitude across a distance of about 1,000 ft (appendix 1). Comparison of concentrations of the 16 PAH compounds at the 6 locations where duplicate samples were collected shows that PAH concentrations in the sample and its duplicate vary by less than a factor of 2 for 82 of the 96 analyses, vary by less than a factor of 3 for 90 of the 96 analyses, vary by less than a factor of 4 for 93 of the analysis, and vary by a factor of 7 or less in the remaining 3 analyses (appendix 1). Eleven of the analyses that varied by more than a factor of two were from sample PAH-CE-15 and its duplicate. The generally good agreement between the PAH concentrations in the sample and its duplicate indicates that PAH concentrations in ambient surface soils typically do not vary substantially over distances of less than about 10 ft.

The variability of PAH concentrations in the soils across the entire city, over distances of about 1,000 ft, and between samples and their duplicates indicates that PAH concentrations in ambient soils in Chicago are affected by site-specific factors. The apparent decrease in the variability of PAH concentrations with a decreasing scale of observation indicates that PAH concentrations in ambient soils also are affected by larger-scale processes.

The variability of PAH concentrations within the city is approximated by the distribution of benzo(a)pyrene, which showed a complex distribution (fig. 9). Higher concentrations were detected in the area near Lake Michigan in the northern part of the city, in much of the western part of the city, and in various pockets in the southern part of the city. Lower concentrations were detected in much of the northwestern, south-central, southwestern, and far southern parts of the city. Areas of lower benzo(a)pyrene concentration corresponded to areas where one or more PAH compound was not detected.

Previous investigators have identified an inverse correlation between concentrations of PAH compounds in surface soils and distance from a roadway (Bradley and others, 1994). Therefore, it was anticipated that proximity to a roadway may have been one of the site-specific factors affecting PAH concentrations in the city. However, linear regression of the concentrations of the uncensored PAHs and distance from the nearest roadway indicated no trend,

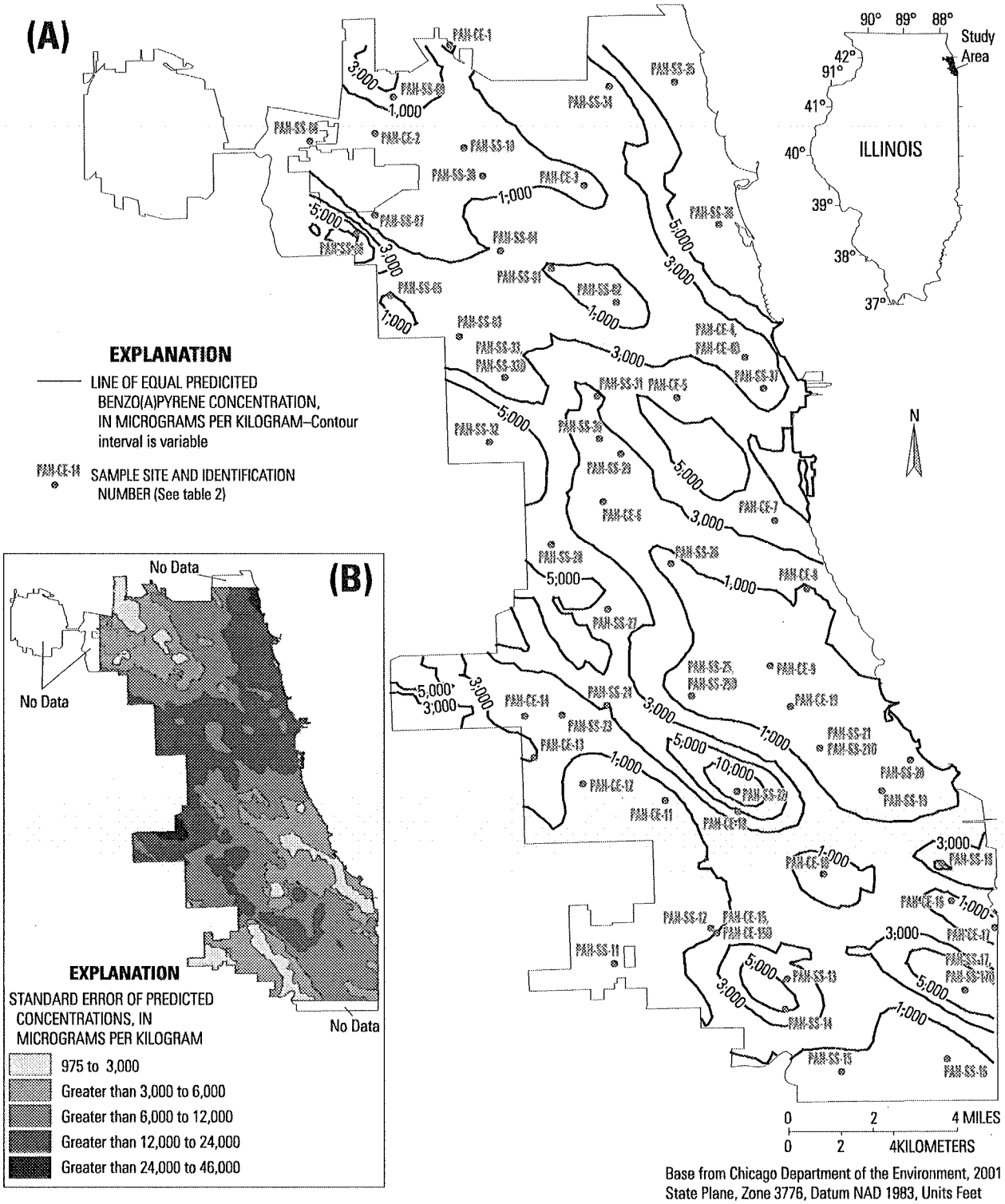

Figure 9. (A) Kriged concentrations of benzo(a)pyrene in ambient surface soils, Chicago, Illinois and (B) standard errors of predicted concentrations.

with all coefficients of determination (R^2) less than 0.02. An analysis of variance did not indicate that mean concentrations of the uncensored PAHs differ in a statistically significant manner with distance from the roadway (table 15). These analyses indicate either that distance from roadways does not have a substantial affect on PAH concentrations in ambient soils in the city of Chicago or that other factors, such as the amount of traffic and the prevailing wind direction, need to be considered.

Analysis was performed to determine if PAH concentrations are related to land use. Results of the multiple-population tests for comparing the natural-log transformed concentrations of individual PAH compounds indicate that there are no statistically significant differences in the mean PAH concentration among land-use categories (tables 16 and 17). It should be cautioned that the unequal sample sizes or "lack of balance" in the statistical tests can result in low power, or diminished capability of the tests to correctly reject the null hypothesis that the means of the land-use categories are not statistically different when the null hypothesis is false.

Linear regression of natural-log transformed PAH concentrations with the percent industrial land use within a 1-mi radius of the sampling location yields a t-statistic for the slope coefficient greater than two for each PAH. Linear regression of natural-log transformed PAH concentrations with percent industrial land use within a 0.5-mi radius of the sampling location yields a t-statistic for the slope coefficient greater than 2 for each PAH except dibenzo(a,h)anthracene. Regressions using percentages of transportation, commercial, vacant, and residential land use showed no relation. A t-statistic for the slope coefficient greater than 2 indicates a statistically significant direct linear relation between the amount of industrial land use in the area and the PAH concentration in the sample (Helsel and Hirsch, 1995) (table 18). The t-statistic for the slope coefficient was near two for each compound and the linear correlation coefficient between percent industrial land use and the PAH concentration is less than 0.10, indicating that this correlation (if present) is weak. Linear regression of natural-log transformed PAH concentrations with percent industrial land use within a 0.25-mi radius of the sampling location yielded a t-statistic for the slope coefficient less than 2 for each PAH. This result indicates no statistically significant direct linear relation between the amount of industrial land use within 0.25 mi of the sample and the PAH concentration in the sample. Simple linear regressions of mean distance to industrial land use and concentrations of uncensored PAH compounds did not show a relation. These data are insufficient to determine if the apparent relation between PAH concentrations and percent industrial land use is because of industrial emissions, increased traffic density in industrial areas, or some other source.

ANALYSIS OF INORGANIC DATA

Surface soils in the city of Chicago are composed of a mixture of compounds, and 34 of the 45 inorganic constituents were detected in more than 75 percent of the samples collected. This frequency of detection allowed the arithmetic mean, standard deviation, and ranges for these analytes to be calculated (table 19). An additional 11 constituents were not quantifiable because all or many samples contained less than the lower limit of detection (LOD). Those elements, with their LOD, are silver (2 mg/Kg), gold (8 mg/Kg), beryllium (1 mg/Kg), bismuth (50 mg/Kg), cadmium (2 mg/Kg), europium (2 mg/Kg), holmium (4 mg/Kg), tin (50 mg/Kg), thallium (40 mg/Kg), uranium (100 mg/Kg), and ytterbium (1 mg/Kg).

The arithmetic mean of the concentration of the 34 inorganic analytes detected in more than 75 percent of the samples of Chicago soils was compared with the arithmetic mean concentration of these analytes in 106 samples of A-horizon soils collected primarily from agricultural areas within 500 kilometers of Chicago (Boerngen and Shacklette, 1981). The mean concentration of arsenic, mercury, calcium, magnesium, phosphorus, copper, molybdenum, zinc, and selenium was from two to six times higher in Chicago soils, and concentrations of lead were about 20 times higher than in soils from the surrounding area (table 20).

Inter-element correlation coefficients for the inorganic analytes were calculated to provide additional insight into the sources of the inorganic constituents (table 21). The sets of elements showing strong mutual correlations can indicate causative factors for the observed concentrations and distribution of these elements.

Concentrations of all of the major element compositions, except for sodium, and many of the trace elements showed trends consistent with naturally developed soils. Bedrock beneath and near Chicago is composed of dolomite (a calcium, magnesium carbonate) and shale, a rock composed largely of clays, which are alumino-silicate minerals often rich in aluminum and potassium. The high (r^2 greater than 0.98) Pearson product moment correlation coefficients among calcium, magnesium, and carbonate carbon reflect the widespread distribution of dolomite in the soils. The lack of other highly correlated elements further suggests that the dolomite does not contain appreciable amounts of other trace elements. Likewise, high correlations (r^2 greater than 0.70) between aluminum and other clay-borne elements such as potassium and trace constituents expected in clays including barium, cerium, gallium, lanthanum, lithium, neodymium, scandium, titanium, vanadium, and yttrium demonstrate the extent the clays affect the soil composition.

Although the bulk of the compositional trends in Chicago soils are explainable by varying proportions of dolomite and shale, which likely are soil parent material, the elevated (in comparison to surrounding agricultural soils) concentrations of arsenic, copper, lead, mercury, molybdenum, nickel, phosphorus, selenium, and zinc indicate a potential anthropogenic source of these elements. Lead (concentration factor of 20.4), zinc (7.4), and mercury (4.5) especially are enriched relative to background soils and all seem likely to indicate substantial and widespread anthropogenic modifications to the trace-element character of the soils.

The high correlation between lead and zinc ($r^2 = 0.91$) suggests that the two elements have been added to soils largely from the same material or process rather than as independently distributed constituents. Mercury shows low correlation with all other constituents, including organic carbon ($r^2 = 0.135$). In many natural settings mercury and organic carbon are highly correlated so the lack of correlation in Chicago soils suggests an anthropogenic addition largely independent of natural processes.

Other correlations of possible significance are among chromium, manganese, iron, and molybdenum. All four of these elements are major or trace constituents in various ferroalloys, which indicates that man-made steel products, or breakdown products from them, might be widely dispersed. The strong correlation among sulfur, organic carbon, and molybdenum also is noteworthy. In Chicago soils, sulfur primarily occurs in organic compounds in contrast to more typical occurrences as naturally occurring iron-sulfide minerals. Conversely, the lack of strong correlation among sulfur and elements that typically concentrate in sulfide minerals, such as copper, lead, zinc, nickel, and cobalt, further indicates that sulfide minerals do not substantially affect the composition of Chicago soils.

SUMMARY AND CONCLUSIONS

The U.S. Geological Survey, in cooperation with the Chicago Department of Environment, assessed the concentration of polynuclear aromatic hydrocarbons (PAHs) and inorganic constituents in ambient surface soils within the city of Chicago. At least 11 of the 16 polynuclear aromatic hydrocarbon constituents were detected in each of the 57 soil samples collected. The distribution of the uncensored PAH compounds in the surface soils can be considered log normal once the data from the outlier location were excluded from the analysis.

PAH concentrations, from highest to lowest, were typically in the following order: fluoranthene, pyrene, benzo(b)fluoranthene, phenanthrene, benzo(a)pyrene, chrysene, benzo(a)anthracene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, and anthracene. Naphthalene, acenaphthene, acenaphthylene, and fluorene consistently were at the lowest concentrations in each sample. Concentrations of the PAH compounds were highly correlated, but did show some variation with the molecular weight of the compound. PAH compounds appear to be derived from similar combinations of sources, and most of the PAHs tend to behave similarly once released into the air, water, and soil.

Concentrations of individual PAH compounds in soils typically varied by at least 3 orders of magnitude for each compound across the city and varied by more than an order of magnitude over a distance of about 1,000 ft. Data from duplicate

samples indicate that PAH concentrations typically varied by less than a factor of two over a distance of a few feet. Variations in the concentrations of a given PAH in ambient surface soils may be affected by proximity to industrial areas. Variations in the concentrations of a given PAH in ambient surface soils did not appear to be affected by proximity to roadways or non-industrial land uses and did not appear to be strongly affected by the organic carbon content of the soil.

The concentration of the different PAH compounds in ambient surface soils appears to have been affected by the physical properties of the compound, which are affected by its molecular weight. Lower molecular-weight PAH compounds, which were in lower concentrations in the soils, were primarily in the vapor phase in the atmosphere. Higher molecular-weight PAH compounds, which often were in higher concentrations in the soils, were primarily in the particulate phase in the atmosphere. The apparent effect of the phase of the PAH in the atmosphere on the concentration of a PAH in ambient surface soils indicated that atmospheric settling of particulate matter is an important source of the PAH compounds in ambient Chicago soils.

The distribution of benzo(a)pyrene, which approximated the distribution of the remaining PAH compounds within the city, was complex. Elevated concentrations (greater than 4,084 micrograms per kilogram) were detected near Lake Michigan in the northern part of the city, in much of the western part of the city, and in isolated areas in the southern part of the city. Comparatively low concentrations (less than 419 micrograms per kilogram) were detected in much of the northwestern, south-central, southwestern, and far southern parts of the city.

Concentrations of various inorganic constituents in surface soils in the city of Chicago appeared to be affected by the natural development of the soils. The arithmetic mean concentration of arsenic, mercury, calcium, magnesium, phosphorus, copper, molybdenum, zinc, selenium were from 2 to 8 times higher, and concentrations of lead were about 20 times higher, than in typical soils from the surrounding area and may indicate an anthropogenic source for these analytes. Elevated concentrations of calcium and magnesium appeared to be related to the effects of dolomite bedrock on the chemical composition of the soil.

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Tables

Table 1. Illinois Environmental Protection Agency Tier 1 remediation objectives for polynuclear aromatic hydrocarbons in soils

[na, not applicable]

Constituent	Remedial objective for residential soil				Remedial objective for industrial or commercial soil					
	Exposure route-specific values for soils		Soil component of the ground-water ingestion exposure route values		Exposure route-specific values for soils				Soil component of the ground-water ingestion exposure route values	
					Industrial commercial		Construction worker			
	Ingestion (milligrams per kilogram)	Inhalation (milligrams per kilogram)	Class I (milligrams per kilogram)	Class II (milligrams per kilogram)	Ingestion (milligrams per kilogram)	Inhalation (milligrams per kilogram)	Ingestion (milligrams per kilogram)	Inhalation (milligrams per kilogram)	Class I (milligrams per kilogram)	Class II (milligrams per kilogram)
Acenaphthene	4,700.	na	570	2,900.	120,000.	na	120,000	na	570	2,900
Acenaphthylene	na	na	na	na	na	na	na	na	na	na
Anthracene	23,000.	na	12,000	59,000.	610,000.	na	610,000	na	12,000	59,000
Benzo(a)anthracene	.9	na	2	8.	8.	na	170	na	2	8
Benzo(b)fluoranthene	.9	na	5	25.	8.	na	170	na	2	8
Benzo(k)fluoranthene	9.	na	49	250.	78.	na	1,700	na	49	250
Benzo(g,h,i)perylene	na	na	na	na	na	na	na	na	na	na
Benzo(a)pyrene	.09	na	8	82.	.8	na	17	na	8	82
Chrysene	88.	na	160	800.	780.	na	17,000	na	160	800
Dibenzo(a,h)anthracene	.09	na	2	7.6	.8	na	17	na	2	8
Fluoranthene	3,100.	na	4,300	21,000.	82,000.	na	82,000	na	4,300	21,000
Fluorene	3,100.	na	560	2,800.	82,000.	na	82,000	na	560	2,800
Indeno(1,2,3-cd)pyrene	.9	na	14	69.	8.	na	170	na	14	69
Naphthalene	3,100.	na	84	420.	82,000.	na	82,000	na	84	420
Phenanthrene	na	na	na	na	na	na	na	na	na	na
Pyrene	2,300.	na	4,200	21,000.0	61,000.	na	61,000	na	4,200	21,000

Table 2. Soil-sampling site data collected during the investigation, Chicago, Illinois
[D, duplicate sample; USGS, U.S. Geological Survey]

Sample number (location shown in figure 4)	Latitude	Longitude	USGS site identification number	Land use at site	Distance from nearest roadway (feet)	Date of sample collection
PAH-CE-1	42°00'35"	87°46'20"	420003508746201	Commercial	25	1/24/2002
PAH-CE-2	41°58'46"	87°48'25"	415846087482501	Transportation	40	1/24/2002
PAH-CE-3	41°57'40"	87°42'41"	415740087424101	Commercial	61	1/24/2002
PAH-CE-4	41°54'04"	87°38'18"	415404087381801	Commercial	190	1/24/2002
PAH-CE-4D	41°54'04"	87°38'18"	415404087381802	Commercial	190	1/24/2002
PAH-CE-5	41°53'16"	87°40'11"	415316087401101	Industrial	118	1/24/2002
PAH-CE-6	41°51'07"	87°42'14"	415107087421401	Commercial	7	1/24/2002
PAH-CE-7	41°50'42"	87°37'31"	415042087373101	Industrial	74	1/24/2002
PAH-CE-8	41°49'17"	87°36'38"	414917087363801	Residential	78	1/24/2002
PAH-CE-9	41°47'43"	87°37'41"	414743087374101	Vacant or wetland	125	1/24/2002
PAH-CE-10	41°43'24"	87°36'16"	414324087361601	Transportation	16	1/24/2002
PAH-CE-11	41°44'57"	87°40'37"	414457087403701	Industrial	221	1/24/2002
PAH-CE-12	41°45'18"	87°42'51"	414518087425101	Residential	37	1/24/2002
PAH-CE-13	41°45'51"	87°44'12"	414551087441201	Industrial	626	1/24/2002
PAH-CE-14	41°46'42"	87°44'26"	414642087442601	Commercial	41	1/24/2002
PAH-CE-15	41°42'11"	87°39'13"	414211087391301	Industrial	140	1/25/2002
PAH-CE-15D	41°42'11"	87°39'13"	414211087391302	Industrial	140	1/25/2002
PAH-CE-16	41°42'49"	87°32'45"	414249087324501	Vacant or wetland	85	1/25/2002
PAH-CE-17	41°42'15"	87°31'33"	414215087313301	Transportation	69	1/25/2002
PAH-CE-18	41°44'42"	87°38'37"	414442087383701	Commercial	69	1/25/2002
PAH-CE-19	41°46'52"	87°37'08"	414652087370801	Vacant or wetland	120	1/25/2002
PAH-SS-01	41°55'57"	87°43'37"	415557087435701	Industrial	30	6/5/2001
PAH-SS-02	41°55'15"	87°41'50"	415515087415001	Commercial	10	6/5/2001
PAH-SS-03	41°54'33"	87°46'08"	415433087460801	Commercial	10	6/5/2001
PAH-SS-04	41°56'20"	87°45'00"	415620087450001	Commercial	45	6/5/2001
PAH-SS-05	41°55'25"	87°48'02"	415525087480201	Commercial	35	6/5/2001
PAH-SS-06	41°56'42"	87°48'57"	415642087485701	Residential	1	6/5/2001
PAH-SS-07	41°57'05"	87°48'26"	415705087482601	Commercial	45	6/5/2001
PAH-SS-08	41°58'37"	87°50'12"	415837087501201	Residential	16	6/5/2001
PAH-SS-09	41°59'31"	87°47'54"	415931087475401	Open space	22	6/5/2001
PAH-SS-10	41°58'27"	87°45'59"	415827087455901	Commercial	32	6/5/2001
PAH-SS-11	41°41'35"	87°42'03"	414135087420301	Commercial	30	6/5/2001
PAH-SS-12	41°42'18"	87°39'24"	414218087392401	Transportation	25	6/5/2001
PAH-SS-13	41°41'14"	87°37'18"	414114087371801	Commercial	20	6/5/2001
PAH-SS-14	41°40'36"	87°31'21"	414036087312101	Residential	10	6/5/2001

Table 2. Soil-sampling site data collected during the investigation, Chicago, Illinois—Continued

[D, duplicate sample; USGS, U.S. Geological Survey]

Sample number (location shown in figure 4)	Latitude	Longitude	USGS site identification number	Land use at site	Distance from nearest roadway (feet)	Date of sample collection
PAH-SS-15	41°39'19"	87°35'50"	413919087355001	Commercial	50	6/5/2001
PAH-SS-16	41°39'34"	87°32'55"	413934087325501	Vacant or wetland	10	6/5/2001
PAH-SS-17	41°40'58"	87°32'24"	414058087322401	Vacant or wetland	23	6/5/2001
PAH-SS-17D	41°40'58"	87°32'24"	414058087322402	Vacant or wetland	23	6/5/2001
PAH-SS-18	41°43'35"	87°33'00"	414335087330001	Vacant or wetland	10	6/5/2001
PAH-SS-19	41°45'06"	87°34'38"	414506087343801	Commercial	20	6/5/2001
PAH-SS-20	41°45'44"	87°33'50"	414544087335001	Residential	20	6/5/2001
PAH-SS-21	41°46'00"	87°36'20"	414600087362001	Commercial	10	6/5/2001
PAH-SS-21D	41°46'00"	87°36'20"	414600087362002	Commercial	10	6/5/2001
PAH-SS-22	41°45'07"	87°38'38"	414507087383801	Commercial	5	6/5/2001
PAH-SS-23	41°46'43"	87°43'25"	414643087432501	Commercial	5	6/6/2001
PAH-SS-24	41°46'55"	87°42'11"	414655087421101	Commercial	5	6/6/2001
PAH-SS-25	41°47'06"	87°39'51"	414706087395101	Commercial	10	6/6/2001
PAH-SS-25D	41°47'06"	87°39'51"	414706087395102	Commercial	10	6/6/2001
PAH-SS-26	41°49'49"	87°40'24"	414949087402401	Commercial	5	6/6/2001
PAH-SS-27	41°48'54"	87°42'09"	414854087420901	Commercial	20	6/6/2001
PAH-SS-28	41°50'14"	87°43'41"	415014087434101	Residential	20	6/6/2001
PAH-SS-29	41°52'06"	87°41'45"	415206087414501	Residential	20	6/6/2001
PAH-SS-30	41°52'25"	87°42'50"	415225087425001	Institutional	10	6/6/2001
PAH-SS-31	41°53'18"	87°42'23"	415318087422301	Institutional	10	6/6/2001
PAH-SS-32	41°52'22"	87°45'20"	415222087452001	Transportation	10	6/6/2001
PAH-SS-33	41°53'42"	87°44'54"	415342087445401	Commercial	10	6/6/2001
PAH-SS-33D	41°53'42"	87°44'54"	415342087445402	Commercial	10	6/6/2001
PAH-SS-34	41°59'42"	87°41'58"	415942087415801	Commercial	10	6/6/2001
PAH-SS-35	41°59'47"	87°40'10"	415947087401001	Residential	50	6/6/2001
PAH-SS-36	41°56'50"	87°38'58"	415650087385801	Institutional	10	6/6/2001
PAH-SS-37	41°53'27"	87°37'48"	415327087374801	Transportation	20	1/25/2002
PAH-SS-38	41°57'52"	87°45'28"	415752087452801	Commercial	10	1/25/2002

