TA-19 (r) 04-001

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Date: May 18, 2004
Refer to: ER2004-0277

RECEIVED
MAY 2004
NMED Hazardous Waste Bureau

Mr. James Bearzi, Bureau Chief
NMED – Hazardous Waste Bureau
2905 Rodeo Park Drive East
Building 1
Santa Fe, NM 87505-6303

SUBJECT: RESPONSE TO THE NOTICE OF DISAPPROVAL FOR THE ACA WORKPLAN FOR TECHNICAL AREA (TA) 19, FORMER EAST GATE LABORATORY

Dear Mr. Bearzi:

Attached please find the Laboratory's response to your Notice of Disapproval for the Accelerated Corrective Action Work Plan for Investigation and Remediation of Consolidated Solid Waste Management Unit 19-001-99 (Former TA-19/East Gate Laboratory).

If you have any questions regarding these responses, or to arrange a site visit, please contact Terry Rust at 505 665 8843.

Sincerely,

David McInroy, Deputy Project Director
Remediation Services
Los Alamos National Laboratory

Sincerely,

David Gregory, Federal Project Director
Department of Energy
Los Alamos Site Operations

DM/DG/RCR/dwt

1598

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IM-5, MS A150
RPF, MS M707

CERTIFICATION

CERTIFICATION BY THE RISK REDUCTION AND ENVIRONMENTAL STEWARDSHIP–REMEDIATION SERVICES (RRES–RS) PROJECT TECHNICAL REPRESENTATIVES

Document Title: **RESPONSES TO NMED COMMENTS ON THE ACA WORK PLAN FOR THE INVESTIGATION AND REMEDIATION OF CONSOLIDATED SOLID WASTE MANANGEMENT UNIT 19-001-99 (FORMER TA-19/EAST GATE LABORATORY)**

I certify under penalty of law that these documents and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gathered and evaluated the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violation.

Name: _____ Date: 5/19/04

David McInroy, Deputy Project Director
Remediation Services
Los Alamos National Laboratory

or

_____ Date: _____

Beverly A. Ramsey, Division Leader
Risk Reduction and Environmental Stewardship Division
Los Alamos National Laboratory

_____ Date: 5/20/04

David Gregory, Federal Project Director
Environmental Restoration Program
Department Of Energy/Los