Table 3. Summary of polynuclear aromatic hydrocarbon data in ambient surface soils, Chicago, Illinois

[<, less than; na, not applicable]

Constituent	Number of samples collected	Number of detections	Percentage of samples with analyte detected	Range of detected concentrations including sample PAH-CE-19 (micrograms per kilogram)	Range of detected concentrations without sample PAH-CE-19 (micrograms per kilogram)	Number of samples exceeding Tier 1 remedial objectives for residential soil because of ingestion[1]	Number of samples exceeding Tier 1 remedial objectives for industrial or commercial soil because of ingestion[1]	Number of samples exceeding Tier 1 remedial objectives for construction workers because of ingestion[1]
Acenaphthene	57	51	89	<5-43,000	<5-1,500	0	0	0
Acenaphthylene	57	43	75	<6-1,035	<6-1,035	na	na	na
Anthracene	57	54	95	<7-120,000	<7-4,600	0	0	0
Benzo(a)anthracene	57	57	100	26-370,000	26-16,000	27	5	1
Benzo(b)fluoranthene	57	57	100	40-550,000	40-18,000	32	6	1
Benzo(k)fluoranthene	57	57	100	36-280,000	36-10,000	3	1	0
Benzo(g,h,i)perylene	57	57	100	24-290,000	24-8,100	na	na	na
Benzo(a)pyrene	57	57	100	39-460,000	39-17,000	51	31	2
Chrysene	57	57	100	31-350,000	31-15,000	1	0	0
Dibenzo(a,h)anthracene	57	57	100	8-41,000	8-1,600	38	7	1
Fluoranthene	57	57	100	52-1,100,000	52-35,000	0	0	0
Fluorene	57	51	89	<6-36,000	<6-2,000	0	0	0
Indeno(1,2,3-cd)pyrene	57	57	100	31-370,000	31-9,900	22	3	1
Naphthalene	57	35	61	<13-2,500	<13-700	0	0	0
Phenanthrene	57	57	100	22-520,000	22-19,000	na	na	na
Pyrene	57	57	100	51-720,000	51-30,000	0	0	0

[1] Illinois Pollution Control Board, 2002

Table 4. Mean distance from sample locations to nearby major land-use categories, Chicago, Illinois

[--, no data]

Sample number (location shown in figure 4)	Mean distance to unclassified land use (feet)	Mean distance to residential land use (feet)	Mean distance to commercial land use (feet)	Mean distance to institutional land use (feet)	Mean distance to industrial, warehousing, and wholesale land use (feet)	Mean distance to transportation, communication, and utilities land use (feet)	Mean distance to agricultural land use (feet)	Mean distance to open space land use (feet)	Mean distance to vacant or wetland land use (feet)	Mean distance to water (feet)
PAH-CE-1	--	4,356	4,265	5,216	2,395	8,144	--	4,936	6,384	--
PAH-CE-2	5,253	3,403	2,645	3,441	--	1,970	--	2,294	1,361	--
PAH-CE-3	--	4,911	4,974	6,659	6,082	6,244	--	5,373	6,979	5,111
PAH-CE-4	--	4,967	5,055	4,288	4,737	4,944	--	5,459	3,786	5,235
PAH-CE-5	--	5,073	4,787	6,209	3,516	4,838	--	4,939	3,947	--
PAH-CE-6	--	3,767	3,531	3,957	4,944	4,428	--	2,922	4,585	6,241
PAH-CE-7	--	5,086	5,436	3,846	5,595	5,536	--	5,017	5,503	6,224
PAH-CE-8	--	4,727	4,621	4,601	6,503	5,926	--	5,385	3,801	--
PAH-CE-9	--	4,479	4,415	4,592	6,564	3,681	--	4,572	3,907	--
PAH-CE-10	--	4,973	5,277	4,041	5,024	5,901	--	7,191	6,299	--
PAH-CE-11	9,308	4,924	4,597	4,531	3,720	3,549	--	5,767	5,197	--
PAH-CE-12	10,330	5,321	5,448	7,313	2,457	3,294	--	4,829	3,933	4,874
PAH-CE-13	4,376	4,523	4,736	2,909	2,531	2,102	--	2,320	2,054	--
PAH-CE-14	11,084	9,809	9,386	10,373	10,686	5,856	--	8,757	5,353	--
PAH-CE-15	10,271	5,054	4,971	5,196	6,916	5,514	--	5,525	7,751	--
PAH-CE-16	--	4,386	3,752	5,079	3,195	5,434	--	5,964	6,269	2,825
PAH-CE-17	--	2,963	1,882	3,162	1,260	1,939	--	4,104	2,331	--
PAH-CE-18	--	4,829	4,670	4,213	3,401	4,642	--	4,908	4,800	--
PAH-CE-19	--	5,081	4,985	5,618	2,469	3,748	--	6,244	4,103	4,854
PAH-SS-01	--	4,130	3,963	3,865	4,061	5,186	--	3,497	5,280	--
PAH-SS-02	--	4,772	5,106	5,193	6,193	5,571	--	4,559	5,644	6,288
PAH-SS-03	4,951	3,904	4,059	4,690	3,946	3,012	--	4,016	3,757	--
PAH-SS-04	--	4,269	4,200	4,708	3,253	5,039	--	4,270	3,086	--
PAH-SS-05	5,112	4,083	4,035	3,988	3,297	5,758	--	4,542	3,632	--
PAH-SS-06	3,942	3,482	4,513	5,343	9,768	--	--	7,798	5,695	9,734
PAH-SS-07	4,008	4,556	3,244	3,868	4,659	--	--	4,504	5,144	--
PAH-SS-08	6,461	8,073	7,135	14,488	19,612	19,974	25,114	6,211	19,443	13,079
PAH-SS-09	12,046	6,017	5,384	4,158	3,059	4,909	--	4,396	6,918	--
PAH-SS-10	6,691	4,678	3,765	4,720	4,678	4,054	--	5,734	7,861	--

Table 4. Mean distance from sample locations to nearby major land-use categories, Chicago, Illinois—Continued

[--, no data]

Sample number (location shown in figure 4)	Mean distance to unclassified land use (feet)	Mean distance to residential land use (feet)	Mean distance to commercial land use (feet)	Mean distance to institutional land use (feet)	Mean distance to industrial, warehousing, and wholesale land use (feet)	Mean distance to transportation, communication, and utilities land use (feet)	Mean distance to agricultural land use (feet)	Mean distance to open space land use (feet)	Mean distance to vacant or wetland land use (feet)	Mean distance to water (feet)
PAH-SS-11	7,930	5,957	6,824	5,864	9,956	7,545	5,100	4,773	9,022	8,472
PAH-SS-12	9,651	5,263	6,921	4,228	4,723	3,305	--	5,157	4,614	--
PAH-SS-13	--	4,071	3,364	3,495	5,610	5,632	--	7,401	7,434	9,507
PAH-SS-14	9,539	5,118	4,268	6,900	5,639	4,961	--	4,125	6,320	7,822
PAH-SS-15	6,413	3,198	2,922	2,360	6,322	4,260	--	3,128	5,162	6,367
PAH-SS-16	--	3,092	3,149	1,965	4,905	4,658	--	4,534	4,836	5,619
PAH-SS-17	--	3,126	1,875	2,911	5,158	4,474	--	3,609	5,864	6,788
PAH-SS-18	--	4,660	3,464	3,910	5,408	4,188	--	4,147	4,286	4,422
PAH-SS-19	--	3,958	3,961	3,745	3,807	3,729	--	4,842	4,620	--
PAH-SS-20	--	3,460	3,179	3,261	7,256	6,708	--	5,963	3,163	7,755
PAH-SS-21	--	4,331	4,516	3,113	3,236	3,680	--	7,257	4,838	7,231
PAH-SS-22	--	4,080	3,679	4,115	3,914	4,162	--	3,911	3,804	--
PAH-SS-23	--	3,492	3,705	3,033	6,983	7,376	--	3,410	1,243	--
PAH-SS-24	--	3,738	3,586	5,390	6,296	5,196	--	4,974	2,384	4,936
PAH-SS-25	--	4,606	4,585	4,682	5,326	5,788	--	4,556	4,311	--
PAH-SS-26	--	4,776	5,471	5,451	5,491	4,644	--	3,512	5,365	5,106
PAH-SS-27	--	4,472	4,286	5,376	5,175	4,607	--	6,033	6,008	6,165
PAH-SS-28	4,916	4,148	4,412	4,414	5,242	5,287	--	4,592	5,995	5,768
PAH-SS-29	--	4,666	4,839	4,706	3,737	5,070	--	3,823	4,047	2,323
PAH-SS-30	--	3,954	3,596	3,410	3,009	3,201	--	3,723	3,457	--
PAH-SS-31	--	4,316	4,518	3,347	3,486	3,529	--	3,914	3,455	3,401
PAH-SS-32	4,696	4,580	4,329	3,628	4,288	3,680	--	4,197	5,107	3,300
PAH-SS-33	--	4,077	4,636	3,977	4,068	4,148	--	4,630	4,471	--
PAH-SS-34	--	5,083	4,959	5,919	7,734	4,692	--	5,801	5,036	3,950
PAH-SS-35	--	5,303	5,328	4,591	5,361	7,664	--	6,556	4,915	4,792
PAH-SS-36	--	5,728	5,115	5,708	7,533	5,392	--	6,121	6,529	7,589
PAH-SS-37	--	4,946	3,944	4,716	5,538	5,058	--	5,559	4,974	3,570
PAH-SS-38	--	4,175	3,898	6,574	4,395	3,785	--	5,187	--	--

Table 5. Percentages of major land-use categories around soil-sampling sites, Chicago, Illinois

Sample number (location shown in figure 4)	Residential	Commercial and services	Institutional	Industrial, warehousing, and wholesale	Transportation, communication, and utilities	Open space	Vacant or wetland	Agricul-ture	Water	Unclassified (outside of city boundary)
	Percent land use within a 0.25-mile radius (0.5-mile diameter) around the sampling site									
PAH-CE-1	46.9	28.9	0	15.3	0	0	0	0	0	8.9
PAH-CE-2	66.3	13.6	0	0	19.3	0	.8	0	0	0
PAH-CE-3	71.2	26.3	2.5	0	0	0	0	0	0	0
PAH-CE-4	37.1	8.9	10	11.5	3.3	13.1	16.2	0	0	0
PAH-CE-5	7.9	3.7	1.4	68.8	10.9	.2	7.0	0	0	0
PAH-CE-6	59.4	30.7	5.6	1.0	0	0.9	2.4	0	0	0
PAH-CE-7	19.6	11.4	14.9	22.0	6.8	3.8	21.5	0	0	0
PAH-CE-8	60.5	10.3	7.2	3.1	.0	1.3	17.6	0	0	0
PAH-CE-9	33.2	24.9	1.9	6.6	12.5	6.9	14.1	0	0	.0
PAH-CE-10	31.5	7.0	16.8	21.2	16.2	.7	6.6	0	0	0
PAH-CE-11	45.2	15.5	0	16.0	14.5	8.8	0	0	0	0
PAH-CE-12	59.9	0	0	21.6	16.9	0	1.6	0	0	0
PAH-CE-13	0	0	0	48.0	33.6	0	18.4	0	0	0
PAH-CE-14	48.4	26.2	.2	0	15.3	3.5	6.4	0	0	0
PAH-CE-15	39.5	2.8	11.1	21.4	19.2	0	6.0	0	0	0
PAH-CE-16	0	0.7	0	31.0	32.3	4.3	20.0	0	11.7	0
PAH-CE-17	27.8	16.0	0	9.3	14.1	0	1.3	0	0	31.5
PAH-CE-18	58.6	12.5	.6	25.5	0	1.0	1.8	0	0	0
PAH-CE-19	44.0	8.7	4.8	10.5	25.3	0	6.7	0	0	0
PAH-SS-01	47.4	15.2	.7	28.3	0	7.7	.7	0	0	0
PAH-SS-02	61.4	28.6	6.3	2.1	0	1.5	0.1	0	0	0
PAH-SS-03	77.1	14.7	3.6	1.6	0	3.0	0	0	0	0
PAH-SS-04	63.9	21.6	10.6	2.6	.8	0	.5	0	0	0
PAH-SS-05	62.7	25.5	4.9	4.5	0	1.9	.5	0	0	0
PAH-SS-06	94.4	2.5	3.1	0	0	0	0	0	0	0
PAH-SS-07	59.7	15.1	11.6	0	0	0	0.5	0	0	13.1
PAH-SS-08	80.7	9.7	5.9	0	0	0	0	0	0	3.7
PAH-SS-09	68.9	15.5	10.8	2.5	0	2.3	0	0	0	0
PAH-SS-10	54.7	14.5	3.3	6.5	21.0	0	0	0	0	0
PAH-SS-11	76.1	20.7	3.2	0	0	0	0	0	0	0

Table 5. Percentages of major land-use categories around soil-sampling sites, Chicago, Illinois—Continued

Sample number (location shown in figure 4)	Residential	Commercial and services	Institutional	Industrial, warehousing, and wholesale	Transportation, communication, and utilities	Open space	Vacant or wetland	Agricul-ture	Water	Unclassified (outside of city boundary)
PAH-SS-12	31.7	10.2	14.5	16.6	17.8	0.4	8.8	0	0	0
PAH-SS-13	52.5	41.2	5.1	0	0	.2	1.0	0	0	0
PAH-SS-14	84.6	14.2	0	0	0	0	1.2	0	0	0
PAH-SS-15	55.6	14.1	10.4	0	1.3	16.5	2.1	0	0	0
PAH-SS-16	58.4	2.9	2.8	0	10.0	13.6	12.3	0	0	0
PAH-SS-17	5.8	28.9	0	23.8	0	9.6	31.8	0	0	0
PAH-SS-18	15.9	31.7	0.8	11.1	20.0	0	20.5	0	0	0
PAH-SS-19	78.9	14.8	5.9	0	0	0	.4	0	0	0
PAH-SS-20	82.5	11.5	2.4	1.0	0	0	2.6	0	0	0
PAH-SS-21	28.2	11.4	28.8	8.3	17.1	0	2.8	0	3.4	0
PAH-SS-22	60.4	26.8	8.0	0	1.3	0	3.5	0	0	0
PAH-SS-23	66.6	31.1	1.8	0	0	0	.5	0	0	0
PAH-SS-24	78.2	17.7	3.5	0	0	0	.6	0	0	0
PAH-SS-25	60.7	24.0	4.5	1.4	0	2.4	7.0	0	0	0
PAH-SS-26	60.8	26.1	1.8	3.3	0	.7	7.3	0	0	0
PAH-SS-27	54.8	28.6	4.3	12.3	0	0	0	0	0	0
PAH-SS-28	78.4	5.3	2.5	.9	0	12.2	.7	0	0	0
PAH-SS-29	36.6	7.1	5.7	15.5	4.7	9.7	20.7	0	0	0
PAH-SS-30	42.5	14.6	10.8	12.2	11.0	5.1	3.8	0	0	0
PAH-SS-31	43.1	4.2	16.8	15.1	1.7	8.1	11.0	0	0	0
PAH-SS-32	43.2	12.8	7.9	11.9	21.9	0	2.3	0	0	0
PAH-SS-33	66.3	23.7	2.8	6.3	0	0	.9	0	0	0
PAH-SS-34	68.5	25.0	6.5	0	0	0	0	0	0	0
PAH-SS-35	66.6	25.0	6.0	0	0	1.1	1.3	0	0	0
PAH-SS-36	63.7	23.2	10.4	0	2.4	0	.3	0	0	0
PAH-SS-37	1.8	56.2	8.6	3.8	22.1	0.3	3.7	0	3.5	0
PAH-SS-38	66.4	18.9	4.1	0	3.6	7.0	0	0	0	0

Table 5. Percentages of major land-use categories around soil-sampling sites, Chicago, Illinois—Continued

Sample number (location shown in figure 4)	Residential	Commercial and services	Institutional	Industrial, warehousing, and wholesale	Transportation, communication, and utilities	Open space	Vacant or wetland	Agricul-ture	Water	Unclassified (outside of city boundary)
	Percent landuse within a 1/2-mile radius (1-mile diameter) around the sampling site									
PAH-CE-1	48.4	9.3	1.9	19.5	0	1.2	0	0	0	19.8
PAH-CE-2	71.5	10.0	4.5	0	9.6	3.9	.6	0	0	0
PAH-CE-3	79.5	15.9	4.3	0	.3	0	.1	0	0	0
PAH-CE-4	29.7	15.7	9.1	21.4	7.1	5.1	9.7	0	2.1	0
PAH-CE-5	25.6	10.7	5.3	39.2	5.0	3.6	10.7	0	0	0
PAH-CE-6	55.9	19.2	8.0	0.3	1.8	11.8	3.1	0	0	0
PAH-CE-7	23.7	10.5	14.5	16.7	16.2	8.3	10.1	0	0	0
PAH-CE-8	58.1	9.9	4.3	1.1	.9	8.4	17.5	0	0	0
PAH-CE-9	47.2	12.5	4.6	1.9	14.4	4.2	15.2	0	0	0
PAH-CE-10	45.2	6.3	20.9	12.8	7.9	2.3	4.6	0	0	0
PAH-CE-11	53.5	12.4	6.4	8.9	10.1	8.1	0.7	0	0	0
PAH-CE-12	57.9	3.8	4.1	18.7	13.2	1.0	1.2	0	0	0
PAH-CE-13	8.4	2.1	2.4	44.2	27.8	1.7	13.4	0	0	0
PAH-CE-14	48.9	14.0	1.6	9.0	20.1	2.1	4.4	0	0	0
PAH-CE-15	63.3	5.1	5.8	7.7	9.7	4.0	4.4	0	0	0
PAH-CE-16	20.7	2.8	0.7	26.5	17.7	2.7	17.3	0	11.6	0
PAH-CE-17	33.5	8.3	.7	2.9	9.2	1.1	1.6	0	0	42.7
PAH-CE-18	56.4	10.5	6.8	15.1	4.0	1.5	5.7	0	0	0
PAH-CE-19	44.0	8.5	2.6	13.9	19.2	2.6	9.2	0	0	0
PAH-SS-01	56.9	12.4	3.5	23.4	.9	2.7	.3	0	0	0
PAH-SS-02	65.2	20.7	5.2	2.8	0.2	4.8	1.1	0	0	0
PAH-SS-03	75.4	8.2	2.1	5.8	5.5	1.2	1.8	0	0	0
PAH-SS-04	72.9	13.6	3.5	9.5	.2	0	.4	0	0	0
PAH-SS-05	61.3	15.2	4.4	6.3	0	3.3	0.5	0	0	9.1
PAH-SS-06	83.7	4.5	10.7	0	0	1.1	0	0	0	0
PAH-SS-07	53.6	8.2	12.2	0	0	0	0.1	0	0	25.9
PAH-SS-08	77.7	12.3	4.8	0	4.3	0	0	0	0	1.0
PAH-SS-09	79.5	6.6	7.0	1.9	0	5.1	0	0	0	0
PAH-SS-10	71.0	12.2	2.2	2.5	9.0	3.1	0	0	0	0
PAH-SS-11	69.0	7.1	23.2	0	0	.7	0	0	0	0

Table 5. Percentages of major land-use categories around soil-sampling sites, Chicago, Illinois—Continued

Sample number (location shown in figure 4)	Residential	Commercial and services	Institutional	Industrial, warehousing, and wholesale	Transportation, communication, and utilities	Open space	Vacant or wetland	Agricul-ture	Water	Unclassified (outside of city boundary)
PAH-SS-12	65.9	4.7	5.6	7.7	10.0	1.3	4.9	0	0	0
PAH-SS-13	61.2	24.6	6.2	0	0	7.2	.9	0	0	0
PAH-SS-14	81.8	9.6	2.4	.4	1.7	1.1	2.6	0	.5	0
PAH-SS-15	30.6	3.5	10.1	0	17.2	26.8	6.3	0	5.6	0
PAH-SS-16	51.3	4.6	2.8	.5	23.2	6.2	11.4	0	0	0
PAH-SS-17	15.9	9.7	4.1	32.6	6.0	5.4	26.2	0	0	0
PAH-SS-18	34.9	14.3	3.4	14.5	14.3	1.3	12.3	0	5.0	0
PAH-SS-19	71.1	8.6	5.5	2.9	7.0	3.1	1.8	0	0	0
PAH-SS-20	65.1	11.1	2.0	.3	0	8.3	2.9	0	0	10.4
PAH-SS-21	45.3	8.2	28.1	4.9	9.1	.7	1.7	0	1.9	0
PAH-SS-22	66.0	13.1	3.5	4.2	4.2	1.5	7.6	0	0	0
PAH-SS-23	77.1	15.2	3.1	0	0	4.4	.2	0	0	0
PAH-SS-24	80.9	16.1	2.3	0	0	0	.7	0	0	0
PAH-SS-25	69.4	17.2	4.4	.8	.8	1.0	6.4	0	0	0
PAH-SS-26	55.4	12.8	2.2	15.5	2.4	7.3	4.4	0	0	0
PAH-SS-27	60.7	15.8	4.6	18.7	0	0.2	0	0	0	0
PAH-SS-28	60.4	5.7	2.1	19.5	5.8	4.8	1.8	0	0	0
PAH-SS-29	35.8	6.2	7.4	16.6	7.5	12.0	13.0	0	1.6	0
PAH-SS-30	45.6	11.2	7.7	11.3	7.6	2.5	14.1	0	0	0
PAH-SS-31	44.0	4.9	5.9	20.9	4.8	7.4	12.3	0	0	0
PAH-SS-32	44.2	5.8	6.2	24.4	16.6	1.5	1.4	0	0	0
PAH-SS-33	60.2	11.0	4.0	19.9	4.0	0	.8	0	0	0
PAH-SS-34	73.5	18.0	3.7	.3	0	4.3	.3	0	0	0
PAH-SS-35	68.6	15.5	8.5	3.3	.1	2.4	1.6	0	0	0
PAH-SS-36	58.7	22.7	4.4	.7	4.6	7.7	.7	0	0	.6
PAH-SS-37	1.9	56.3	6.9	5.9	17.9	2.9	2.4	0	5.9	0
PAH-SS-38	68.1	15.9	1.7	3.7	6.8	3.8	0	0	0	0
Percent landuse within a 1-mile radius (2-mile diameter) around the sampling site										
PAH-CE-1	32.0	3.8	1.8	8.5	0	17.1	0.1	0	0	36.9
PAH-CE-2	74.2	3.9	9.7	.5	4.2	2.5	.2	0	0	4.8

Table 5. Percentages of major land-use categories around soil-sampling sites, Chicago, Illinois—Continued

Sample number (location shown in figure 4)	Residential	Commercial and services	Institutional	Industrial, warehousing, and wholesale	Transportation, communication, and utilities	Open space	Vacant or wetland	Agricul-ture	Water	Unclassified (outside of city boundary)
PAH-CE-3	71.4	15.5	4.0	0.8	0.3	6.5	0.2	0	1.4	0
PAH-CE-4	25.1	19.1	6.5	19.6	10.1	5.3	7.7	0	3.0	3.6
PAH-CE-5	32.8	15.7	7.1	25.0	7.8	2.7	9.0	0	0	0
PAH-CE-6	49.4	12.7	8.6	8.8	3.8	10.3	5.8	0	.6	0
PAH-CE-7	23.6	13.5	10.1	11.3	20.2	7.5	9.5	0	.9	3.4
PAH-CE-8	42.9	11.1	5.8	1.5	4.9	10.5	12.5	0	0	10.9
PAH-CE-9	39.6	9.5	4.9	4.2	15.6	13.8	12.0	0	.5	0
PAH-CE-10	52.2	3.7	10.8	14.5	9.2	3.9	5.8	0	0	0
PAH-CE-11	53.9	8.5	4.1	8.3	9.6	12.8	2.8	0	0	0
PAH-CE-12	55.5	7.0	7.4	11.1	9.6	5.4	3.5	0	.6	0
PAH-CE-13	28.8	10.4	6.0	24.8	11.5	1.9	5.7	0	0	11.0
PAH-CE-14	39.1	7.3	1.0	6.4	30.5	3.3	6.1	0	0	6.3
PAH-CE-15	75.7	6.8	4.9	2.2	5.5	2.5	2.5	0	0	0
PAH-CE-16	33.7	6.0	1.3	17.9	13.4	6.3	15.0	0	5.8	.6
PAH-CE-17	30.3	3.5	1.4	4.3	4.5	5.9	1.5	0	.7	47.9
PAH-CE-18	58.4	10.0	3.8	12.4	6.2	3.2	6.0	0	0	0
PAH-CE-19	45.1	9.3	7.7	6.2	12.1	10.3	8.5	0	.9	0
PAH-SS-01	68.2	12.0	3.3	12.2	1.3	2.4	.6	0	0	0
PAH-SS-02	59.9	17.1	3.5	6.2	3.4	6.6	3.0	0	.4	0
PAH-SS-03	65.7	9.0	3.3	9.1	3.1	4.5	1.8	0	0	3.4
PAH-SS-04	72.7	13.0	3.7	7.4	0.5	2.6	0.3	0	0	0
PAH-SS-05	49.8	12.7	2.2	8.7	0	2.8	1.1	0	0	22.7
PAH-SS-06	67.0	5.0	13.7	0	0	1.8	.0	0	0	12.5
PAH-SS-07	46.5	5.1	20.3	.3	0	1.0	2.8	0	0	24.0
PAH-SS-08	56.4	10.3	2.8	0	4.7	17.4	.6	0	.1	7.8
PAH-SS-09	62.8	6.3	16.8	1.5	3.5	8.2	0.2	0	0	0.8
PAH-SS-10	69.4	10.2	2.8	5.5	5.0	6.9	.2	0	0	0
PAH-SS-11	65.0	5.0	14.1	.1	0	7.6	1.2	2.6	.1	4.4
PAH-SS-12	77.5	5.8	4.3	2.2	5.4	2.5	2.4	0	0	0
PAH-SS-13	64.7	11.3	5.3	10.3	2.6	2.5	3.2	0	.2	0

Table 5. Percentages of major land-use categories around soil-sampling sites, Chicago, Illinois—Continued

Sample number (location shown in figure 4)	Residential	Commercial and services	Institutional	Industrial, warehousing, and wholesale	Transportation, communication, and utilities	Open space	Vacant or wetland	Agricul-ture	Water	Unclassified (outside of city boundary)
PAH-SS-14	59.3	8.8	2.4	9.9	11.6	2.6	4.6	0	0.9	0
PAH-SS-15	14.7	1.5	3.5	13.5	39.5	13.2	6.6	0	7.5	0
PAH-SS-16	24.0	2.2	.8	18.8	19.5	5.3	17.6	0	11.9	0
PAH-SS-17	14.4	3.4	2.8	26.2	10.8	15.7	13.7	0	7.7	5.3
PAH-SS-18	40.3	7.1	2.7	14.9	13.9	3.2	13.8	0	4.0	0
PAH-SS-19	71.1	11.9	5.0	3.3	4.6	2.4	1.6	0	0	0
PAH-SS-20	53.4	7.2	2.4	.5	.6	9.1	1.5	0	25.3	0
PAH-SS-21	58.0	11.1	12.4	4.4	7.2	1.5	5.0	0	.5	0
PAH-SS-22	61.1	10.6	4.1	12.6	3.0	3.5	5.1	0	0	0
PAH-SS-23	77.1	9.7	2.4	1.1	2.5	4.7	2.4	0	0	0
PAH-SS-24	77.5	9.4	3.4	0	1.2	7.0	0.4	0	1.1	0
PAH-SS-25	61.6	10.6	4.6	4.6	1.4	8.3	8.9	0	0	0
PAH-SS-26	22.3	8.2	1.2	40.3	10.7	5.1	8.3	0	4.0	0
PAH-SS-27	40.1	9.4	1.7	34.1	12.4	1.0	1.4	0	0	0
PAH-SS-28	34.0	7.1	1.3	31.9	13.0	1.2	4.0	0	2.1	5.3
PAH-SS-29	35.6	11.8	6.9	14.2	10.1	9.2	11.5	0	0.6	0
PAH-SS-30	43.3	8.9	5.7	9.0	5.8	12.9	13.0	0	1.3	0
PAH-SS-31	43.2	8.0	4.6	15.1	7.4	11.7	9.3	0	.7	0
PAH-SS-32	35.8	10.6	3.0	22.6	7.4	7.2	3.0	0	.3	10.2
PAH-SS-33	55.0	8.8	3.6	20.0	6.2	1.8	4.5	0	0	0
PAH-SS-34	56.7	13.9	10.3	1.6	0.6	8.8	1.8	0	1.1	5.3
PAH-SS-35	56.3	10.2	16.4	2.9	.2	4.8	1.3	0	.2	7.7
PAH-SS-36	47.2	14.5	8.7	.7	2.8	8.8	.8	0	0	16.6
PAH-SS-37	11.0	36.0	5.6	7.5	15.8	8.5	7.5	0	4.0	4.1
PAH-SS-38	67.3	13.1	2.8	5.7	7.5	3.5	.1	0	0	0

Table 6. Number of soil-sampling sites near each major land-use category, Chicago, Illinois.

	Land-use category						
	Residential	Commercial and services	Institutional	Industrial, warehousing and wholesale	Transportation, communication, and utilities	Open space	Vacant or wetland
Code	1100	1200	1300	1400	1500	3000	4000
Number of samples in the category	9	26	3	5	5	2	6

Table 7. Shapiro-Wilk test statistic for normal distribution of natural-log-transformed polynuclear aromatic hydrocarbon data in ambient surface soils, Chicago, Illinois

[Alpha = 0.1. Null hypothesis (H_0) is that the distribution is lognormal.]

Constituent (natural-log transformed)	Shapiro-Wilk test statistic					
	Excluding sample PAH-CE-19			Including sample PAH-CE-19		
	Value	p-value	Conclusion	Value	p-value	Conclusion
Phenanthrene	0.968	0.14	Fail to reject H_0	0.971	0.19	Fail to reject H_0
Fluoranthene	.969	.16	Fail to reject H_0	.967	.13	Fail to reject H_0
Pyrene	.969	.16	Fail to reject H_0	.962	.07	Reject H_0
Benzo(a)anthracene	.973	.24	Fail to reject H_0	.971	.18	Fail to reject H_0
Chrysene	.977	.35	Fail to reject H_0	.971	.19	Fail to reject H_0
Benzo(b)fluoranthene	.976	.31	Fail to reject H_0	.965	.10	Reject H_0
Benzo(k)fluoranthene	.970	.17	Fail to reject H_0	.961	.08	Reject H_0
Benzo(a)pyrene	.977	.35	Fail to reject H_0	.966	.11	Fail to reject H_0
Dibenzo(a,h)anthracene	.981	.50	Fail to reject H_0	.937	.01	Reject H_0
Benzo(g,h,i)perylene	.974	.26	Fail to reject H_0	.931	.00	Reject H_0
Indeno(1,2,3-cd)pyrene	.978	.40	Fail to reject H_0	.939	.01	Reject H_0

Table 8. Statistical summary of log-transformed polynuclear aromatic hydrocarbon data for censored compounds in ambient surface soils, Chicago, Illinois

[Bold denotes retained estimates]

Constituent (natural-log transformed)	Number of samples	Number less than detection limit	Number of detection limits	Maximum detection limit (micro-grams per kilogram)	Mean (micro-grams per kilogram)	Standard deviation (micro-grams per kilogram)	Value of 25th percentile (micro-grams per kilogram)	Median (micro-grams per kilogram)	Value of 75th percentile (micro-grams per kilogram)
Estimates using log-probability regression of samples with concentrations greater than the detection limit									
All Samples									
Acenaphthene	57	7	5	3.05	4.24	1.86	2.41	4.44	5.63
Acenaphthylene	57	16	6	3.18	3.22	1.55	1.91	2.83	4.18
Anthracene	57	3	3	3.05	5.22	1.89	3.68	5.39	6.48
Fluorene	57	7	5	3.05	4.36	1.88	2.53	4.51	5.75
Naphthalene	57	22	7	3.18	3.56	1.44	2.42	3.00	4.54
Excluding Sample PAH-CE-19									
Acenaphthene	56	7	5	3.05	**4.14**	**1.65**	2.45	4.44	5.52
Acenaphthylene	56	16	6	3.18	**3.16**	**1.47**	1.90	2.80	4.10
Anthracene	56	3	3	3.05	**5.10**	**1.69**	3.66	5.32	6.44
Fluorene	56	7	5	3.05	**4.25**	**1.69**	2.53	4.43	5.72
Naphthalene	56	22	7	3.18	**3.51**	**1.30**	2.46	2.97	4.49
Estimates using adjusted lognormal maximum likelihood regression of samples with concentrations above the detection limit									
All Samples									
Acenaphthene	57	7	5	3.05	4.26	2.32	2.66	4.44	5.63
Acenaphthylene	57	16	6	3.18	3.22	1.76	2.00	2.83	4.18
Anthracene	57	3	3	3.05	5.24	2.15	3.68	5.39	6.48
Fluorene	57	7	5	3.05	4.38	2.27	2.79	4.51	5.75
Naphthalene	57	22	7	3.18	3.51	1.65	2.35	3.18	4.54
Excluding Sample PAH-CE-19									
Acenaphthene	56	7	5	3.05	4.15	2.17	**2.64**	**4.44**	**5.52**
Acenaphthylene	56	16	6	3.18	3.16	1.68	**1.99**	**2.79**	**4.10**
Anthracene	56	3	3	3.05	5.13	2.02	**3.66**	**5.32**	**6.44**
Fluorene	56	7	5	3.05	4.27	2.13	**2.78**	**4.43**	**5.72**
Naphthalene	56	22	7	3.18	3.44	1.54	**2.36**	**3.14**	**4.49**

Table 9. Test for outliers in polynuclear aromatic hydrocarbon concentrations in sample PAH-CE-19, Chicago, Illinois

[%, percent; unk, unknown]

Constituent	Lowest value (0%)	First quartile (Q1) (25%)	Median (50%)	Third quartile (Q3) (75%)	Interquartile range (IQR) (Q3-Q1)	Value in sample PAH-CE-19	Next highest value below PAH-CE-19	Standard deviation	1 Step (1.5 * IQR)	Number of steps between Q3 and the value in PAH-CE-19	Number of standard deviations between maximum value and the next highest value
Phenanthrene	22	230	1,200	3,700	3,470	520,000	19,000	68,633	5,205	99	7
Fluoranthene	52	495	2,100	7,100	6,605	1,100,000	35,000	145,200	9,907	110	7
Pyrene	51	350	1,700	5,000	4,650	720,000	30,000	95,044	6,975	103	7
Benzo(a)anthracene	26	210	880	2,700	2,490	370,000	16,000	48,825	3,735	98	7
Chrysene	31	245	910	2,900	2,655	350,000	15,000	46,176	3,982	87	7
Benzo(b)fluoranthene	40	350	1,100	3,700	3,350	550,000	18,000	72,593	5,025	109	7
Benzo(k)fluoranthene	36	230	820	2,200	1,970	280,000	10,000	36,932	2,955	94	7
Benzo(a)pyrene	39	270	1,000	3,200	2,930	460,000	17,000	60,710	4,395	104	7
Dibenzo(a,h)anthracene	8	70	140	290	220	41,000	1,600	5,404	330	123	7
Benzo(g,h,i)perylene	24	190	490	1,200	1,010	290,000	8,100	38,298	1,515	191	7
Indeno(1,2,3-cd)pyrene	31	220	610	1,500	1,280	370,000	9,900	48,861	1,920	192	7
Naphthalene	unk	8	26	94	86	2,500	700	350	128	19	5
Acenaphthene	unk	16	85	279	263	43,000	1,500	5,678	393	109	7
Anthracene	unk	40	220	655	616	120,000	4,600	15,848	923	129	7
Fluorene	unk	18	91	315	297	36,000	2,000	4,753	445	80	7

Table 10. Statistical summary of natural-log transformed polynuclear aromatic hydrocarbon concentrations in ambient surface soils, Chicago, Illinois

[na, not applicable.]

Constituent (natural-log transformed)	Number of samples collected[1]	Censored data	Mean concentration (micrograms per kilogram)	Standard deviation (micrograms per kilogram)	Median (micrograms per kilogram)	95th percentile of the distribution (micrograms per kilogram)	Upper 95-percent confidence limit on the mean (micrograms per kilogram)	Lower 95-percent confidence limit on the mean (micrograms per kilogram)
Acenaphthene	56	yes	4.14	1.65	4.44	7.00	na	na
Acenaphthylene	56	yes	3.16	1.47	2.79	6.09	na	na
Anthracene	56	yes	5.10	1.69	5.32	7.84	na	na
Benzo(a)anthracene	56	no	6.58	1.65	6.75	9.12	7.03	6.14
Benzo(b)fluoranthene	56	no	6.90	1.56	6.96	9.32	7.32	6.49
Benzo(k)fluoranthene	56	no	6.52	1.51	6.64	8.97	6.92	6.11
Benzo(g,h,i)perylene	56	no	6.19	1.34	6.13	8.75	6.55	5.83
Benzo(a)pyrene	56	no	6.78	1.56	6.88	9.24	7.19	6.36
Chrysene	56	no	6.65	1.59	6.78	9.08	7.08	6.23
Dibenzo(a,h)anthracene	56	no	5.03	1.16	4.94	7.00	5.34	4.72
Fluoranthene	56	no	7.49	1.67	7.63	9.90	7.93	7.04
Fluorene	56	yes	4.25	1.69	4.43	7.24	na	na
Indeno(1,2,3-cd)pyrene	56	no	6.41	1.37	6.39	8.87	6.77	6.04
Naphthalene	56	yes	3.51	1.30	3.14	6.02	na	na
Phenanthrene	56	no	6.75	1.76	7.00	9.39	7.22	6.28
Pyrene	56	no	7.14	1.61	7.41	9.39	7.57	6.71

[1] Excludes data from sample PAH-CE-19

Table 11. Results of Wilcoxon-Rank-Sum test comparing polynuclear aromatic hydrocarbon concentrations in surface soils collected at city properties and Commonwealth Edison properties, Chicago, Illinois

[Value of detection limit used to compute rank for censored data. Data from site PAH-CE-19 excluded from analysis. Alpha = 0.05. Null hypothesis (H_0) is that city and Commonwealth Edison properties have the same mean value.]

Constituent	Rank sum normal statistic with correction	p-value	Conclusion
	Uncensored Data		
Phenanthrene	1.26	0.207	Fail to reject H_0
Fluoranthene	1.09	.277	Fail to reject H_0
Pyrene	1.00	.317	Fail to reject H_0
Benzo(a)anthracene	.98	.326	Fail to reject H_0
Chrysene	1.16	.247	Fail to reject H_0
Benzo(b)fluoranthene	.75	.456	Fail to reject H_0
Benzo(k)fluoranthene	.54	.593	Fail to reject H_0
Benzo(a)pyrene	.90	.366	Fail to reject H_0
Dibenzo(a,h)anthracene	1.85	.064	Fail to reject H_0
Benzo(g,h,i)perylene	1.40	.160	Fail to reject H_0
Indeno(1,2,3-cd)pyrene	1.16	.247	Fail to reject H_0
	Censored Data		
Naphthalene	1.82	0.069	Fail to reject H_0
Acenaphthylene	-.46	.648	Fail to reject H_0
Acenaphthene	-.48	.629	Fail to reject H_0
Fluorene	-.64	.522	Fail to reject H_0
Anthracene	-.97	.335	Fail to reject H_0

Table 12. Pearson product-moment correlation coefficients for natural-log transformed concentrations of polynuclear aromatic hydrocarbons and total organic carbon in ambient surface soils, Chicago, Illinois

[Italic denotes constituents with censored data. --, not applicable]

Constituent	*Acenaphthene*	*Acenaphthylene*	*Anthracene*	Benzo(a)anthracene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(g,h,i)perylene	Benzo(a)pyrene	Chrysene	Dibenzo(a,h)anthracene	Fluoranthene	*Fluorene*	Indeno(1,2,3-cd)pyrene	*Naphthalene*	Phenanthrene	Pyrene	Total organic carbon
Acenaphthene	--	0.79	0.97	0.93	0.92	0.92	0.86	0.92	0.92	0.81	0.94	0.98	0.88	0.73	0.95	0.94	0.48
Acenaphthylene	--	--	.83	.87	.87	.87	.84	.87	.86	.75	.85	.83	.86	.78	.83	.87	.49
Anthracene	--	--	--	.98	.97	.96	.92	.97	.98	.87	.98	.98	.94	.76	.99	.97	.52
Benzo(a)anthracene	--	--	--	--	.99	.99	.95	1.00	1.00	.89	1.00	.95	.97	.74	.99	.99	.55
Benzo(b)fluoranthene	--	--	--	--	--	.99	.95	1.00	.99	.89	.99	.94	.97	.74	.98	.98	.56
Benzo(k)fluoranthene	--	--	--	--	--	--	.94	.99	.98	.88	.98	.94	.96	.75	.97	.97	.57
Benzo(g,h,i)perylene	--	--	--	--	--	--	--	.96	.96	.95	.95	.88	.99	.72	.94	.95	.57
Benzo(a)pyrene	--	--	--	--	--	--	--	--	1.00	.90	.99	.94	.98	.74	.98	.99	.57
Chrysene	--	--	--	--	--	--	--	--	--	.90	.99	.94	.98	.73	.98	.99	.56
Dibenzo(a,h)anthracene	--	--	--	--	--	--	--	--	--	--	.88	.82	.95	.70	.89	.88	.57
Fluoranthene	--	--	--	--	--	--	--	--	--	--	--	.95	.96	.72	.99	.99	.55
Fluorene	--	--	--	--	--	--	--	--	--	--	--	--	.90	.77	.96	.95	.48
Indeno(1,2,3-cd)pyrene	--	--	--	--	--	--	--	--	--	--	--	--	--	.73	.96	.96	.57
Naphthalene	--	--	--	--	--	--	--	--	--	--	--	--	--	--	.75	.75	.40
Phenanthrene	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	.99	.53
Pyrene	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	.54

Table 13. Physical properties of select polynuclear aromatic hydrocarbons
[°C, degrees Celsius]

Constituent	Molecular weight (grams per mole)	Solubility in water at 25°C (micrograms per liter)	Octonal-water partition coefficient (dimensionless)	Organic carbon partition coefficient (milliliters water per gram carbon)	Henry's Law Constant (cubic meters atmosphere per mole)
Acenaphthene	154	3,930.	9,600	4,600	1.40E-04
Acenaphthylene	154	3,420.	5,300	2,500	1.45E-03
Anthracene	178	59.	14,000	28,000	5.87E-05
Benzo(a)anthracene	228	11.	410,000	200,000	3.01E-06
Benzo(b)fluoranthene	252	2.4	1,100,000	550,000	1.22E-05
Benzo(k)fluoranthene	252	2.4	1,150,000	550,000	7.48E-07
Benzo(g,h,i)perylene	276	.3	3,200,000	1,600,000	1.44E-07
Benzo(a)pyrene	252	3.8	1,550,000	5,500,000	1.28E-09
Chrysene	228	1.9	410,000	200,000	8.45E-05
Dibenzo(a,h)anthracene	278	.4	6,900,000	3,300,000	1.33E-08
Fluoranthene	202	260.	79,000	38,000	1.45E-05
Fluorene	166	800.	15,000	7,300	5.74E-05
Indeno(1,2,3-cd)pyrene	276	.5	3,200,000	1,600,000	6.95E-08
Naphthalene	128	12,500.	2,344	1,290	1.08E-03
Phenanthrene	178	435.	28,000	14,000	1.45E-04
Pyrene	202	133.	80,000	38,000	9.92E-06

Table 14. Summary of average polynuclear aromatic hydrocarbon concentrations in air samples, Chicago, Illinois
[bdl, below detection limit]

Constituent	Chicago-Washington School [1] (micrograms per cubic meter)	Coke ovens [2] (micrograms per cubic meter)	Warm diesel engines[2] (microgram per cubic meter)	Highway tunnel[2] (micrograms per cubic meter)	Gasoline engines[2] (micrograms per cubic meter)	Wood combustion[2] (micrograms per cubic meter)
Acenaphthene	12.8	0.023	0.566	0.168	0.0377	0.0515
Acenaphthylene	3.6	.747	.464	.445	.0708	1.83
Anthracene	1.5	.158	.251	.177	.0446	.0959
Benzo(a)anthracene	1.	.0076	.249	.09	.0059	.0187
Benzo(b)fluoranthene	.6	.0048	.137	.044	.033	.0234
Benzo(k)fluoranthene	bdl	.008	.098	.041	.0255	.0446
Benzo(g,h,i)perylene	bdl	.0007	.108	.017	.0092	bdl
Benzo(a)pyrene	.1	.0053	.302	.063	.027	.203
Chrysene	1.2	.0147	.143	.078	.0283	.0328
Dibenzo(a,h)anthracene	bdl	bdl	.170	.015	bdl	bdl
Fluoranthene	8.6	.0883	.081	.117	.0446	.0959
Fluorene	14.7	.502	.651	.406	.123	.128
Indeno(1,2,3-cd)pyrene	bdl	.0011	.250	.02	bdl	bdl
Naphthalene	202.9	22.4	.386	8.03	2.46	.402
Phenanthrene	46.8	.5	.472	.3	.0398	.219
Pyrene	4.9	.0563	.049	.193	.0719	.100

[1] From Illinois Environmental Protection Agency, 2002

[2] From Khalili and others, 1995

Table 15. Results of one-way analysis of variance of polynuclear aromatic hydrocarbon concentrations and distance from nearest roadway, Chicago, Illinois
[Alpha = 0.05. Null hypothesis (H_0) is that all means are equal.]

Constituent (natural-log transformed)	F value	Probability of (F)[1]	Conclusion
Benzo(a)anthracene	0.31	0.93	Fail to reject H_0
Benzo(a)pyrene	.29	.94	Fail to reject H_0
Benzo(b)fluoranthene	.36	.90	Fail to reject H_0
Benzo(g,h,i)perylene	.34	.91	Fail to reject H_0
Benzo(k)fluoranthene	.32	.93	Fail to reject H_0
Chrysene	.42	.86	Fail to reject H_0
Dibenzo(a,h)anthracene	.39	.88	Fail to reject H_0
Fluoranthene	.31	.93	Fail to reject H_0
Indeno(1,2,3-cd)pyrene	.56	.76	Fail to reject H_0
Phenanthrene	.26	.95	Fail to reject H_0
Pyrene	.43	.86	Fail to reject H_0

[1] Probability of observing an F value this large by chance alone. Probabilities less than 0.05 are considered statistically significant.

Table 16. Statistical description of polynuclear aromatic hydrocarbons in ambient soils for different land-use categories, Chicago, Illinois

[Bold denotes rejection of the assumption of normal distribution for the constituent. %, percent]

Constituent (natural-log transformed)	Mean	Standard deviation	Lowest value (0%)	First quartile (25%)	Median (50%)	Third quartile (75%)	Highest value (100%)	Shapiro-Wilk test (p-value)
Vacant or Wetland (6 cases)								
Phenanthrene	6.34	2.37	3.40	4.03	6.46	8.65	9.02	0.47
Fluoranthene	7.22	2.43	4.16	5.08	7.38	9.31	10.02	.45
Pyrene	6.74	2.20	4.09	4.61	6.87	8.67	9.31	.41
Benzo(a)anthracene	6.34	2.39	3.33	4.08	6.49	8.50	9.13	.53
Chrysene	6.45	2.28	3.58	4.37	6.53	8.61	9.08	.51
Benzo(b)fluoranthene	6.83	2.30	3.91	4.57	7.17	8.82	9.32	.35
Benzo(k)fluoranthene	6.49	2.23	3.78	4.06	6.96	8.19	8.97	.28
Benzo(a)pyrene	6.72	2.30	3.81	4.39	7.11	8.63	9.24	.36
Dibenzo(a,h)anthracene	4.95	1.58	2.30	4.23	5.08	6.25	6.72	.74
Benzo(g,h,i)perylene	6.23	2.11	3.18	4.79	6.22	8.22	8.75	.88
Indeno(1,2,3-cd)pyrene	6.38	2.09	3.43	4.87	6.40	8.32	8.87	.83
Transportation, Communication, and Utilities (5 cases)								
Phenanthrene	5.69	2.33	3.09	4.87	5.08	6.02	9.39	0.54
Fluoranthene	6.42	2.04	4.30	5.44	6.02	6.59	9.74	.46
Pyrene	6.09	2.05	3.93	5.01	5.86	6.25	9.39	.52
Benzo(a)anthracene	5.62	1.99	3.40	4.70	5.35	5.89	8.76	.66
Chrysene	5.66	1.95	3.56	4.79	5.30	5.89	8.79	.56
Benzo(b)fluoranthene	5.94	1.79	3.91	5.01	5.77	6.29	8.70	.78
Benzo(k)fluoranthene	5.71	1.98	3.58	4.55	5.30	6.36	8.75	.77
Benzo(a)pyrene	5.84	1.91	3.71	4.87	5.52	6.31	8.79	.78
Dibenzo(a,h)anthracene	4.30	1.80	2.08	3.30	4.22	5.08	6.85	.99
Benzo(g,h,i)perylene	5.38	1.88	3.18	4.60	4.87	6.06	8.19	.84
Indeno(1,2,3-cd)pyrene	5.58	1.85	3.50	4.87	4.94	6.15	8.43	.66
Commercial (26 cases)								
Phenanthrene	6.54	1.60	3.30	5.44	6.76	7.65	9.85	0.67
Fluoranthene	7.29	1.56	3.95	6.36	7.55	8.27	10.46	.76
Pyrene	6.99	1.49	4.48	6.06	7.27	7.86	10.31	.40
Benzo(a)anthracene	6.39	1.55	3.26	5.39	6.59	7.31	9.68	.89
Chrysene	6.47	1.46	3.43	5.52	6.71	7.31	9.62	.91
Benzo(b)fluoranthene	6.70	1.47	3.69	5.83	6.85	7.65	9.80	.95
Benzo(k)fluoranthene	6.29	1.40	3.58	5.39	6.53	7.17	9.21	.80
Benzo(a)pyrene	6.57	1.44	3.66	5.58	6.80	7.38	9.74	.90
Dibenzo(a,h)anthracene	4.94	.98	3.64	4.22	4.74	5.39	7.38	**.01**
Benzo(g,h,i)perylene	6.07	1.10	4.61	5.30	6.02	6.36	9.00	.09
Indeno(1,2,3-cd)pyrene	6.26	1.16	4.59	5.42	6.29	6.77	9.20	.36

Table 16. Statistical description of polynuclear aromatic hydrocarbons in ambient soils for different land-use categories, Chicago, Illinois—Continued

[Bold denotes rejection of the assumption of normal distribution for the constituent. %, percent]

Constituent (natural-log transformed)	Mean	Standard deviation	Lowest value (0%)	First quartile (25%)	Median (50%)	Third quartile (75%)	Highest value (100%)	Shapiro-Wilk test (p-value)
Industrial, Warehousing, and Wholesale (5 cases)								
Phenanthrene	7.15	1.28	5.19	6.55	7.65	8.10	8.27	0.34
Fluoranthene	7.91	1.14	6.13	7.44	8.40	8.70	8.87	.28
Pyrene	7.55	1.14	6.06	6.72	7.74	8.56	8.68	.48
Benzo(a)anthracene	7.00	1.17	5.35	6.40	7.09	8.07	8.10	.49
Chrysene	7.04	1.10	5.39	6.58	7.17	7.97	8.07	.52
Benzo(b)fluoranthene	7.37	1.01	5.86	6.91	7.63	8.13	8.34	.57
Benzo(k)fluoranthene	6.95	1.13	5.44	6.11	7.33	7.90	7.97	.31
Benzo(a)pyrene	7.18	1.08	5.60	6.63	7.41	8.07	8.19	.51
Dibenzo(a,h)anthracene	5.07	1.01	3.30	5.25	5.39	5.56	5.83	**.03**
Benzo(g,h,i)perylene	6.35	1.02	4.70	6.02	6.84	7.09	7.09	.12
Indeno(1,2,3-cd)pyrene	6.59	0.98	5.08	6.15	7.04	7.31	7.38	.21
Residential (9 cases)								
Phenanthrene	7.33	1.77	4.87	5.48	7.60	8.67	9.68	0.40
Fluoranthene	8.03	1.61	5.70	6.48	8.37	9.39	9.90	.33
Pyrene	7.65	1.63	5.52	5.86	8.24	8.73	9.74	.22
Benzo(a)anthracene	7.10	1.64	4.94	5.35	7.44	8.54	9.12	.24
Chrysene	7.14	1.64	5.08	5.39	7.44	8.67	9.31	.27
Benzo(b)fluoranthene	7.38	1.61	5.25	5.91	7.55	8.88	9.55	.47
Benzo(k)fluoranthene	6.91	1.52	4.61	5.67	7.17	8.29	9.11	.82
Benzo(a)pyrene	7.24	1.60	5.08	5.67	7.50	8.73	9.39	.45
Dibenzo(a,h)anthracene	5.28	1.21	3.33	4.44	5.30	6.23	7.00	.82
Benzo(g,h,i)perylene	6.52	1.51	4.79	5.14	6.59	7.60	8.84	.41
Indeno(1,2,3-cd)pyrene	6.81	1.54	4.87	5.39	6.82	8.37	9.00	.37

Table 17. Results of analysis of variance of uncensored polynuclear aromatic hydrocarbon concentrations in ambient soil by land use, Chicago, Illinois

[Alpha = 0.05. Null hypothesis (H_0) is that mean concentrations are not significantly different among land-use categories.]

Constituent (natural-log transformed)	F value	Probability[1]	Conclusion
Benzo(a)anthracene	0.92	0.49	Fail to reject H_0
Benzo(a)pyrene	.94	.48	Fail to reject H_0
Benzo(b)fluoranthene	.93	.48	Fail to reject H_0
Benzo(g,h,i)perylene	.66	.68	Fail to reject H_0
Benzo(k)fluoranthene	.81	.57	Fail to reject H_0
Chrysene	.92	.49	Fail to reject H_0
Dibenzo(a,h)anthracene	.85	.54	Fail to reject H_0
Fluoranthene	1.01	.43	Fail to reject H_0
Indeno(1,2,3-cd)pyrene	.69	.66	Fail to reject H_0
Phenanthrene	1.01	.43	Fail to reject H_0
Pyrene	1.12	.37	Fail to reject H_0

[1] Probability of observing an F value this large by chance alone. Probabilities less than 0.05 are considered statistically significant.

Table 18. Regression of polynuclear aromatic hydrocarbon concentrations in surface soils and percent industrial land use within a 1-mile radius of the sample, Chicago, Illinois.

Constituent (natural-log transformed)	T-ratio of slope coefficient	p-value	Correlation coefficient
Phenanthrene	2.01	0.049	0.070
Fluoranthene	2.27	.027	.087
Pyrene	2.33	.023	.092
Benzo(a)anthracene	2.41	.019	.097
Chrysene	2.32	.024	.091
Benzo(b)fluoranthene	2.34	.023	.092
Benzo(k)fluoranthene	2.38	.021	.095
Benzo(a)pyrene	2.43	.019	.098
Dibenzo(a,h)anthracene	2.11	.040	.076
Benzo(g,h,i)perylene	2.22	.030	.084
Indeno(1,2,3-cd)pyrene	2.24	.030	.085

Table 19. Summary of data on inorganic constituents in ambient surface soils, Chicago, Illinois

[<, less than; nc, not calculated]

Constituent	Number of samples collected	Number of detections	Percentage of samples with analyte detected	Arithmetic mean	Standard deviation	Range of detected concentrations
Aluminum (weight percent)	57	57	100	4.8	1.7	0.775-7.45
Arsenic (milligrams per kilogram)	57	47	82	19.5	31.8	<10-220
Barium (milligrams per kilogram)	57	57	100	427.2	126.	100-697
Beryllium (milligrams per kilogram)	57	49	86	nc	nc	<1-14
Bismuth (milligrams per kilogram)	57	1	2	nc	nc	<50-57
Cadmium (milligrams per kilogram)	57	18	32	nc	nc	<2-7
Calcium (weight percent)	57	57	100	4.1	3.4	0.61-16.4
Cerium (milligrams per kilogram)	57	55	96	47.4	21.8	6-104
Chromium (milligrams per kilogram)	57	57	100	71.2	49.6	8-363
Cobalt (milligrams per kilogram)	57	57	100	11.1	3.7	4-26
Copper (milligrams per kilogram)	57	57	100	150.5	373.7	9-2,780
Europium (milligrams per kilogram)	57	1	2	nc	nc	<2-3
Gallium (milligrams per kilogram)	57	54	95	13.9	4.3	5-23
Gold (milligrams per kilogram)	57	0	0	nc	nc	<8
Holmium (milligrams per kilogram)	57	0	0	nc	nc	<4
Iron (weight percent)	57	57	100	3.3	2.1	0.56-14.5
Lanthanum (milligrams per kilogram)	57	57	100	25.7	9.3	6.5-52
Lead (milligrams per kilogram)	57	57	100	395.	494.2	13-1,910
Lithium (milligrams per kilogram)	57	57	100	31.3	14.3	5-67
Magnesium (weight percent)	57	57	100	2.5	2.2	0.504-11.3
Manganese (milligrams per kilogram)	57	57	100	583.4	511.	158-3,670
Mercury (milligrams per kilogram)	57	56	98	.6	1.9	<0.02-13.1
Molybdenum (milligrams per kilogram)	57	52	91	5.7	3.7	<2-17
Neodymium (milligrams per kilogram)	57	51	89	24.8	7.7	<9-49
Nickel (milligrams per kilogram)	57	57	100	36.4	23.5	5-154
Niobium (milligrams per kilogram)	57	56	98	9.7	3.3	<4-23
Phosphorus (weight percent)	57	57	100	.1	.1	0.01-.28
Potassium (weight percent)	57	57	100	1.8	.6	0.33-2.86
Scandium (milligrams per kilogram)	57	55	96	8.6	3.3	3-18
Selenium (milligrams per kilogram)	57	55	96	1.	.6	<0.2-3.1
Silver (milligrams per kilogram)	57	0	0	nc	nc	<2
Sodium (weight percent)	57	57	100	0.5	0.2	0.0825-8.05
Strontium (milligrams per kilogram)	57	57	100	113.6	31.5	66-299
Sulfur (weight percent)	57	57	100	.1	.1	0.05-0.63
Tantalum (milligrams per kilogram)	57	0	0	nc	nc	<40
Thorium (milligrams per kilogram)	57	44	77	9.	1.7	6-13
Tin (milligrams per kilogram)	57	4	7	nc	nc	<50-248
Titanium (weight percent)	57	57	100	.2	.1	0.045-3.83
Uranium (milligrams per kilogram)	57	0	0	nc	nc	<100
Vanadium (milligrams per kilogram)	57	57	100	76.5	26.9	24-145
Ytterbium (milligrams per kilogram)	57	48	84	nc	nc	<1-3
Yttrium (milligrams per kilogram)	57	57	100	15.8	5.2	6-38
Zinc (milligrams per kilogram)	57	57	100	396.6	410.8	79-1,690
Carbonate carbon (weight percent)	57	57	100	1.9	2.3	0.04-11.15
Organic carbon (weight percent)	57	57	100	5.7	3.9	0.22-22.31

Table 20. Comparison of arithmetic mean concentrations of select inorganic constituents in ambient surface soils, Chicago, Illinois with mean concentrations from surrounding agricultural soils

[Bold denotes analytes concentrated by a factor of two or more; mg/Kg, milligrams per kilogram]

Constituent	Arithmetic mean concentration in 57 Chicago soil samples	Arithmetic mean concentration in 106 soil samples collected within 500 kilometers of Chicago	Concentration factor in Chicago soils relative to soils within 500 kilometers of Chicago
Aluminum (weight percent)	4.8	4.86	0.99
Arsenic (mg/Kg)	**19.5**	**6.56**	**2.97**
Barium (mg/Kg)	427.3	499.3	.86
Beryllium (mg/Kg)	2.2	1.2	1.83
Calcium (weight percent)	**4.06**	**.82**	**4.95**
Total Carbon (weight percent)	**7.61**	**2.55**	**2.98**
Chromium (mg/Kg)	71.2	44.1	1.61
Cobalt (mg/Kg)	11.	8.51	1.29
Copper (mg/Kg)	**150.5**	**18.4**	**8.18**
Gallium (mg/Kg)	13.9	12.8	1.09
Iron (weight percent)	3.3	1.85	1.78
Lanthanum (mg/Kg)	25.7	36.2	.71
Lead (mg/Kg)	**395.3**	**19.4**	**20.38**
Lithium (mg/Kg)	31.3	19.74	1.59
Magnesium (weight percent)	**2.47**	**.4**	**6.18**
Manganese (mg/Kg)	583.4	460.4	1.27
Mercury (mg/Kg)	**.64**	**.14**	**4.57**
Molybdenum (mg/Kg)	**5.74**	**2.46**	**2.33**
Nickel (mg/Kg)	**36.44**	**15.95**	**2.28**
Phosphorus (weight percent)	**.086**	**.043**	**2.00**
Potassium (weight percent)	1.75	1.56	1.12
Scandium (mg/Kg)	8.6	8.2	1.05
Selenium (mg/Kg)	**1.**	**.46**	**2.17**
Sodium (weight percent)	.52	.73	.71
Strontium (mg/Kg)	113.6	122.1	.93
Thorium (mg/Kg)	9.	8.2	1.10
Titanium (weight percent)	.22	.27	.81
Vanadium (mg/Kg)	76.5	61.1	1.25
Yttrium (mg/Kg)	15.8	20.8	.76
Zinc (mg/Kg)	**396.68**	**53.57**	**7.40**

Table 21. Pearson product-moment correlation coefficients for selected inorganic constituents in ambient surface soils, Chicago, Illinois

[Positive coefficients greater than 0.70 in bold]

	ALUMINUM	ARSENIC	BARIUM	CALCIUM	CARBONATE CARBON	ORGANIC CARBON	CERIUM	CHROMIUM	COBALT	COPPER	GALLIUM	IRON	LANTHANUM	LEAD	LITHIUM	MAGNESIUM
ALUMINUM	1.00															
ARSENIC	-.13	1.00														
BARIUM	**.71**	.13	1.00													
CALCIUM	-.73	.07	-.71	1.00												
CARBONATE CARBON	-.75	.07	-.73	**.99**	1.00											
ORGANIC CARBON	.02	.19	.13	-.17	-.26	1.00										
CERIUM	**.94**	-.17	.69	-.62	-.62	-.14	1.00									
CHROMIUM	.25	.16	.33	-.15	-.24	.29	.27	1.00								
COBALT	**.75**	.14	.66	-.44	-.50	.39	**.72**	.34	1.00							
COPPER	-.07	.17	.12	.08	.05	.21	-.05	.13	.11	1.00						
GALLIUM	**.92**	-.07	**.72**	-.62	-.65	.08	**.89**	.30	**.79**	.02	1.00					
IRON	.29	.22	.39	-.28	-.35	.68	.20	.57	.62	.21	.37	1.00				
LANTHANUM	**.96**	-.14	**.71**	-.64	-.65	-.05	**.98**	.30	**.76**	-.08	**.90**	.25	1.00			
LEAD	-.22	.46	.33	.12	.07	.42	-.19	.29	.25	.51	-.01	.48	-.18	1.00		
LITHIUM	**.93**	-.13	.62	-.52	-.55	.03	**.91**	.30	**.80**	-.03	**.91**	.30	**.92**	-.13	1.00	
MAGNESIUM	-.70	.05	-.71	**.98**	**1.00**	-.28	-.57	-.23	-.47	.07	-.59	-.35	-.60	.06	-.49	1.00
MANGANESE	.17	-.04	.18	-.11	-.19	.21	.21	**.93**	.20	.05	.17	.53	.23	.11	.18	-.19
MERCURY	.00	.13	.14	.14	.14	.03	.02	.10	.20	.10	.06	.06	.05	.29	.10	.14
MOLYBDENUM	.21	.31	.34	-.11	-.22	.66	.10	**.75**	.57	.34	.26	**.79**	.19	.51	.27	-.22
NICKEL	.27	.18	.44	-.12	-.19	.39	.28	.47	.53	**.78**	.39	.55	.29	.61	.37	-.16
PHOSPHOROUS	.41	.08	.55	-.30	-.35	.30	.51	.47	.61	.26	.57	.53	.50	.44	.49	-.32
POTASSIUM	**.88**	-.22	.55	-.68	-.67	-.27	**.83**	.11	.47	-.13	**.80**	.01	**.80**	-.39	**.81**	-.61
SCANDIUM	**.96**	-.08	.67	-.61	-.64	.15	**.91**	.29	**.86**	-.01	**.91**	.39	**.94**	-.10	**.95**	-.59
SELENIUM	.29	.24	.48	-.26	-.31	.57	.32	.41	.66	.24	.48	.65	.32	.60	.36	-.30
SODIUM	.49	-.02	.58	-.74	-.74	-.04	.45	.04	.21	-.06	.44	.14	.44	-.09	.25	-.73
SULFUR	-.06	.22	.11	-.04	-.13	**.90**	-.25	.26	.36	.17	-.03	.68	-.15	.46	-.06	-.16
STRONTIUM	.29	.17	.46	-.21	-.29	.39	.32	.33	.58	.11	.36	.42	.36	.40	.35	-.31
THORIUM	.22	.12	.28	-.39	-.35	-.12	.17	-.17	.13	-.23	.06	-.15	.22	-.17	.14	-.38
TITANIUM	**.95**	-.10	**.71**	-.68	-.70	.14	**.89**	.30	**.78**	.00	**.87**	.40	**.94**	-.12	**.87**	-.66
VANADIUM	**.89**	-.02	.66	-.56	-.61	.27	**.83**	.55	**.86**	.01	**.85**	.60	**.88**	.01	**.88**	-.57
YTTRIUM	**.83**	.01	.66	-.48	-.54	.30	**.81**	.35	**.91**	.05	**.81**	.53	**.87**	.07	**.84**	-.50
ZINC	-.19	.46	.32	.16	.09	.52	-.18	.30	.32	.54	.00	.49	-.14	**.91**	-.08	.08

Table 21. Pearson product-moment correlation coefficients for selected inorganic constituents in ambient surface soils, Chicago, Illinois–Continued

[Positive coefficients greater than 0.70 in bold]

	MANGANESE	MERCURY	MOLYBDENUM	NICKEL	PHOSPHOROUS	POTASSIUM	SCANDIUM	SELENIUM	SODIUM	SULFUR	STRONTIUM	THORIUM	TITANIUM	VANADIUM	YTTRIUM	ZINC
ALUMINUM																
ARSENIC																
BARIUM																
CALCIUM																
CARBONATE CARBON																
ORGANIC CARBON																
CERIUM																
CHROMIUM																
COBALT																
COPPER																
GALLIUM																
IRON																
LANTHANUM																
LEAD																
LITHIUM																
MAGNESIUM																
MANGANESE	1.00															
MERCURY	-.03	1.00														
MOLYBDENUM	.62	.12	1.00													
NICKEL	.31	.16	.65	1.00												
PHOSPHOROUS	.37	.28	.42	.60	1.00											
POTASSIUM	.07	-.06	-.06	.07	.20	1.00										
SCANDIUM	.17	.08	.34	.39	.49	**.78**	1.00									
SELENIUM	.28	.20	.57	.56	.70	.02	.40	1.00								
SODIUM	.08	-.15	-.09	-.03	.22	.49	.32	.12	1.00							
SULFUR	.17	.04	**.74**	.33	.13	-.34	.08	.46	-.14	1.00						
STRONTIUM	.22	.23	.48	.43	.59	-.02	.41	.56	.22	.35	1.00					
THORIUM	-.20	.05	-.10	-.14	-.10	.19	.16	-.09	.24	-.12	.19	1.00				
TITANIUM	.20	.01	.30	.36	.43	**.74**	**.94**	.33	.42	.06	.33	.15	1.00			
VANADIUM	.45	.08	.55	.47	.56	.64	**.93**	.49	.26	.22	.43	.10	**.90**	1.00		
YTTRIUM	.24	.16	.47	.47	.60	.51	**.92**	.52	.27	.24	.61	.14	**.89**	**.92**	1.00	
ZINC	.11	.37	.59	.68	.43	-.41	-.04	.57	-.15	.56	.50	-.11	-.06	.07	.16	1.00

Appendix 1. Polynuclear aromatic hydrocarbons in ambient surface soils, Chicago, Illinois.

Appendix 1. Polynuclear aromatic hydrocarbons in ambient surface soils, Chicago, Illinois

[µg/Kg, micrograms per kilogram; 15 U, constituent not detected and detection limit; J, estimated; D, duplicate sample]

Sample Number	Constituent							
	Naphthalene (µg/Kg)	Acenaph-thylene (µg/Kg)	Acenaph-thene (µg/Kg)	Fluorene (µg/Kg)	Phenanthrene (µg/Kg)	Anthracene (µg/Kg)	Fluoranthene (µg/Kg)	Pyrene (µg/Kg)
PAH-SS-01	15 UJ	9 UJ	44	49	700	150	1,700	830 J
PAH-SS-02	14 U	6 UJ	9	11	200	38	580	240 J
PAH-SS-03	15 U	7 J	93	77	1,000	220	2,100	1,300 J
PAH-SS-04	14 U	14 J	57	53	900	140	2,000	1,700 J
PAH-SS-05	13 U	6 J	37	36	690	97	1,600	1,200 J
PAH-SS-06	160	340	370	400	8,100	1,000	20,000	12,000
PAH-SS-07	14 U	7 U	7 UJ	8 UJ	83	14 J	130	100 J
PAH-SS-08	15 U	7 U	14 J	10 J	190	37	480	290 J
PAH-SS-09	15 J	23	450	680	5,900	1,300	7,800	4,400 J
PAH-SS-10	14 U	7 U	6 U	7 U	27	7 U	52	88 J
PAH-SS-11	14 U	6 U	5 U	7 U	33	8 J	81	98 J
PAH-SS-12	14 U	6 U	8 J	11 J	130	28	230	150 J
PAH-SS-13	30	62	320	260	4,600	890	8,400	4,100
PAH-SS-14	41	440	110	330	5,800	680	12,000	6,200 J
PAH-SS-15	16 U	7 U	8 J	8 J	130	25	340	220 J
PAH-SS-16	14 U	6 U	5 U	7 U	56	11 J	160	100
PAH-SS-17	290	970	520	990	11,000	3,200	26,000	13,000
PAH-SS-17D	240	1,100	74	460	5,600	1,900	19,000	9,200
PAH-SS-18	15 U	77	640	420	5,700	980	11,000	5,800
PAH-SS-19	13 U	6 U	5 U	6 U	84	14 J	220	110
PAH-SS-20	13 UJ	7 J	7 J	7 J	130	22	300	250
PAH-SS-21	19 J	21	8 J	12 J	210	39	460	430
PAH-SS-21D	19 J	26	10 J	16 J	250	53	530	430
PAH-SS-22	350 J	480	1,500	2,000	19,000	4,600	35,000	30,000
PAH-SS-23	15 J	28	39	46	820	150	2,000	1,600
PAH-SS-24	58 J	390	98	310	3,700	540	7,200	5,500
PAH-SS-25	14 UJ	10 J	12 J	12 J	220	39	570	490
PAH-SS-25D	14 UJ	11 J	17 J	18 J	280	48	650	560
PAH-SS-26	17 J	16 J	41	43	670	120	1,300	1,000
PAH-SS-27	90 J	130	220	210	3,500	620	8,400	7,000
PAH-SS-28	40 J	51	140	130	2,000	380	4,300	3,800
PAH-SS-29	78 J	35	380	390	4,000	620	5,300	4,500
PAH-SS-30	65 J	37	190	170	1,800	400	3,600	2,900
PAH-SS-31	290 J	74	330	340	4,500	1,000	6,000	5,000
PAH-SS-32	610 J	100	1,100	1,400	12,000	2,500	17,000	12,000
PAH-SS-33	36 J	39	150	170	1,900	390	3,200	2,700

Appendix 1. Polynuclear aromatic hydrocarbons in ambient surface soils, Chicago, Illinois—Continued

[µg/Kg, micrograms per kilogram; 15 U, constituent not detected and detection limit; J, estimated; D, duplicate sample]

Sample Number	Constituent							
	Benzo(a)-anthracene (µg/Kg)	Chrysene (µg/Kg)	Benzo(b)-fluoranthene (µg/Kg)	Benzo(k)-fluoranthene (µg/Kg)	Benzo(a)-pyrene (µg/Kg)	Dibenzo-(a,h)anthra-cene (µg/Kg)	Benzo-(g,h,i)-perylene (µg/Kg)	Indeno-(1,2,3-cd)-pyrene (µg/Kg)
PAH-SS-01	600	720	1,000	450	760	190	410	470
PAH-SS-02	200	250	340	220	260	93	200	210
PAH-SS-03	720	800	920	650	850	140	430	500
PAH-SS-04	740	910	1,100	900	1,000	150	490	610
PAH-SS-05	510	650	760	530	680	110	360	430
PAH-SS-06	9,100	11,000	14,000	9,000	12,000	770	6,900	8,100
PAH-SS-07	47	54	100	53	81	68	120	110
PAH-SS-08	180	220	260	220	250	96	170	200
PAH-SS-09	2,700	2,900	3,000	2,200	3,000	290	1,000	1,300
PAH-SS-10	26	31	40	36	39	62	110	98
PAH-SS-11	43	61	63	59	66	62	100	110
PAH-SS-12	110	120	150	95	130	68	130	140
PAH-SS-13	3,400	3,500	4,000	1,900	3,700	640	1,300	1,500
PAH-SS-14	5,100	5,800	7,200	4,400	6,200	510	2,000	4,300
PAH-SS-15	160	180	240	140	200	82	160	170
PAH-SS-16	59	79	97	58	81	69	120	130
PAH-SS-17	10,000	9,300	13,000	7,100	11,000	870	7,100	8,100
PAH-SS-17D	8,400	8,200	9,400	8,600	9,700	780	5,500	6,100
PAH-SS-18	4,900	5,500	6,800	3,600	5,600	520	3,700	4,100
PAH-SS-19	77	99	99	70	95	70	130	140
PAH-SS-20	140	160	190	100	160	28	120	130
PAH-SS-21	210	230	300	170	250	44	180	210
PAH-SS-21D	230	260	330	190	280	52	200	240
PAH-SS-22	16,000	15,000	18,000	10,000	17,000	1,600	8,100	9,900
PAH-SS-23	880	980	970	1,000	1,000	110	490	620
PAH-SS-24	2,500	2,600	3,700	2,000	3,000	290	1,500	1,800
PAH-SS-25	240	280	340	210	280	59	210	250
PAH-SS-25D	280	330	380	270	340	70	230	280
PAH-SS-26	550	540	530	340	570	71	280	370
PAH-SS-27	3,800	4,200	5,700	2,900	4,200	760	3,200	3,800
PAH-SS-28	2,000	1,900	2,600	1,300	2,100	280	920	1,100
PAH-SS-29	1,700	1,700	1,900	1,300	1,800	200	730	920
PAH-SS-30	1,700	1,600	1,600	1,500	1,600	280	640	830
PAH-SS-31	2,400	2,500	3,000	1,700	2,400	370	930	1,200
PAH-SS-32	6,400	6,600	6,000	6,300	6,600	940	3,600	4,600
PAH-SS-33	1,300	1,300	1,300	1,400	1,400	220	570	700

Appendix 1. Polynuclear aromatic hydrocarbons in ambient surface soils, Chicago, Illinois—Continued

[µg/Kg, micrograms per kilogram; 15 U, constituent not detected and detection limit; J, estimated; D, duplicate sample]

	Constituent							
Sample Number	Naphthalene (µg/Kg)	Acenaph-thylene (µg/Kg)	Acenaph-thene (µg/Kg)	Fluorene (µg/Kg)	Phenanthrene (µg/Kg)	Anthracene (µg/Kg)	Fluoranthene (µg/Kg)	Pyrene (µg/Kg)
PAH-SS-33D	50 J	48	130	150	1,700	340	3,000	2,500
PAH-SS-34	50 J	17 J	190	180	2,100	380	3,900	3,100
PAH-SS-35	700 J	300	1,200	1,500	16,000	3,000	20,000	17,000
PAH-SS-36	190 J	250	510	630	8,200	1,400	16,000	12,000
PAH-SS-37	68	54	210	210	2,200	470	4,700	2,000
PAH-SS-38	24 UJ	24 UJ	33	40	430	84	990	500
PAH-CE-1	21 UJ	21 UJ	17 J	18 J	330	48	880	610
PAH-CE-2	18 U	18 U	18 U	18 U	22	18 UJ	74	51
PAH-CE-3	110	8 J	46	52	620	120	1,100	840
PAH-CE-4	20	13 J	170	170	2,100	300	3,500	2,600
PAH-CE-4D	14 J	9 J	100	110	1,400	200	3,100	1,800
PAH-CE-5	97	72	140	180	2,100	510	6,000	5,200
PAH-CE-6	50	17 J	84	91	1,200	190	1,800	1,800
PAH-CE-7	410	50	260	320	3,900	680	7,100	5,900
PAH-CE-8	20	7 J	110	120	1,200	290	2,300	1,500
PAH-CE-9	21 U	21 U	21 U	21 U	30	21 U	64	60
PAH-CE-10	21 UJ	7 J	9 J	9 J	160	29	410	350
PAH-CE-11	18 UJ	18 U	9 J	9 J	180	28	460	430
PAH-CE-12	14 J	13 J	36	31	240	49	650	350
PAH-CE-13	51	69	85	110	1,500	260	5,700	2,800
PAH-CE-14	110	55	110	130	1,700	260	3,400,	2,100
PAH-CE-15	180 J	17 J	920 J	950 J	5,100	980 J	6,200	3,400
PAH-CE-15D	38	11 J	250	220	1,500	280	2,700	1,200
PAH-CE-16	84	14 J	9 J	13 J	270	41	450	330
PAH-CE-17	98	20	17 J	17 J	410	53	730	520
PAH-CE-18	86	40	310	290	3,600	770	8,600	6,000
PAH-CE-19	2,500	1,000	43,000	36,000	520,000	120,000	1,100,000	720,000 J

Appendix 1. Polynuclear aromatic hydrocarbons in ambient surface soils, Chicago, Illinois—Continued

[µg/Kg, micrograms per kilogram; 15 U, constituent not detected and detection limit; J, estimated; D, duplicate sample]

Sample Number	Constituent							
	Benzo(a)-anthracene (µg/Kg)	Chrysene (µg/Kg)	Benzo(b)-fluoranthene (µg/Kg)	Benzo(k)-fluoranthene (µg/Kg)	Benzo(a)-pyrene (µg/Kg)	Dibenzo-(a,h)anthra-cene (µg/Kg)	Benzo-(g,h,i)-perylene (µg/Kg)	Indeno-(1,2,3-cd)-pyrene (µg/Kg)
PAH-SS-33D	1,300	1,300	1,700	950	1,400	220	540	700
PAH-SS-34	1,500	1,600	2,100	720	1,600	220	920	1,200
PAH-SS-35	8,100	7,800	9,000	4,000	7,500	1,100	4,100	5,000
PAH-SS-36	6,100	6,400	8,500	3,900	6,600	1,100	4,000	5,200
PAH-SS-37	1,800 J	1,500	2,600	1,300	1,700	130	570	870 J
PAH-SS-38	300 J	310	440 J	490	490	140	220	360 J
PAH-CE-1	320	380	480	330	410	38	200	270
PAH-CE-2	30	35	50	36	41	8 J	24	33
PAH-CE-3	430	430	550	410	480	48	200	260
PAH-CE-4	1,400	1,400	1,800	1,400	1,600	120	560	790
PAH-CE-4D	1,000	1,000	1,300	950 J	1,200	130 J	560	770
PAH-CE-5	3,200	2,900	3,400	2,900	3,600	260 J	1,200	1,500
PAH-CE-6	880	850	1,200	820	950	120	580	700
PAH-CE-7	3,300	3,200	4,200	2,700	3,200	340 J	1,200	1,600
PAH-CE-8	830	730	830	620	780	78	290	410
PAH-CE-9	28	36	50	44	45	10 J	24	31
PAH-CE-10	210	200	320	200	250	27	99	130
PAH-CE-11	210	220	350	230	270	27	110	160
PAH-CE-12	210 J	200	370 J	290	290	85	130	220 J
PAH-CE-13	1,800 J	1,800	3,900	2,900	3,500	200	820 J	1,200
PAH-CE-14	1,300 J	1,300	2,100	1,800	1,600	200	390	580 J
PAH-CE-15	1,600 J	1,800 J	2,600	2,100	2,100	220 J	1,300 J	1,500 J
PAH-CE-15D	810 J	790	1,500 J	960	1,200	220	560	780 J
PAH-CE-16	240 J	260	430 J	380	430	130	310	300 J
PAH-CE-17	360 J	360	540 J	580	550	160	430	470
PAH-CE-18	4,100	3,700	4,000	3,200	4,100	980	2,100	3,100
PAH-CE-19	370,000	350,000 J	550,000	280,000	460,000	41,000	290,000	370,000

Appendix 2. Inorganic constituents in ambient surface soils, Chicago, Illinois.

Appendix 2. Inorganic constituents in ambient surface soils, Chicago, Illinois

[percent, percent-weight; D, duplicate sample; <50, constituent not detected and detection limit]

	Constituent							
Sample Number	Carbon Dioxide (percent)	Carbonate Carbon (percent)	Total Carbon (percent)	Total Organic Carbon (percent)	Aluminum (percent)	Calcium (percent)	Iron (percent)	Magnesium (percent)
PAH-SS-01	0.91	0.25	6.01	5.76	5.66	1.27	2.78	0.92
PAH-SS-02	2.02	.55	4.50	3.95	5.83	1.77	2.29	1.16
PAH-SS-03	2.38	.65	5.64	4.99	6.90	1.94	3.50	1.47
PAH-SS-04	3.77	1.03	6.79	5.76	5.68	2.65	2.63	1.77
PAH-SS-05	16.30	4.45	7.77	3.32	4.33	7.95	2.57	5.25
PAH-SS-06	16.40	4.48	11.50	7.02	4.58	8.95	3.19	5.65
PAH-SS-07	1.97	.54	2.49	1.95	7.13	1.68	3.23	1.43
PAH-SS-08	1.54	.42	4.85	4.43	6.26	1.48	2.90	1.18
PAH-SS-09	1.88	.51	5.99	5.48	5.89	1.70	2.97	1.23
PAH-SS-10	.14	.04	2.21	2.17	6.04	.62	2.99	.59
PAH-SS-11	2.76	0.75	4.88	4.13	5.54	2.34	2.83	1.39
PAH-SS-12	.35	.10	2.39	2.29	6.12	.86	2.88	.74
PAH-SS-13	3.15	.86	5.13	4.27	6.74	2.64	3.63	1.71
PAH-SS-14	3.38	.92	6.95	6.03	6.52	2.77	3.94	1.68
PAH-SS-15	3.49	.95	3.50	2.55	6.39	2.66	3.30	1.67
PAH-SS-16	1.46	0.40	3.32	2.92	6.48	1.67	3.21	1.04
PAH-SS-17	4.40	1.20	8.26	7.06	5.42	4.15	5.27	1.82
PAH-SS-17D	4.54	1.24	7.94	6.70	5.32	4.58	5.61	1.82
PAH-SS-18	3.85	1.05	16.00	14.95	3.78	3.43	14.50	1.52
PAH-SS-19	1.33	.36	2.62	2.26	6.49	1.32	3.05	1.16
PAH-SS-20	4.23	1.15	9.30	8.15	4.58	3.30	3.83	1.76
PAH-SS-21	.76	.21	3.21	3.00	6.71	1.15	3.00	.94
PAH-SS-21D	.80	.22	3.16	2.94	6.78	1.18	3.02	.98
PAH-SS-22	15.10	4.12	7.93	3.81	4.82	8.55	2.76	4.58
PAH-SS-23	1.83	.50	5.91	5.41	5.86	1.80	3.07	1.09
PAH-SS-24	0.61	0.17	5.69	5.52	6.26	1.15	3.19	0.94
PAH-SS-25	.90	.25	3.55	3.30	5.78	1.15	2.63	.86
PAH-SS-25D	.94	.26	3.56	3.30	5.83	1.23	2.70	.95
PAH-SS-26	6.97	1.90	7.98	6.08	4.92	4.42	2.75	2.53
PAH-SS-27	9.55	2.61	10.50	7.89	4.73	5.45	4.18	3.46
PAH-SS-28	2.18	0.59	6.07	5.48	7.00	1.89	3.98	1.67
PAH-SS-29	26.90	7.34	9.77	2.43	3.09	12.90	2.24	8.06
PAH-SS-30	1.97	.54	4.73	4.19	6.44	1.79	4.28	1.22
PAH-SS-31	3.07	.84	10.90	10.06	4.56	2.41	5.75	1.39
PAH-SS-32	5.49	1.50	8.99	7.49	5.89	3.96	3.67	2.09

Appendix 2. Inorganic constituents in ambient surface soils, Chicago, Illinois—Continued

[percent, percent-weight; D, duplicate sample; <50, constituent not detected and detection limit]

	Constituent							
Sample Number	Carbon Dioxide (percent)	Carbonate Carbon (percent)	Total Carbon (percent)	Total Organic Carbon (percent)	Aluminum (percent)	Calcium (percent)	Iron (percent)	Magnesium (percent)
PAH-SS-33	4.25	1.16	8.38	7.22	5.97	3.10	3.36	1.95
PAH-SS-33D	4.30	1.17	8.34	7.17	5.86	3.18	3.31	1.94
PAH-SS-34	6.89	1.88	5.53	3.65	5.44	3.85	2.79	2.82
PAH-SS-35	5.68	1.55	11.50	9.95	7.46	4.55	5.51	1.94
PAH-SS-36	6.97	1.90	11.80	9.90	4.30	4.53	4.32	2.59
PAH-SS-37	7.35	2.01	6.94	4.93	2.60	3.89	2.15	2.16
PAH-SS-38	.65	.18	7.35	7.17	5.26	1.23	2.44	.81
PAH-CE-01	16.00	4.37	13.40	9.03	2.33	7.38	1.23	4.60
PAH-CE-02	29.20	7.97	8.19	.22	1.21	12.30	.56	7.84
PAH-CE-03	18.40	5.02	9.11	4.09	3.44	8.10	2.38	5.44
PAH-CE-04	40.00	10.92	12.10	1.18	0.83	15.90	0.80	10.80
PAH-CE-04D	41.70	11.38	12.20	.82	.73	16.90	.73	11.80
PAH-CE-05	7.13	1.95	11.60	9.65	3.81	4.09	5.59	2.20
PAH-CE-06	9.89	2.70	6.60	3.90	1.92	5.29	2.52	3.03
PAH-CE-07	5.22	1.42	16.20	14.78	3.45	3.38	6.36	1.76
PAH-CE-08	8.46	2.31	3.46	1.15	2.91	4.68	0.91	2.44
PAH-CE-09	.28	.08	2.71	2.63	5.94	.75	2.75	.77
PAH-CE-10	1.79	.49	3.78	3.29	3.07	1.37	1.24	.68
PAH-CE-11	33.20	9.06	10.20	1.14	1.47	14.20	.78	9.42
PAH-CE-12	5.35	1.46	6.37	4.91	5.34	3.00	2.96	2.02
PAH-CE-13	1.44	0.39	22.70	22.31	5.74	3.48	9.31	0.50
PAH-CE-14	9.11	2.49	8.44	5.95	3.45	5.23	2.90	2.76
PAH-CE-15	1.50	.41	8.48	8.07	4.48	1.74	2.10	.89
PAH-CE-15D	1.38	.38	8.33	7.95	4.47	1.69	2.09	.87
PAH-CE-16	9.29	2.54	5.50	2.96	2.64	4.85	1.47	2.88
PAH-CE-17	5.25	1.43	5.99	4.56	3.04	3.85	2.69	1.68
PAH-CE-18	4.02	1.10	5.59	4.49	3.70	2.74	2.52	1.40
PAH-CE-19	11.20	3.06	18.70	15.64	1.75	6.04	1.45	3.31

Appendix 2. Inorganic constituents in ambient surface soils, Chicago, Illinois—Continued

[percent, percent-weight; D, duplicate sample; <50, constituent not detected and detection limit]

	Constituent							
Sample Number	Phosphorus (percent)	Potassium (percent)	Sodium (percent)	Sulfur (percent)	Titanium (percent)	Arsenic (milligrams per kilogram)	Barium (milligrams per kilogram)	Beryllium (milligrams per kilogram)
PAH-SS-01	0.080	2.04	0.56	0.08	0.273	15	445	2
PAH-SS-02	.090	1.84	.74	.05	.273	<10	449	1
PAH-SS-03	.070	2.45	.47	.09	.278	16	453	2
PAH-SS-04	.175	2.19	.49	.10	.247	10	403	2
PAH-SS-05	.070	1.71	.56	.06	.210	12	278	1
PAH-SS-06	0.090	1.62	0.67	0.12	0.221	12	403	2
PAH-SS-07	.055	2.63	.59	.05	.305	11	475	2
PAH-SS-08	.085	2.31	.76	.06	.284	<10	481	2
PAH-SS-09	.110	2.24	.70	.08	.252	11	463	2
PAH-SS-10	.065	1.98	.81	<0.05	.305	13	540	1
PAH-SS-11	0.095	1.84	0.61	0.05	0.268	11	499	1
PAH-SS-12	.065	1.88	.69	<0.05	.310	10	543	1
PAH-SS-13	.210	2.60	.51	.09	.257	20	572	2
PAH-SS-14	.100	2.28	.54	.13	.268	12	666	3
PAH-SS-15	.055	2.34	.52	.05	.289	17	442	2
PAH-SS-16	.070	2.43	0.53	0.05	0.326	15	485	2
PAH-SS-17	.120	1.91	.45	.16	.252	<10	426	2
PAH-SS-17D	.130	1.87	.44	.14	.247	<10	436	2
PAH-SS-18	.240	.94	.64	.30	.200	25	477	3
PAH-SS-19	.060	2.45	.58	<0.05	.305	13	505	2
PAH-SS-20	0.140	1.55	0.70	0.14	0.210	19	397	2
PAH-SS-21	.065	2.51	.60	<0.05	.305	<10	473	2
PAH-SS-21D	.065	2.53	.60	.05	.294	14	483	2
PAH-SS-22	.055	1.93	.42	.11	.221	11	450	2
PAH-SS-23	.125	1.94	.58	.09	.289	17	588	2
PAH-SS-24	0.090	2.25	0.66	0.08	0.294	15	498	2
PAH-SS-25	.080	2.16	.62	.05	.305	10	494	1
PAH-SS-25D	.085	2.20	.63	.05	.294	15	536	2
PAH-SS-26	.075	1.91	.53	.17	.226	13	394	1
PAH-SS-27	.150	1.72	.46	.13	.242	13	451	2
PAH-SS-28	.095	2.86	0.46	0.10	0.268	21	460	3
PAH-SS-29	.050	1.24	.29	.11	.158	11	284	1
PAH-SS-30	.100	2.34	.63	.07	.284	16	494	2
PAH-SS-31	.120	1.53	.54	.25	.221	27	414	2
PAH-SS-32	.125	2.16	.41	.14	.257	18	519	3

Appendix 2. Inorganic constituents in ambient surface soils, Chicago, Illinois—Continued

[percent, percent-weight; D, duplicate sample; <50, constituent not detected and detection limit]

	Constituent							
Sample Number	Phosphorus (percent)	Potassium (percent)	Sodium (percent)	Sulfur (percent)	Titanium (percent)	Arsenic (milligrams per kilogram)	Barium (milligrams per kilogram)	Beryllium (milligrams per kilogram)
PAH-SS-33	0.095	2.09	0.50	0.14	0.268	13	431	2
PAH-SS-33D	.090	2.06	.51	.13	.273	12	428	2
PAH-SS-34	.075	2.25	.53	.07	.226	<10	394	2
PAH-SS-35	.280	1.32	.49	.20	.383	32	697	9
PAH-SS-36	.140	1.30	.49	.17	.236	28	541	2
PAH-SS-37	0.095	1.10	0.48	0.11	0.145	<10	390	<1
PAH-SS-38	.100	1.84	.49	.07	.245	14	437	1
PAH-CE-01	.080	1.12	.38	.12	.090	31	227	<1
PAH-CE-02	.010	.82	.20	<0.05	.045	<10	106	<1
PAH-CE-03	.090	1.51	.35	.10	.155	51	412	1
PAH-CE-04	0.020	0.35	0.10	<0.05	0.050	35	110	<1
PAH-CE-04D	.015	.31	.07	.05	.040	31	91	<1
PAH-CE-05	.080	1.18	.60	.24	.180	220	521	4
PAH-CE-06	.075	.85	.35	.09	.125	35	506	1
PAH-CE-07	.050	.98	.56	.52	.180	20	693	3
PAH-CE-08	0.025	1.62	0.78	<0.05	0.075	11	349	<1
PAH-CE-09	.045	2.34	.50	<0.05	.275	13	468	1
PAH-CE-10	.070	1.45	.65	.05	.105	13	378	<1
PAH-CE-11	.020	.88	.13	<0.05	.075	<10	113	<1
PAH-CE-12	.070	2.35	.46	.09	.230	14	366	2
PAH-CE-13	0.020	1.08	0.25	0.63	0.345	<10	257	14
PAH-CE-14	.045	1.45	.44	.19	.140	16	362	2
PAH-CE-15	.065	1.62	.52	.16	.175	11	413	1
PAH-CE-15D	.060	1.63	.53	.14	.180	13	408	1
PAH-CE-16	.020	1.32	.67	.10	.085	11	295	1
PAH-CE-17	0.040	1.22	0.71	0.11	0.120	<10	371	2
PAH-CE-18	.075	1.51	.57	.08	.150	15	407	2
PAH-CE-19	.030	.75	.42	.20	.090	<10	169	<1

Appendix 2. Inorganic constituents in ambient surface soils, Chicago, Illinois—Continued

[percent, percent-weight; D, duplicate sample; <50, constituent not detected and detection limit]

	Constituent							
Sample Number	Bismuth (milligrams per kilogram)	Cadmium (milligrams per kilogram)	Cesium (milligrams per kilogram)	Chromium (milligrams per kilogram)	Cobalt (milligrams per kilogram)	Copper (milligrams per kilogram)	Europium (milligrams per kilogram)	Gallium (milligrams per kilogram)
PAH-SS-01	<50	<2	63	65	11	43	<2	14
PAH-SS-02	<50	<2	61	53	10	37	<2	15
PAH-SS-03	<50	<2	63	75	13	57	<2	18
PAH-SS-04	<50	3	54	66	11	69	<2	17
PAH-SS-05	<50	<2	41	44	9	51	<2	16
PAH-SS-06	<50	6	44	78	12	343	<2	17
PAH-SS-07	<50	<2	72	70	14	39	<2	19
PAH-SS-08	<50	<2	62	64	12	35	<2	16
PAH-SS-09	<50	<2	61	64	11	43	<2	16
PAH-SS-10	<50	<2	64	54	11	28	<2	13
PAH-SS-11	<50	<2	61	56	9	36	<2	16
PAH-SS-12	<50	<2	71	68	11	38	<2	15
PAH-SS-13	<50	<2	69	78	14	66	<2	20
PAH-SS-14	<50	<2	67	102	13	73	<2	17
PAH-SS-15	<50	<2	68	63	14	42	<2	16
PAH-SS-16	<50	<2	75	66	15	36	<2	15
PAH-SS-17	<50	<2	55	340	11	75	<2	16
PAH-SS-17D	<50	<2	60	387	11	76	<2	13
PAH-SS-18	<50	7	38	192	16	395	<2	14
PAH-SS-19	<50	<2	69	61	12	42	<2	16
PAH-SS-20	<50	<2	43	66	11	67	<2	13
PAH-SS-21	<50	<2	70	76	11	44	<2	18
PAH-SS-21D	<50	<2	73	72	12	47	<2	17
PAH-SS-22	<50	<2	46	57	13	89	<2	15
PAH-SS-23	<50	<2	63	69	12	74	<2	16
PAH-SS-24	<50	<2	64	73	13	57	<2	17
PAH-SS-25	<50	<2	58	59	10	35	<2	16
PAH-SS-25D	<50	<2	63	61	10	37	<2	14
PAH-SS-26	<50	<2	51	64	11	48	<2	10
PAH-SS-27	<50	5	48	94	12	2,780	<2	14
PAH-SS-28	<50	2	70	78	16	117	<2	23
PAH-SS-29	<50	3	33	50	9	208	<2	8
PAH-SS-30	<50	<2	66	76	14	99	<2	18
PAH-SS-31	<50	<2	44	82	13	214	<2	17
PAH-SS-32	<50	<2	60	79	14	134	<2	18

Appendix 2. Inorganic constituents in ambient surface soils, Chicago, Illinois—Continued

[percent, percent-weight; D, duplicate sample; <50, constituent not detected and detection limit]

Sample Number	Constituent							
	Bismuth (milligrams per kilogram)	Cadmium (milligrams per kilogram)	Cesium (milligrams per kilogram)	Chromium (milligrams per kilogram)	Cobalt (milligrams per kilogram)	Copper (milligrams per kilogram)	Europium (milligrams per kilogram)	Gallium (milligrams per kilogram)
PAH-SS-33	<50	<2	60	77	12	84	<2	17
PAH-SS-33D	<50	<2	59	81	14	83	<2	18
PAH-SS-34	<50	<2	54	61	11	46	<2	16
PAH-SS-35	<50	3	104	129	26	234	3	23
PAH-SS-36	<50	7	45	118	12	355	<2	17
PAH-SS-37	<50	3	15	67	7	73	<2	7
PAH-SS-38	57	<2	52	45	12	35	<2	13
PAH-CE-01	<50	3	19	29	8	47	<2	6
PAH-CE-02	<50	<2	<5	8	5	9	<2	<4
PAH-CE-03	<50	4	23	90	10	66	<2	10
PAH-CE-04	<50	3	<5	20	5	98	<2	<4
PAH-CE-04D	<50	2	<5	17	4	77	<2	<4
PAH-CE-05	<50	7	23	131	14	475	<2	11
PAH-CE-06	<50	6	8	87	5	419	<2	6
PAH-CE-07	<50	7	16	88	14	484	<2	11
PAH-CE-08	<50	<2	11	19	5	12	<2	7
PAH-CE-09	<50	<2	60	55	13	25	<2	17
PAH-CE-10	<50	<2	18	31	4	24	<2	8
PAH-CE-11	<50	<2	13	23	5	24	<2	<4
PAH-CE-12	<50	<2	47	54	13	78	<2	15
PAH-CE-13	<50	5	13	82	16	45	<2	11
PAH-CE-14	<50	<2	29	45	10	63	<2	9
PAH-CE-15	<50	<2	41	43	11	46	<2	12
PAH-CE-15D	<50	<2	38	42	9	42	<2	11
PAH-CE-16	<50	<2	16	26	6	13	<2	6
PAH-CE-17	<50	<2	25	56	6	59	<2	8
PAH-CE-18	<50	3	30	45	9	200	<2	11
PAH-CE-19	<50	3	6	26	5	59	<2	5

Appendix 2. Inorganic constituents in ambient surface soils, Chicago, Illinois—Continued

[percent, percent-weight; D, duplicate sample; <50, constituent not detected and detection limit]

Sample Number	Constituent							
	Gold (milligrams per kilogram)	Holmium (milligrams per kilogram)	Lanthanum (milligrams per kilogram)	Lead (milligrams per kilogram)	Lithium (milligrams per kilogram)	Manganese (milligrams per kilogram)	Mercury (milligrams per kilogram)	Molybdenum (milligrams per kilogram)
PAH-SS-01	<8	<4	32	93	36	561	0.11	4
PAH-SS-02	<8	<4	33	40	32	327	.09	2
PAH-SS-03	<8	<4	34	198	52	461	.86	5
PAH-SS-04	<8	<4	30	283	43	365	.31	4
PAH-SS-05	<8	<4	23	150	29	433	.17	4
PAH-SS-06	<8	<4	25	654	37	628	0.32	6
PAH-SS-07	<8	<4	35	42	52	390	.07	5
PAH-SS-08	<8	<4	33	87	40	507	.09	3
PAH-SS-09	<8	<4	31	224	38	582	.38	3
PAH-SS-10	<8	<4	34	27	28	751	.08	3
PAH-SS-11	<8	<4	33	35	30	699	0.08	3
PAH-SS-12	<8	<4	36	39	29	651	.19	2
PAH-SS-13	<8	<4	34	323	51	524	1.89	6
PAH-SS-14	<8	<4	33	504	55	821	.33	6
PAH-SS-15	<8	<4	34	47	42	694	.07	5
PAH-SS-16	<8	<4	36	65	44	795	0.08	5
PAH-SS-17	<8	<4	30	240	39	3,250	.18	15
PAH-SS-17D	<8	<4	33	246	38	4,090	.16	17
PAH-SS-18	<8	<4	21	1,690	28	2,330	.93	14
PAH-SS-19	<8	<4	35	44	43	634	.07	3
PAH-SS-20	<8	<4	24	239	25	802	0.25	4
PAH-SS-21	<8	<4	34	72	51	427	.27	3
PAH-SS-21D	<8	<4	35	70	51	420	.59	3
PAH-SS-22	<8	<4	25	303	36	541	1.91	6
PAH-SS-23	<8	<4	33	198	39	442	.28	5
PAH-SS-24	<8	<4	34	109	38	683	0.17	5
PAH-SS-25	<8	<4	31	82	33	471	.06	2
PAH-SS-25D	<8	<4	33	90	35	549	.06	3
PAH-SS-26	<8	<4	27	105	31	459	.14	6
PAH-SS-27	<8	<4	24	1,310	33	697	1.65	11
PAH-SS-28	<8	<4	35	275	49	415	0.39	7
PAH-SS-29	<8	<4	18	473	25	512	.70	5
PAH-SS-30	<8	<4	34	355	42	544	.25	6
PAH-SS-31	<8	<4	24	469	26	631	.31	7
PAH-SS-32	<8	<4	29	528	42	495	.21	7

Appendix 2. Inorganic constituents in ambient surface soils, Chicago, Illinois—Continued

[percent, percent-weight; D, duplicate sample; <50, constituent not detected and detection limit]

Sample Number	Constituent							
	Gold (milligrams per kilogram)	Holmium (milligrams per kilogram)	Lanthanum (milligrams per kilogram)	Lead (milligrams per kilogram)	Lithium (milligrams per kilogram)	Manganese (milligrams per kilogram)	Mercury (milligrams per kilogram)	Molybdenum (milligrams per kilogram)
PAH-SS-33	<8	<4	31	281	46	411	0.44	6
PAH-SS-33D	<8	<4	31	283	45	405	.43	6
PAH-SS-34	<8	<4	28	175	36	533	.12	4
PAH-SS-35	<8	<4	52	1,270	67	710	5.13	12
PAH-SS-36	<8	<4	24	1,910	28	642	.75	6
PAH-SS-37	<8	<4	13	1,000	12	390	0.25	4
PAH-SS-38	<8	<4	28	85	32	484	.08	3
PAH-CE-01	<8	<4	13	260	13	240	.12	2
PAH-CE-02	<8	<4	10	13	7	196	<0.02	<2
PAH-CE-03	<8	<4	18	886	24	335	13.10	5
PAH-CE-04	<8	<4	7	270	5	166	0.08	<2
PAH-CE-04D	<8	<4	6	200	5	150	.12	<2
PAH-CE-05	<8	<4	19	1,450	20	415	.38	13
PAH-CE-06	<8	<4	11	1,500	8	327	.21	6
PAH-CE-07	<8	<4	17	1,680	17	517	.41	15
PAH-CE-08	<8	<4	12	70	7	276	0.03	<2
PAH-CE-09	<8	<4	32	30	42	479	.03	3
PAH-CE-10	<8	<4	12	98	8	241	.28	<2
PAH-CE-11	<8	<4	13	66	15	236	.02	2
PAH-CE-12	<8	<4	28	167	40	368	.06	6
PAH-CE-13	<8	<4	21	49	32	579	0.03	17
PAH-CE-14	<8	<4	18	977	22	405	.11	6
PAH-CE-15	<8	<4	23	135	32	346	.10	6
PAH-CE-15D	<8	<4	22	114	32	333	.07	6
PAH-CE-16	<8	<4	11	30	8	311	.03	2
PAH-CE-17	<8	<4	17	332	14	954	0.48	4
PAH-CE-18	<8	<4	20	428	22	414	.44	3
PAH-CE-19	<8	<4	10	90	7	320	.09	<2

Appendix 2. Inorganic constituents in ambient surface soils, Chicago, Illinois—Continued

[percent, percent-weight; D, duplicate sample; <50, constituent not detected and detection limit]

Sample Number	Constituent							
	Niobium (milligrams per kilogram)	Neodymium (milligrams per kilogram)	Nickel (milligrams per kilogram)	Scandium (milligrams per kilogram)	Selenium (milligrams per kilogram)	Silver (milligrams per kilogram)	Strontium (milligrams per kilogram)	Tantalum (milligrams per kilogram)
PAH-SS-01	9	27	29	10	0.7	<2	98	<40
PAH-SS-02	7	31	27	9	.7	<2	102	<40
PAH-SS-03	7	30	41	12	1.0	<2	100	<40
PAH-SS-04	8	27	37	10	.8	<2	125	<40
PAH-SS-05	10	24	26	7	.6	<2	100	<40
PAH-SS-06	11	24	52	8	0.9	<2	123	<40
PAH-SS-07	6	29	38	13	.5	<2	98	<40
PAH-SS-08	8	30	30	11	.7	<2	99	<40
PAH-SS-09	6	32	29	10	.8	<2	107	<40
PAH-SS-10	10	32	25	9	.7	<2	98	<40
PAH-SS-11	7	28	24	9	0.7	<2	122	<40
PAH-SS-12	10	31	27	10	.6	<2	99	<40
PAH-SS-13	12	33	41	13	1.2	<2	106	<40
PAH-SS-14	13	31	45	12	1.3	<2	106	<40
PAH-SS-15	9	30	32	11	.8	<2	104	<40
PAH-SS-16	10	32	31	12	0.9	<2	94	<40
PAH-SS-17	10	25	54	10	1.2	<2	132	<40
PAH-SS-17D	13	32	57	9	1.2	<2	127	<40
PAH-SS-18	16	21	77	7	2.7	<2	143	<40
PAH-SS-19	7	29	30	11	.6	<2	91	<40
PAH-SS-20	9	23	28	8	1.5	<2	122	<40
PAH-SS-21	10	30	34	12	.8	<2	141	<40
PAH-SS-21D	7	32	33	12	.7	<2	141	<40
PAH-SS-22	11	23	34	9	.7	<2	133	<40
PAH-SS-23	7	30	34	10	.7	<2	131	<40
PAH-SS-24	11	28	34	11	1.0	<2	101	<40
PAH-SS-25	11	29	25	9	.7	<2	98	<40
PAH-SS-25D	10	30	25	10	.7	<2	99	<40
PAH-SS-26	10	24	32	9	1.0	<2	112	<40
PAH-SS-27	14	22	154	9	1.3	<2	115	<40
PAH-SS-28	11	34	51	14	1.9	<2	94	<40
PAH-SS-29	11	19	35	6	.7	<2	97	<40
PAH-SS-30	9	28	43	11	1.3	<2	114	<40
PAH-SS-31	10	26	43	8	2.7	<2	102	<40
PAH-SS-32	11	27	53	11	1.2	<2	146	<40

Appendix 2. Inorganic constituents in ambient surface soils, Chicago, Illinois—Continued

[percent, percent-weight; D, duplicate sample; <50, constituent not detected and detection limit]

Sample Number	Constituent							
	Niobium (milligrams per kilogram)	Neodymium (milligrams per kilogram)	Nickel (milligrams per kilogram)	Scandium (milligrams per kilogram)	Selenium (milligrams per kilogram)	Silver (milligrams per kilogram)	Strontium (milligrams per kilogram)	Tantalum (milligrams per kilogram)
PAH-SS-33	10	31	41	11	1.2	<2	116	<40
PAH-SS-33D	10	27	40	11	1.2	<2	114	<40
PAH-SS-34	8	29	31	10	.9	<2	94	<40
PAH-SS-35	18	49	93	18	3.1	<2	299	<40
PAH-SS-36	10	23	55	8	3.1	<2	144	<40
PAH-SS-37	7	<9	22	3	0.5	<2	104	<40
PAH-SS-38	10	25	24	9	1.0	<2	108	<40
PAH-CE-01	6	<9	26	3	.8	<2	103	<40
PAH-CE-02	6	<9	5	<2	<0.2	<2	78	<40
PAH-CE-03	13	13	25	6	.9	<2	93	<40
PAH-CE-04	12	9	15	<2	0.3	<2	65	<40
PAH-CE-04D	6	<9	12	<2	.3	<2	67	<40
PAH-CE-05	10	18	48	7	1.5	<2	153	<40
PAH-CE-06	8	12	88	3	.7	<2	94	<40
PAH-CE-07	16	10	48	6	1.6	<2	125	<40
PAH-CE-08	5	<9	8	3	0.2	<2	128	<40
PAH-CE-09	13	23	28	10	.8	<2	87	<40
PAH-CE-10	9	<9	10	3	.5	<2	117	<40
PAH-CE-11	8	13	11	3	<0.2	<2	83	<40
PAH-CE-12	12	20	39	9	.8	<2	91	<40
PAH-CE-13	23	11	50	13	0.9	<2	142	<40
PAH-CE-14	8	16	24	6	.8	<2	114	<40
PAH-CE-15	13	14	27	7	1.4	<2	114	<40
PAH-CE-15D	7	17	26	7	1.7	<2	113	<40
PAH-CE-16	<4	11	11	3	.3	<2	115	<40
PAH-CE-17	4	10	19	4	0.6	<2	153	<40
PAH-CE-18	6	18	23	6	.8	<2	121	<40
PAH-CE-19	6	<9	12	3	.7	<2	83	<40

Appendix 2. Inorganic constituents in ambient surface soils, Chicago, Illinois

[percent, percent-weight; D, duplicate sample; <50, constituent not detected and detection limit]

	Constituent						
Sample Number	Thorium (milligrams per kilogram)	Tin (milligrams per kilogram)	Uranium (milligrams per kilogram)	Vanadium (milligrams per kilogram)	Ytterbium (milligrams per kilogram)	Yttrium (milligrams per kilogram)	Zinc (milligrams per kilogram)
PAH-SS-01	9	<50	<100	84	2	17	137
PAH-SS-02	8	<50	<100	82	2	19	83
PAH-SS-03	10	<50	<100	104	2	19	213
PAH-SS-04	<6	<50	<100	83	2	17	380
PAH-SS-05	<6	<50	<100	63	2	14	109
PAH-SS-06	<6	<50	<100	70	2	16	804
PAH-SS-07	8	<50	<100	106	3	19	97
PAH-SS-08	9	<50	<100	91	2	17	112
PAH-SS-09	9	<50	<100	85	2	17	170
PAH-SS-10	9	<50	<100	89	2	18	79
PAH-SS-11	9	<50	<100	83	2	18	90
PAH-SS-12	9	<50	<100	93	2	20	105
PAH-SS-13	10	<50	<100	105	2	19	235
PAH-SS-14	8	<50	<100	106	2	20	388
PAH-SS-15	9	<50	<100	99	3	19	112
PAH-SS-16	9	<50	<100	95	3	18	108
PAH-SS-17	<6	<50	<100	116	2	18	325
PAH-SS-17D	7	<50	<100	122	2	17	320
PAH-SS-18	<6	105	<100	105	1	19	1,180
PAH-SS-19	8	<50	<100	94	3	18	99
PAH-SS-20	<6	<50	<100	70	2	18	239
PAH-SS-21	9	<50	<100	95	2	18	173
PAH-SS-21D	8	<50	<100	95	3	18	165
PAH-SS-22	<6	<50	<100	72	2	16	359
PAH-SS-23	9	<50	<100	90	2	20	243
PAH-SS-24	9	<50	<100	92	3	18	172
PAH-SS-25	9	<50	<100	81	2	16	115
PAH-SS-25D	9	<50	<100	86	2	17	124
PAH-SS-26	<6	<50	<100	73	2	16	172
PAH-SS-27	<6	248	<100	78	1	17	1,240
PAH-SS-28	7	<50	<100	115	2	20	260
PAH-SS-29	<6	<50	<100	47	1	12	623
PAH-SS-30	8	<50	<100	93	2	19	243
PAH-SS-31	<6	<50	<100	79	1	14	507
PAH-SS-32	7	<50	<100	96	2	18	760

Appendix 2. Inorganic constituents in ambient surface soils, Chicago, Illinois

[percent, percent-weight; D, duplicate sample; <50, constituent not detected and detection limit]

	Constituent						
Sample Number	Thorium (milligrams per kilogram)	Tin (milligrams per kilogram)	Uranium (milligrams per kilogram)	Vanadium (milligrams per kilogram)	Ytterbium (milligrams per kilogram)	Yttrium (milligrams per kilogram)	Zinc (milligrams per kilogram)
PAH-SS-33	8	<50	<100	91	2	18	348
PAH-SS-33D	8	<50	<100	88	2	18	339
PAH-SS-34	<6	<50	<100	81	2	17	191
PAH-SS-35	13	<50	<100	145	3	38	1,500
PAH-SS-36	<6	<50	<100	79	1	16	1,140
PAH-SS-37	6	<50	<100	42	1	9	431
PAH-SS-38	11	<50	<100	71	2	16	133
PAH-CE-01	7	<50	<100	35	<1	9	606
PAH-CE-02	10	<50	<100	24	<1	6	100
PAH-CE-03	8	101	<100	62	1	13	930
PAH-CE-04	8	<50	<100	34	<1	7	242
PAH-CE-04D	<6	<50	<100	32	<1	8	187
PAH-CE-05	11	<50	<100	73	2	16	1,260
PAH-CE-06	10	<50	<100	38	<1	8	1,400
PAH-CE-07	8	51	<100	70	1	14	1,690
PAH-CE-08	11	<50	<100	27	<1	7	83
PAH-CE-09	10	<50	<100	88	3	17	80
PAH-CE-10	8	<50	<100	30	<1	7	106
PAH-CE-11	<6	<50	<100	34	<1	9	142
PAH-CE-12	13	<50	<100	82	2	15	174
PAH-CE-13	8	<50	<100	124	3	26	490
PAH-CE-14	7	<50	<100	58	2	13	251
PAH-CE-15	11	<50	<100	65	2	14	163
PAH-CE-15D	12	<50	<100	63	2	14	158
PAH-CE-16	10	<50	<100	34	<1	8	89
PAH-CE-17	12	<50	<100	50	2	11	528
PAH-CE-18	7	<50	<100	53	2	13	371
PAH-CE-19	6	<50	<100	34	<1	7	264

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March 15, 2013

Judy Cearley
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Re: USGS-2011-00093

Dear Judy:

Based upon your earlier emails and correspondence, it would appear that the USGS, after two years, is in the process of completing its initial response to my FOIA request. As I understand your position, there may be a couple of more boxes coming that contain QA/QC lab reports. I think you would agree that I have waited patiently after being advised that the delays were due in large part to several of the USGS scientists having research duties that repeatedly pulled them away from my FOIA request. I have tried to be accommodating.

Having reviewed the documents produced thus far, I am concerned that certain aspects of my FOIA request have been overlooked by several of these same USGS scientists, and for reasons that are not clear. Indeed, over the past two years, I have never been advised that my FOIA request was somehow inappropriate or requested documents that I was not entitled to review. Naturally, I had assumed that the USGS scientists would be willing to share their underlying data and thought processes regarding the alleged impact of coal tar sealants upon the environment, especially since transparency is the foundation of sound scientific reasoning.

I have attached for your review another copy of my FOIA request so that I may more clearly outline below the areas in which deficiencies in the USGS response seem to exist. Please note that a virtually identical FOIA request was sent to the Minnesota Pollution Control Agency ("MPCA"). This was done because it became apparent several years ago that two of the USGS scientists who have been involved with coal tar sealant research, Dr. Barbara Mahler and Dr. Peter Van Metre, had developed a close relationship with Dr. Judy Crane of the MPCA, who also shared their interest in coal tar sealants. By cross referencing some of Dr. Crane's emails that were exchanged between herself and the USGS scientists, it would be relatively simple to determine if Drs. Van Metre and Mahler had withheld or deleted certain emails and documents from the anticipated USGS FOIA response.

EXHIBIT
H

This small group of government sponsored sealant researchers includes several other individuals who have frequently interacted with the USGS and the MPCA. One such person is Tom Ennis, Environmental Resource Manager for the City of Austin. Another is Dr. Alison Watts, Research Assistant Professor at the University of New Hampshire. Emails from Dr. Crane confirm that the members of this group have become inextricably connected to each other and to the proposition that coal tar sealants are the single greatest source of PAHs in sediment and house dust east of the Rockies. Given the numerous presentations that each has given on this topic, the number of articles written, their high media visibility - and in the case of Mr. Ennis, the anti-coal tar sealant blog that he has created - it cannot be reasonably disputed that the professional reputation of each person is largely dependent upon the above mentioned proposition being correct.

The purpose behind this letter is not to debate the validity or merits of the proposition offered by this group. That can be left for another day. The point to be made is that once a small group of researchers has become vested in offering a new proposition to the scientific community and the public, the need for transparency becomes paramount since it is human nature to see what one wants to see and overlook the rest. Certainly, this precise argument has been directed toward researchers who are funded by industry. Science has recognized this human foible for over a century, which is why scientists must not only produce all underlying data and methodologies that lead to their conclusions, but they should also welcome related challenges, as difficult as that may be personally. Unfortunately, that does not seem to be the case when it comes to USGS research regarding coal tar sealants.

In reviewing Dr. Crane's emails, the resentment the research group displayed behind closed doors toward anyone who questioned their conclusions is unmistakable, and should be a red warning flag. Consider, for example, Dr. Crane's pride in advising the group that she had temporarily stalled and dissuaded the PCTC from filing a FOIA request, only to be told by her superiors at the MPCA two weeks later that she needed to respond in a more substantive manner. (See Group Exhibit 1). Similarly, the group's disdain for any research that does not comport with their findings, particularly industry sponsored research, is evident throughout, as is their mutual admiration for each other's work. (See Group Exhibit 2). Ultimately, Mr. Ennis became such an extreme advocate for his anti-coal tar sealant stance that the group eventually agreed they should no longer send emails to him at his City of Austin job, but would continue to communicate with him through his private email account. (See Exhibit 3).

The extent to which this dynamic has permeated and affected the research of Drs. Mahler and Van Metre is not presently known because, unlike Dr. Crane and the MPCA, the USGS has produced virtually no emails, correspondence or internal communications from the files of these two scientists. The few emails that have been produced by the USGS appear to come from another staff member, Jennifer Wilson. This would appear to be the case even though paragraphs 1-7 of my attached FOIA request clearly call for any and all correspondence and emails related to

coal tar sealant research being conducted by Drs. Mahler and Van Metre from 2003 to the present.

Despite the large quantities of emails that appear to be missing, I was able to locate one document that seems to contain Dr. Mahler's responses to questions raised by Dr. Rosalind Schoof with regard to a house dust study that was published by the USGS in 2010. Specifically, Dr. Schoof had asked for details regarding the manner in which the underlying data were obtained and tabulated and how variables were controlled or accounted for by the USGS. Instead of expressing a willingness to share her data and methodologies, Dr. Mahler repeatedly characterized Dr. Schoof's requests as being an "obfuscation" or "not relevant." (See Exhibit 4, italicized responses to paragraphs 2, 3, 6 & 7). The tone of these responses should be another warning flag. The fact that Dr. Mahler is married to Dr. Van Metre raises yet another question as to whether Dr. Van Metre would ever produce emails and data that Dr. Mahler thought should be withheld for some reason, or vise versa. The normal checks and balances that one might expect to see between two scientists have been eroded.

Given Dr. Mahler's perspective, I was not surprised when my initial review of the USGS records failed to disclose any field notes for the house dust study. Once again, my FOIA request clearly covered such documents (see paragraphs 8 & 9). As strange as it may seem, the blank field note forms that were to be used for this study were produced (see Exhibit 5), but not the completed forms with the observations of Drs. Mahler and Van Metre. If I am mistaken, please let me know. Similarly, Drs. Mahler and Van Metre apparently prepared cover letters for participants in the house dust study letting them know that specific data and findings for each home would be provided. (See template marked as Exhibit 6). This is precisely the type of data that has been requested by my FOIA request and by Dr. Schoof, but to the best of my knowledge, not produced.

The significance of the house dust study cannot be overstated. The house dust data provide the foundation for all of the subsequent risk assessments that were performed by the USGS in conjunction with Dr. Spencer Williams of Baylor. Dr. Schoof anticipated that Drs. Mahler and Van Metre would attempt to use the house dust study for this purpose, which is why she asked for all of the underlying sampling procedures, original data and field notes for each apartment and parking lot tested. This is what scientists do to check the merits of conclusions reached by others. As mentioned above, Dr. Mahler not only responded by calling such a request an "obfuscation," she also implied that the house dust study was not be used for risk assessment purposes. (See Exhibit 4, italicized response to paragraphs 3 & 8). It would appear that Dr. Mahler later changed her mind.

Other documents that should have been produced in response to my FOIA request, but appear to be missing, are as follows:

EDWARDS WILDMAN

- Complete dust study results for each apartment and parking lot sampled, giving minimum, maximum and median concentrations of all analytes that were tested, including pesticides, flame retardants, PCBs and phthalates (not just PAHs) (Para. 8 & 9 of FOIA Request)
- Notes regarding field sampling equipment calibrations and cleaning procedures (Para. 8 & 9 of FOIA Request)
- Chains of custody for the samples (it appears as though there are no chains of custody for any sample collected by the USGS) (Para. 8 & 9 of FOIA Request)
- Individual and compiled results of questions asked of households participating in the dust study and responses given (Para. 8 & 9 of FOIA Request)
- A means for identifying individual samples and correlating them to specific apartments or parking lots that were identified in the USGS house dust study. It is presently impossible to evaluate which dust samples were included, or just as importantly, excluded from the published summaries (Para. 8 & 9 of FOIA Request)
- Internal or external reviews of manuscripts that became published papers by the USGS regarding coal tar sealants (Para. 5 of FOIA Request)
- Documents that either proposed or authorized USGS work to be performed on coal tar sealants (Para. 12 of FOIA Request)
- Documentation regarding any joint funding between the USGS and the City of Austin on coal tar sealants (Para. 12 of FOIA Request)
- All communications and emails regarding coal tar sealants that may have been exchanged internally or externally between scientists, legislators or members of the media. (Para. 1, 4, 6, 7, 10 & 12 of FOIA Request).

As I mentioned above, if I am mistaken regarding any of the documents that appear to be missing, please let me know. I continue to appreciate your personal efforts to track down these documents and will be happy to answer any questions you may have. I look forward to your response.

Very truly yours,

Leonard S. Kurfirst

LSK:cs
Enclosures

Crane, Judy (MPCA)

From: Crane, Judy (MPCA)
Sent: Tuesday, January 11, 2011 1:47 PM
To: 'Peter C VanMetre'
Cc: Barbara J Mahler
Subject: RE: ES&T Feature Article

Great! I just had an email from someone we know threatening me with a data practices request; I think I've diffused her for awhile.

From: Peter C VanMetre [mailto:pcvanmet@usgs.gov]
Sent: Tuesday, January 11, 2011 1:45 PM
To: Crane, Judy (MPCA)
Cc: Barbara J Mahler
Subject: RE: ES&T Feature Article

Judy,
Good start on the letter! I'll incorporate your thoughts in my first cut...
Pete

Peter Van Metre
Research Hydrologist
USGS
1505 Ferguson Lane
Austin, TX 78754
512-927-3506

From: "Crane, Judy (MPCA)" <Judy.Crane@state.mn.us>
To: Peter C VanMetre <pcvanmet@usgs.gov>, Barbara J Mahler <bjmahler@usgs.gov>
Date: 01/11/2011 12:01 PM
Subject: RE: ES&T Feature Article

Good idea, Pete. In the email/letter, I would mention the widespread attention this issue has received from media outlets in response to USGS press releases and publications and the keen interest policy makers have about this issue. Having a comprehensive feature article will be very useful to frame our current understanding of the role coal-tar-based sealants play in contributing PAHs to urban environments, the potential human health and ecological consequences of this contamination, and the challenges policy makers face in addressing this issue.

Judy

From: Peter C VanMetre [mailto:pcvanmet@usgs.gov]
Sent: Tuesday, January 11, 2011 11:49 AM
To: Barbara J Mahler
Cc: Crane, Judy (MPCA)
Subject: Re: ES&T Feature Article

Yes, I think the time is ripe...

PENGAD 800-631-6989
EXHIBIT

Crane, Judy (MPCA)

From: Crane, Judy (MPCA)
Sent: Monday, January 24, 2011 10:55 AM
To: Alison Watts (alison.watts@unh.edu); Barbara Mahler (bjmahler@usgs.gov); Peter Van Metre (pcvanmet@usgs.gov)
Subject: Kirk O'Reilly and Paul Boehm's comment to ES&T

See Anne LeHuray's email below regarding a comment submitted to ES&T. It seems most likely this would pertain to Alison's recent paper.

MPCA management instructed me to provide my PAH—stormwater SETAC presentations to LeHuray after she threatened us with a data practices request.

Judy

From: alehuray [mailto:alehuray@pavementcouncil.org]
Sent: Monday, January 24, 2011 10:31 AM
To: Crane, Judy (MPCA); 'Paul Boehm'; koreilly@exponent.com
Cc: Thompson, Dale (MPCA); Berger, Donald (MPCA)
Subject: RE: request a copy of SETAC 2010 North America conference presentation #434

Hi Judy -

Sorry not to have seen your email. I was out of the country on the 13th and days following.

Kirk and Paul do not need any permission from me to share their presentation. It's also up to them whether they wish to share their just-submitted comment to ES&T which you surely will be interested in.

Thanks for keeping me in the loop.

Anne

From: Crane, Judy (MPCA) [mailto:Judy.Crane@state.mn.us]
Sent: Monday, January 24, 2011 10:55 AM
To: Paul Boehm (pboehm@exponent.com); koreilly@exponent.com
Cc: alehuray
Subject: request a copy of SETAC 2010 North America conference presentation #434

Kirk and Paul--

I am requesting a copy of your SETAC 2010 North America conference presentation #434 that was done for the Pavement Coating Technology Council on "PAHs in urban sediments: Forensic approaches for assessing the relative contribution of atmospheric deposition and parking lot sealants" by K. O'Reilly, J. Pietari, and P. Boehm. I previously requested this file from Dr. Anne LeHurary on January 13, 2011, and she has not responded to my request. This presentation will only be used internally at the MPCA. Please contact me with any questions. Thanks much.

Regards,

Judy L. Crane, Ph.D.
Research Scientist III
Environmental Analysis & Outcomes Division
Minnesota Pollution Control Agency
520 Lafayette Road North
St. Paul, MN 55155-4194

Crane, Judy (MPCA)

From: Barbara J Mahler [bjmahler@usgs.gov]
Sent: Wednesday, February 24, 2010 2:26 PM
To: Crane, Judy (MPCA)
Cc: Alison.Watts@unh.edu
Subject: RE: meeting w/ Anne LeHuray in Minnesota on March 12

Judy,

Just had a long talk with Dan Chiles, mayor pro-tem of Springfield. Apparently LeHuray and DeMott were in Springfield this afternoon (their third visit), and in his words, they "took apart" our research. He's sending me a transcript and they're going to post the video on their website. But from talking to him, it sounds like what they did was put up a smokescreen, bringing up a bunch of non-relevant points and mixing it in with a few outright lies.

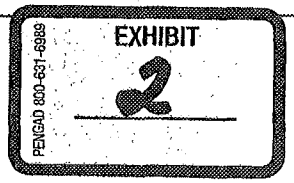
I think it will be important for us to take a look at this and come up with a point-by-point refutation of what they're saying, as well as some powerful points of our own. It sounds like they're not pulling any punches.

Barbara

****

Barbara J. Mahler, Ph.D., P.G.
Research Hydrologist
U.S. Geological Survey
1505 Ferguson Ln., Austin, TX 78754
(512) 927-3566

From: "Crane, Judy (MPCA)" <Judy.Crane@state.mn.us>
To: "Mike Kromrey (mike@watershedcommittee.org)" <mike@watershedcommittee.org>, "Peter Van Metre (pcvanmet@usgs.gov)" <pcvanmet@usgs.gov>, "Barbara Mahler (bjmahler@usgs.gov)" <bjmahler@usgs.gov>, "Tom Ennis (Tom.Ennis@ci.austin.tx.us)" <Tom.Ennis@ci.austin.tx.us>
Cc: "Alison Watts (alison.watts@unh.edu)" <alison.watts@unh.edu>
Date: 02/24/2010 02:11 PM
Subject: RE: meeting w/ Anne LeHuray in Minnesota on March 12



Hi—

As a follow-up to the below email, Don Berger of our staff provided me with some additional info about our upcoming meeting with White Bear Lake city officials and Anne LeHurray & PCTC members. Don has been doing some work on the coal tar sealcoat issue from the policy side of things. He's trying to get the city to put together an agenda for this meeting. Of particular note are the sentences I have highlighted below (for which publication of these results in the peer-reviewed literature will be necessary before we give it much attention).

Purpose:
I believe there are two purposes and I have asked the PCTC to put theirs in writing. I expect the PCTC's purpose to include convincing the City of White Bear Lake that they should not take action to ban coal tar sealcoat within their jurisdiction. I believe our purpose to be much different. I believe our purpose is to support the City in moving toward a coal tar sealer restriction in their jurisdiction, gather as much information from the industry and the legislative lobbyists as possible, and represent the health and welfare of the environment, our stakeholders, and the public well being as best we can. I want you to know that it is not my intention to debate scientific studies, research, or sampling results with the PCTC. My discussions with the City of White Bear Lake

Crane, Judy (MPCA)

From: Barbara J Mahler [bjmahler@usgs.gov]
Sent: Wednesday, February 24, 2010 3:12 PM
To: Crane, Judy (MPCA)
Subject: RE: meeting w/ Anne LeHuray in Minnesota on March 12

Sounds good, I'll be here, as will Pete.

****

Barbara J. Mahler, Ph.D., P.G.
Research Hydrologist
U.S. Geological Survey
1505 Ferguson Ln., Austin, TX 78754
(512) 927-3566

From: "Crane, Judy (MPCA)" <Judy.Crane@state.mn.us>
To: Barbara J Mahler <bjmahler@usgs.gov>
Date: 02/24/2010 02:40 PM
Subject: RE: meeting w/ Anne LeHuray in Minnesota on March 12

Yes, I'm not surprised, Barbara. We've seen this approach many times from responsible parties for contaminated sites. That was one of the reasons I wanted to contact all of you.

I'm hoping the MN Legislature will ban coal tar-based sealcoats this session. It's a bonding session so they usually don't address too many policy issues, but it could get slipped in...there is definitely interest by some Legislators to make this happen.

Can you send me a copy of the transcript, too, and the web link when Dan Chiles provides it to you. I'm thinking we should probably have a MPCA manager at this meeting (the meeting is scheduled for a Friday so that may be tough). I at least want to provide some of the stormwater supervisors/managers with more information on LeHuray's tactics so we're better prepared to address them.

I'll give you a call later today to discuss this issue further.

Judy

From: Barbara J Mahler [mailto:bjmahler@usgs.gov]
Sent: Wednesday, February 24, 2010 2:26 PM
To: Crane, Judy (MPCA)
Cc: Alison.Watts@unh.edu
Subject: RE: meeting w/ Anne LeHuray in Minnesota on March 12

Judy,

Just had a long talk with Dan Chiles, mayor pro-tem of Springfield. Apparently LeHuray and DeMott were in Springfield this afternoon (their third visit), and in his words, they "took apart" our research. He's sending me a transcript and they're going to post the video on their website. But from talking to him, it sounds like what they did was put up a smokescreen,

Crane, Judy (MPCA)

From: Ennis, Tom [Tom.Ennis@ci.austin.tx.us]
Sent: Tuesday, March 02, 2010 10:38 AM
To: Peter C VanMetre; Barbara J Mahler; Crane, Judy (MPCA)
Cc: Scoggins, Mateo; Bashara, Tom
Subject: RE: nice line...
Attachments: PCTC Response to CIC Questions (2).pdf

Pete:

Did you see the PCTC answers to Council questions in Springfield? Dodgeball 2.0 in my opinion. I'll attach a copy. Also interesting is that the PCTC is up and going and that they claim the BAP concentration of their products is 0.002% (we are more like 0.1 to 0.5 percent BAP). Just 2 orders of magnitude off.

Here's a link: http://www.pavementcouncil.org/faqs

Tom

From: Peter C VanMetre [mailto:pcvanmet@usgs.gov]
Sent: Tuesday, March 02, 2010 9:51 AM
To: Barbara J Mahler; Ennis, Tom; Judy.Crane@state.mn.us
Subject: nice line...

OSU has a Superfund Research Program. http://oregonstate.edu/superfund/

The web site opens with this:

Polycyclic Aromatic Hydrocarbons: New Technologies and Emerging Health Risks

Welcome to the Superfund Research Program at Oregon State University.
Polycyclic Aromatic Hydrocarbons (PAHs) are re-emerging as an environmental pollutant of concern. PAHs, found at Superfund sites and urban settings, are formed in the burning of carbon-based energy sources, e.g., diesel, gasoline, coal, petroleum and in cooking or tobacco smoke.

That first sentence is pretty close to our proposed session title for next years SETAC Judy.
Pete

Peter Van Metre
Research Hydrologist
USGS
1505 Ferguson Lane
Austin, TX 78754
512-927-3506

Crane, Judy (MPCA)

From: Crane, Judy (MPCA)
Sent: Thursday, December 02, 2010 11:04 AM
To: 'Peter C VanMetre'
Subject: RE: UNH paper on PAHs in stormwater runoff

Ok—thanks for the heads-up.

From: Peter C VanMetre [mailto:pcvanmet@usgs.gov]
Sent: Thursday, December 02, 2010 10:54 AM
To: Watts, Alison; Crane, Judy (MPCA)
Subject: Re: UNH paper on PAHs in stormwater runoff

Alison,

I gave your paper and your name to a reporter who interviewed me this morning -- hope that's OK! And I've given your name out too Judy.

Cheers,
Pete

Peter Van Metre
Research Hydrologist
USGS
1505 Ferguson Lane
Austin, TX 78754
512-927-3506

From: "Watts, Alison" <Alison.Watts@unh.edu>

To: "'Peter C VanMetre'" <pcvanmet@usgs.gov>, "Crane, Judy (MPCA)" <Judy.Crane@state.mn.us>, "Bert van Hattum (bert.van.hattum@ivm.vu.nl)" <bert.van.hattum@ivm.vu.nl>, "Brian Mulhearn°(bmulhearn@ensafe.com)" <bmulhearn@ensafe.com>, "David Mauro (dmauro@metaenv.com)" <dmauro@metaenv.com>, "Dave Nakles (dnakles@andrew.cmu.edu)" <dnakles@andrew.cmu.edu>, "Greg Durell (durell@battelle.org)" <durell@battelle.org>, Elisa Buckley <ebuckley@langan.com>, "Fred Pinkney (Fred_Pinkney@fws.gov)" <Fred_Pinkney@fws.gov>, "Greg Sower (GSower@environcorp.com)" <GSower@environcorp.com>, "Karey Harris (harris.karey@epa.gov)" <harris.karey@epa.gov>, "Jocelyne Hellou (Hellouj@mar.dfo-mpo.gc.ca)" <Hellouj@mar.dfo-mpo.gc.ca>, "Chip McCarty (hmccarty@csc.com)" <hmccarty@csc.com>, "Ileana Rhodes (ileana.rhodes@shell.com)" <ileana.rhodes@shell.com>, "Jerri Dawn Martin (jerri.martin@ky.gov)" <jerri.martin@ky.gov>, "John Higman (jhigman@sjrwmd.com)" <jhigman@sjrwmd.com>, "Joel Meyer (joel.meyer@duke.edu)" <joel.meyer@duke.edu>, "Charlene Liu (liush@cdm.com)" <liush@cdm.com>, "Dave Mount (mount.dave@epa.gov)" <mount.dave@epa.gov>, "Nick Azzolina (nick.azzolina@gmail.com)" <nick.azzolina@gmail.com>, "John French (pesa@gci.net)" <pesa@gci.net>, "Amy Rowe (rowe@njaes.rutgers.edu)" <rowe@njaes.rutgers.edu>, "Robert (Bob) De Santo (rsdesanto@ct.metrocast.net)" <rsdesanto@ct.metrocast.net>, "Susan Kane Driscoll (sdriscoll@exponent.com)" <sdriscoll@exponent.com>, "Paul Seidel (seidel.paul@deq.state.or.us)" <seidel.paul@deq.state.or.us>, "Hennes, Steven (MPCA)" <Steven.Hennes@state.mn.us>, Steve Geiger <steve.geiger@aecom.com>, "Randy St. Germain (stgermain@dakotatechnologies.com)" <stgermain@dakotatechnologies.com>, "Thomas Webster (twebster@bu.edu)" <twebster@bu.edu>, "Will Gala (WGala@chevron.com)" <WGala@chevron.com>, Christopher G Ingersoll <cingersoll@usgs.gov>

Date: 12/02/2010 10:45 AM

Subject: UNH paper on PAHs in stormwater runoff

And on the subject of papers... We have just published a paper in ES&T on our sealant/runoff work:

Crane, Judy (MPCA)

From: Peter C VanMetre [pcvanmet@usgs.gov]
Sent: Thursday, December 09, 2010 12:59 PM
To: Crane, Judy (MPCA)
Cc: Barbara J Mahler
Subject: Re: FW: [npsinfo] Pavement Sealer Study-Product Ban Fails to Lower or Change Sources of PAHs in Watershed

We've seen much of what's in this paper in various presentations by Bob DeMott. The approaches used are not technically defensible.
Pete

Peter Van Metre
Research Hydrologist
USGS
1505 Ferguson Lane
Austin, TX 78754
512-927-3506

From: "Crane, Judy (MPCA)" <Judy.Crane@state.mn.us>
To: "Tom Ennis (Tom.Ennis@ci.austin.tx.us)" <Tom.Ennis@ci.austin.tx.us>, "Peter Van Metre (pcvanmet@usgs.gov)" <pcvanmet@usgs.gov>, "Barbara Mahler (bjmahler@usgs.gov)" <bjmahler@usgs.gov>
Date: 12/09/2010 12:50 PM
Subject: FW: [npsinfo] Pavement Sealer Study-Product Ban Fails to Lower or Change Sources of PAHs in Watershed

---

I'm sure you've already seen the below article....

Judy

From: Gelbmann, Anne (MPCA)
Sent: Thursday, December 09, 2010 10:45 AM
To: Berger, Donald (MPCA)
Cc: Crane, Judy (MPCA); Thompson, Dale (MPCA)
Subject: FW: [npsinfo] Pavement Sealer Study-Product Ban Fails to Lower or Change Sources of PAHs in Watershed

Don/Judy/Dale-are you on this list serve? Lots of e-mails today about the PAH ban.

Crane, Judy (MPCA)

From: Ennis, Tom [Tom.Ennis@ci.austin.tx.us]
Sent: Friday, April 15, 2011 2:19 PM
To: Crane, Judy (MPCA)
Subject: RE: Other coal tar sealant bans/ordinances in the U.S.

Judy:

It is best that you communicate with me about coal tar stuff via my personal email, enniseng@gmail.com.

I don't do that for the City of Austin anymore.

Thanks...

Tom

From: Crane, Judy (MPCA) [mailto:judy.crane@state.mn.us]
Sent: Friday, April 15, 2011 2:16 PM
To: Ennis, Tom
Subject: RE: Other coal tar sealant bans/ordinances in the U.S.

Hi Tom—

Please add Golden Valley, MN and New Hope, MN to your list, too.

I hadn't seen your blog. Pete mentioned you were taking more of an advocacy role on this issue. I'll check it out further.

Judy

From: Ennis, Tom [mailto:Tom.Ennis@ci.austin.tx.us]
Sent: Friday, April 15, 2011 2:06 PM
To: Crane, Judy (MPCA); Sarah Pasquesi
Cc: Cassandra McKinney; Bob Newport
Subject: RE: Other coal tar sealant bans/ordinances in the U.S.

Judy:

Yes here is my list. I have not added the State of Washington. I thought I would wait for the governor to sign it first (which is due in less than 20 days).

There are some surprises (Winfield, KS and the Commonwealth of Massachusetts (for wetland permits only)).

Let me know if there are some changes.

Tom

From: Crane, Judy (MPCA) [mailto:judy.crane@state.mn.us]
Sent: Friday, April 15, 2011 1:49 PM
To: Sarah Pasquesi
Cc: Cassandra McKinney; Bob Newport; Ennis, Tom
Subject: Other coal tar sealant bans/ordinances in the U.S.

PENGAD 800-631-6989
EXHIBIT
3

Dust Study Questions

1. Describe the approach used to collect samples at each property, including specifying the order in which samples were collected. The sampling period in the Mahler et al. 2010 study is described as between April and July 2008. The weather in Austin, Texas varied considerably during that period. From the beginning of 2008 through mid-April, there was little rain in Austin which would be expected to result in considerable dust build up. From late April through July there were periods of relatively frequent rain. For this reason as we well as others, it's important to understand which samples were collected at which times. Which was sampled first, outdoors or indoors? Was the order the same at every property? Do you have a sampling SOP (standard operating procedure) that you could share with us?

Indoor samples were collected from Mar 28 to May 23. Outdoor samples were collected from Mar 28 to July 23. In all cases the indoor sample was collected prior to the outdoor sample. Seasonal build-up of dust is not relevant to PAH concentrations.

2. Describe the approach used to collect the indoor dust samples. The paper says that dust was collected from the entryways and adjacent living room floors, and that the areas sampled ranged from 1.6 to 13 m^2. Why wasn't a standard area vacuumed? What was the relative area of the entry vs. living area that was vacuumed? Was there any difference between the concentrations of PAHs at the entryway as opposed to the living room?
[USEPA guidance for sampling lead in indoor dust specifies that discrete samples should be collected from a bedroom, most frequently used living space and the most frequently used entrance. It is further recommended that these samples be used to calculate an average concentration based on time-weighted activity patterns for residents.]

A sufficient area was vacuumed to obtain a sufficient amount of dust for analysis. Indoor dust was analyzed as a single composite. This is obfuscating the fact that indoor dust had elevated concentrations of PAHs if the parking lot had a sealcoated parking lot.

3. Were PAH loads calculated? The mass of dust collected indoors was stated to vary from 0.36 to 35 g (median of 4.8 g). Did you evaluate the influence of dust load on PAH concentrations?
[Both PAH concentration and PAH load from each living area are needed to assess exposures because exposure will be a function of transfer of PAH to hands, which will be a function of both concentration and load. Dust load is expected to be highest at the entryway and in carpets; however, PAH concentrations are expected to be highest at the entryway and lowest in carpets. Since most time will be spent in the living areas rather than at the entryway, composite samples that combine both areas do not represent average exposure concentrations. The composite concentrations will overestimate the average exposure concentration both due to higher concentration and due to higher loading.]

DRAFT

PENGAD 800-631-6989
EXHIBIT
4

Yes, they were. PAH loads from apartments with CT lots were 16 times higher than those from apartments with NCT lots (based on median values). Loads for CT apartments ranged from 9 to 480 ug/m^2 with a mean value of 160 ug/m^2.

This publication was not a health risk analysis. The paper demonstrated that PAH concentrations are 25 times in residences with sealcoated parking lots. We did compute PAH loads, but it's not relevant to this discussion.

4. Describe the process of removing samples from the HVS3 and preparing it for collection of the next sample. Describe if/how the HVS3 was cleaned, and the frequency with which the cleaning was performed. Was this done between every sample? [On average, parking lot dust concentrations are 37 times higher than indoor dust concentrations. Consequently, if parking lots were sampled first, and if the HSV3 was not decontaminated according to recommended procedures, residual parking lot dust could account for the elevated indoor dust concentrations. Even if the indoor dust was sampled first, failure to decontaminate between properties could result in high values due to residual contamination from the prior property.]

The HVS3 was cleaned between collection of every sample.

5. Did you evaluate the possible influence of apartment or carpet age on dust PAH concentrations?

Yes. There is no relation.

6. Will you share with us the individual data for the independent variables listed in Table 1 of the paper? How can the alleged impact of these variables be checked if the data for each apartment are not produced? Were data collected for any other parameters not listed in Table 1? When will the USGS produce this data?

Obfuscation.

7. The degree of sealcoat wear is listed in Table 1 as an independent variable potentially related to the levels of PAH detected in SHD and parking lots dust samples. However, there is no information presented as to how this wear was evaluated, nor is there any information in the supporting material that summarizes the range of wear levels for the parking lots examined in the study. If parking lot surface type is believed to be a significant factor in explaining indoor and parking lot dust PAH levels, why wasn't the degree of sealcoat wear estimated? Were such estimates made in earlier USGS "parking lot" articles? If so, why were those USGS techniques for estimating wear abandoned this time around? Is the USGS saying that the "untreated asphalt" parking lots in their study had never been treated with any type of sealant? Did the USGS assume that a parking lot which had no obvious "sealant chips" for the "coffee/tea" screening test was a parking lot that had never been sealed in the past? If so, did the USGS conduct any research to demonstrate that such an assumption was valid?

Obfuscation. The enormous difference between NCT lots and CT lots indicates that wear was not an issue, and unsealcoated lots were not misidentified.

8. Describe the relevance of the German dust PAH guideline of 10 μg/g.
[U.S. EPA (2003) derived a dust PAH guideline of 145 $\mu g/m^2$ for total PAH for the World Trade Center residential studies. This value is based on an incremental risk of 1 x 10^{-4} for ingestion of and dermal contact with dust for 30 years (daily dust intake of 13 mg/d for children and 6 mg/d for adults). The target risk is justified due to limits of analytical methods for PAH in dust and to background concentrations of other COPCs such as dioxins. We can estimate an approximately equivalent T-PAH concentration based on literature reports of typical dust loads in homes. For example, Adgate (1995) report a geometric mean dust load of 38 mg/ft^2 for 216 homes, which is 0.409 g/m^2. At this loading, the U.S. EPA guideline of 145 $\mu g/m^2$ is equivalent to a concentration of 355 μg/g. This compares to a range of coal tar sealcoat indoor dust T-PAH concentrations of 20 to 335 μg/g in the Mahler et al. study. Consequently, the reported indoor dust concentrations do not exceed the health-based benchmarks used in the World Trade Center Indoor Environmental Assessment.]

So, they are accusing us of doing a health-risk analysis when we did not do so, and then they go ahead and do a health-risk analysis on nonexistent data.

The WTC daily dust ingestion value of 13 mg/d for toddlers is very small relative to that presented in other EPA documents: 127 mg/d from one study (Calabrese), 55 mg/d from EPA's own summary of estimates, and that's for the median child. Upper percentile (top 10%) estimate is 432 mg/d. EPA Child-Specific Exposure Factors Handbook. "EPA (1997) recommends central estimates of total soil ingestion rates of 100 mg/d for children and 50 mg/d for adults. It is logical that lower ingestion rates would apply to dust only, however, it is uncertain how much less. ***This uncertainty appears to have more potential for leading to under than over estimates of risk."*** *So they admit that they are probably underestimating the risk.*

Further, the total exposure is based on the assumption that the residue level will dissipate according to first-order kinetics, i.e., that in the case of the WTC the contaminant was delivered only once and from then on it continually decreased as a result of dissipation from cleaning, chemical breakdown, etc. This is clearly not the case with CT sealcoat dust, which is constantly replenished. (Appendix D5, Section 3.3, World Trade Center Indoor Environmental Assessment.)

"Dose rates were estimated based on a number of assumptions—for example, the fraction of dust residues that can be transferred to the skin, daily skin loads, mouthing behaviors for different age groups, and dissipation of surface loading over time."

First of all the content of these papers is not germane as they have not been published. The two included are still in review; to the best of my knowledge, the Demott paper was rejected by ES&T and is now in review at Environmental Forensics; they have been

citing it as "in review" for 18 months now. The one that is listed as "in press" is not included in the .pdf, and is in a trade journal, not a peer-reviewed scientific journal.

Because of this, let's stick to just one stopper for each paper.

Demott – Analytical error

O'Reilly – misleading use of data

There are substantial problems with the two papers submitted.

The Demott paper has so much analytical error that the data cannot be reasonably evaluated. They only collected two sets of duplicates for 44 samples, and the relative percent difference was 42% and 87%. Now, the amount of decrease in PAHs that we might expect to see of the course of 2 years (assuming a half-life of 15 years) is about 9%. How can we possibly see a decrease of 9% if the experimental error is 40% or greater? And in fact, these weren't even field duplicates, they were splits. They collected a bunch of sediment, mixed it in a bowl, divided it in half, and analyzed each half. There are a lot of other very serious issues, such as the fact that collection of streambed sediment is a very poor choice of approach for determining trends, but this one overwhelms them.

The O'Reilly paper has four major flaws. First, they don't specify which data they used for their "forensic" plots, but the data for "coal tar sealed lot" shown on their "forensic" plots don't include any of the data from any of our publications. If you plot our parking lot data on there, it very nicely overlies the stormwater pond data. Second, these are pretty weak "forensic" methods. In fact, they only used three methods, as methods 1 and 2 and methods 4 and 5 are really the same thing. They're fine for screening, but cannot be considered advanced forensic tools. The science has moved on, and the CMB model approach we've taken is much more sophisticated and preferable to any of these approaches. Third, they exclude any consideration of PAH concentrations. How can atmospheric deposition be the principal source of PAHs to stormwater ponds in the Minneapolis area if there is a thousand-fold difference in the PAH concentrations of those ponds? And finally, none of the sources that they consider, with the exception of dust from lots with coal-tar-based sealcoat (and apparently they don't even use that) are actually sources – atmospheric particles, urban soils, and rooftop particles are all themselves receivers of PAHs from different sources, and themselves may (and likely do) include PAHs from coal-tar-based sealcoat.

And note, the atmospheric particle standards used by O'Reilly are either from Simcik, 1999, which were for atmospheric particles in the Chicago area (2 of the 3 points); the other is the NIST atmospheric dust standard, for which O'Reilly does not provide a reference – which NIST standard is this? If it's 8785 (Air particulate matter on filter media), it consists of the fine fraction of the "urban dust" standard SRM 1649a. Urban dust is simply "an atmospheric particulate material collected in an urban area." We have no idea what urban area.

USGS
science for a changing world

Date: _____

Time: _____

HIGH VOLUME SMALL SURFACE SAMPLER DATA SHEET
PART A: INDOOR HOUSEDUST SAMPLE

Address:				Sample ID:	
Bottle tare mass:	(g)	Bottle final mass:	(g)	Dust mass:	(g)
Fines (<0.5 mm) mass:	(g)	NWQL Lab ID:			
Location and size of area(s) sampled (describe and sketch):					
Operator(s):					
Flow rate:	(inches of water)	Nozzle pressure:	(inches of water)		
Total vacuum time:	(min)	(sec)	10 sec. cleaning at end:	Yes	No
Comments:					

PENGAD 800-631-6989

EXHIBIT 5

USGS
science for a changing world

Date: _____

Time: _____

HIGH VOLUME SMALL SURFACE SAMPLER DATA SHEET
PART B: OUTDOOR PARKING LOT DUST SAMPLE

Address:				Sample ID:	
Latitude:			Longitude:		
Bottle tare mass:	(g)	Bottle final mass:	(g)	Dust mass:	(g)
Fines (<0.5 mm) mass:	(g)		NWQL Lab ID:		
Location and size of area(s) sampled (describe and sketch):					
Operator(s):					
Flow rate:	(inches of water)		Nozzle pressure:	(inches of water)	
Total vacuum time:	(min)	(sec)	10 sec. cleaning at end:	Yes	No
Electrical outlet or generator used for power? (circle one)					
Comments:					

Agreement Number: _____

AGREEMENT FOR COLLECTION OF SOLIDS ON PRIVATE PROPERTY

THIS AGREEMENT is entered into this _____ day of _____, 20___, by and between _____, hereinafter called "Licensor", and the United States of America, by and through the U.S. Geological Survey (USGS), U.S. Department of the Interior, hereinafter called "Licensee".

WITNESSETH:

1. Licensor, for and in consideration of the faithful performance by Licensee of all covenants and conditions herein contained, hereby consents and agrees to the collection of solids indoors and outdoors of the property of the Licensor for the use of the Licensee in scientific investigations.

Solids may include any unconsolidated materials such as soils, sediments, matter suspended in water or wastewater, sweepings, dusts, scrapings, or other particulate matter, both indoors and outdoors, of the property of the licensor. The solids shall be collected using a customized vacuum cleaner or other collection equipment deemed appropriate by the Licensee.

2. The said property, either leased or owned, of Licensor is located at the following street address:

_____

3. Collection of solids shall be at a mutually agreeable time after the effective date of this agreement. The solids collection equipment shall be maintained in a good, safe, and workable manner such that it shall cause no harm to the property or Licensor.

4. The solids collection equipment and all tools for the maintenance and use thereof placed in or upon the said property shall remain the property of the Licensee and shall be removed by the Licensee at the conclusion of the solids collection.

5. The Licensee agree to cooperate, to the extent of the law, in the submittal of all claims for alleged loss, injuries, or damages to persons or property arising from the acts of Licensee's employees, acting within the scope of their employment, in the collection of solids from indoors and outdoors of the property, and use and maintenance of solids collection equipment and tools pursuant to the Federal Tort Claims Act (28 U.S.C., 2671 et seq.)

IN WITNESS WHEREOF, the parties have caused this agreement to be executed the day and year first above written.

LICENSOR:	_____	LICENSEE:	United States of America
Printed name:	_____	Department of the Interior Geological Survey	
		By:	_____
		Printed name:	_____
		Title:	Hydrologist

USGS
science for a changing world

Completed by: _____

Sample ID: _____

SAMPLE SITE QUESTIONNAIRE

I. Background info (fill out before going inside)

Date:	Address:	Apartment or house? (circle one)
Describe setup/location of house/apt. unit with respect to parking lot, type of parking lot sealcoat and condition (new, worn, etc.).		
Describe and photograph access to front door, e.g., approximate distance from parking area to front door, steps, pathway.		
Describe nearby businesses – any BBQ or charbroiling (e.g. El Regio) restaurants?		
Describe surrounding neighborhood (e.g., residential, some industrial businesses, commercial, roads, traffic).		

II. Questions for resident

Number of residents:		#Adults/#Children	/
Approx. square footage of house/apt.:		#Bedrooms/#Bathrooms:	/
Are any residents employed in a job that involves contact with petroleum products, e.g., construction worker, maintenance, gas station?			
Does anyone in the household smoke?		How many smokers?	
Describe smoking habits (smoke inside/outside mostly, smoke how much/day, etc):			
Do residents wear shoes in house, or are shoes taken off immediately indoors? (circle one)			
Describe average daily trips to/from residence (e.g., leave for work in AM and come home in PM; in and out several times a day; kids in and out all day, etc.).			
1-4 per day	5-10 per day	too many to count	
How often do residents walk around complex (e.g., to collect mail, go to pool, visit office, do laundry, walk pet): More than once a day	once a day	3-6 times a week	1-3 times a week <1 once a week

II. Questions for resident (continued)

Sample ID:

Heating and cooling system (circle all that apply):			
Heat:	Electric	Gas	None
	Central	Floor unit	Wall unit
A/C:	Central	Window unit	None
Are A/C air filters changed regularly (i.e. every 3 months)?		Any specialized filtration system (e.g., if a house)?	
How much are windows kept open?		Never Rarely (< 1/mo) Sometimes (monthly)	Often (weekly) Whenever possible (2x+ week)
Gas or electric stove? (circle one)		Mostly cook at home or dine/take-out or about equal? (circle one)	
Is there a BBQ grill? Yes No	Charcoal Propane Smoker	If yes, how much is it used? (circle one)	Never Rarely (1-2 x yr) Sometimes (4-6 x yr) Often (1-4x month) Whenever possible (2x+ week)
Where is it located relative to living area?			
Is there a fireplace?		If yes, how much is it used? (circle one)	Never Rarely (1-2 x yr) Sometimes (4-6 x yr) Often (1-4x month) Whenever possible (2x+ week)
Is there a washer/dryer in the residence?		Does resident burn candles/incense regularly?	
Any pets?		How many?	
Type of animal(s)?		Indoor and/or outdoor?	
Does pet walk on parking lots/driveway?			
When the last time living area was vacuumed or swept?			
Is there a regularly scheduled cleaning service?			

III. Indoor description:

Rug type(s) (circle):	Plush	Level loop	Flat
Multi-level	Shag	Other flooring:	
Type and condition of upholstered items (couch, curtains, carpet). Are they newer, older, or especially worn?			
Describe windows in main living area (many/few, floor to ceiling, etc):			
Describe electronics (TV, computers, stereo etc.) in main living area:			

United States Department of the Interior

U.S. GEOLOGICAL SURVEY
WATER RESOURCES DISCIPLINE

Texas Water Science Center
8027 Exchange Dr.
Austin, Texas 78754-4733

Date

Dear *Name of participant*:

Thank you for allowing the U.S. Geological Survey (USGS) to sample dust from your residence on *date of sample collection*. The dust was collected to assess house dust in Texas as part of a USGS reconnaissance study. The USGS is not a regulatory agency, and dust samples were not collected for compliance monitoring. Rather, the purpose of the study was to provide preliminary information about occurrence of a variety of different organic compounds in house dust. Your cooperation and that of other participants was invaluable to this study and we sincerely appreciate your help.

We analyzed your house dust for 96 organic compounds of environmental interest, including 26 pesticides, 18 polychlorinated biphenyls (PCBs), 13 flame retardants and 28 polycyclic hydrocarbons (PAHs). A description of the compounds that were analyzed, their uses, and web sites where you can find more information is included in this packet. The analyses were performed at the USGS National Water Quality Laboratory in Denver, Colorado. A copy of the chemical analysis report for your dust sample is enclosed. For each compound we detected, the chemical analysis report lists the concentration we measured. In all cases, the concentrations are reported as micrograms (μg) of compound per kilogram (kg) of solid (dust). One μg/kg is equivalent to one in 1,000,000,000 (part per billion, or ppb). If the concentration is indicated with a "less than" symbol (<), it means that the compound was not detected at the minimum laboratory reporting level indicated.

Currently no regulatory or health guidelines exist for these compounds in house dust. In fact, for some of these compounds this study represents the first time that they have been analyzed in house dust. However, if you have any health-related questions regarding these compounds, please contact the State Health Department's Environmental Toxicology Group at 800-588-1248 or the Austin/Travis County Health and Human Services at 512-972-5486. Local and state health departments will receive a summary of results from this study, but your name and address will not be provided to them.

If you have any other questions, please contact me at 512-927-3566 or bjmahler@usgs.gov. We will provide you with copies of any reports or other publications that result from this study. Again, thank you for your interest, assistance, and cooperation.

Sincerely,

Barbara Mahler
Research Hydrologist

Attachments (2): Chemical analysis report, compound information sheet

PENGAD 800-631-6989
EXHIBIT
6

Leonard S. Kurfirst
312-201-2707
kurfirst@wildman.com

April 15, 2011

USGS FOIA Officer
Mail Stop 807
National Center
Reston, VA 20192

Re: Coal Tar Sealants

Dear FOIA Officer:

Pursuant to the Freedom of Information Act, 5 U.S.C. §552, I hereby request copies of any documents which constitute, refer to or relate to the following:

1. All communications, including correspondence, emails, notes, reports and memoranda regarding coal tar sealant and asphalt research conducted by USGS or any employee, agent or contractor of USGS between January 1, 2003 and the present.

2. All correspondence, emails, notes, reports and memoranda regarding Society of Environmental Toxicology and Chemistry ("SETAC"), meetings, conferences, sessions and presentations related to coal tar sealants attended, sponsored or coordinated by USGS or any employee, agent or contractor of USGS during 2008, 2009, 2010 and 2011.

3. All USGS communications, including correspondence, emails, notes, reports and memoranda that in any way reference the Pavement Coating and Technology Council ("PCTC") dated between January 1, 2003 and the present.

4. All communications, including correspondence, e-mails, notes, reports and memoranda related to coal tar sealants authored by, received by or copied to Peter Van Metre, Barbara Mahler, Jennifer T. Wilson, T.L. Burbank, M. Scoggins and/or P.A. Hamilton dated between January 1, 2003 and the present.

5. All documents constituting, referring or relating to studies or publications related to coal tar sealants conducted by, authored by, co-authored

by or edited by Peter Van Metre, Barbara Mahler, Jennifer T. Wilson, T.L. Burbank, M. Scoggins and/or P.A. Hamilton including but not limited to notes, drafts, correspondence, e-mails, galley prints, edits, raw data, field notes, QA/QC documentation and chain of custody reports.

6. All communications, including correspondence, emails, notes, reports and memoranda between, among or including Peter Van Metre of the USGS, Judy Crane of the Minnesota Pollution Control Agency and/or Alison Watts of the University of New Hamphsire regarding coal tar sealants and/or asphalt coatings.

7. All communications, including correspondence, emails, notes, reports and memoranda between, among and/or including any employee, agent or contractor of USGS and any employee, agent or contractor of a law firm, corporation, publication or other third party regarding coal tar and/or asphalt sealants and their alleged impact on the environment or human health. Please note that this request is not seeking law firm documents generated as part of an attorney/client relationship.

8. All lab data, field notes, chain of custody and QA/QC reports in the possession, custody or control of USGS related to any research, study or evaluation of coal tar or asphalt sealants or the alleged effect of coal tar or asphalt sealants on human health, aquatic organisms or the environment dated between January 1, 2003 and the present.

9. All lab data, field notes, chain of custody and QA/QC reports in the possession, custody or control of USGS generated as a result of any research, study or evaluation of soil, dust, water and/or sediment purportedly impacted by coal tar or asphalt sealants.

10. All USGS communications, including correspondence, e-mails, notes, reports or memoranda between or among any USGS employees, agents or contractors regarding trade associations that promote asphalt sealants, dated between January 1, 2003 and the present.

11. Copies of all photographs taken as part of or in connection with any research, study or evaluation regarding the alleged environmental impact of coal tar or asphalt sealants.

12. All communications, including correspondence, emails, notes, reports, memoranda and budgets regarding expenditures made and approved by USGS for coal tar and asphalt sealant research, studies or evaluations dated between January 1, 2003 and the present.

If USGS objects to all or any part of these requests, please alert me as soon as possible so that we may discuss those objections and attempt to resolve them. While any objections are pending, please produce copies of any documents to which USGS does not object. I will pay reasonable copying charges up to $250. I would kindly ask for an estimate before incurring any copying charges above $250.

Please call me at (312) 201-2707 to discuss your timeframe for compliance with this request, the format for production (*i.e.,* paper files, electronic files or both) and the cost to copy the documents.

Very truly yours,

WILDMAN, HARROLD, ALLEN & DIXON LLP

Leonard S. Kurfirst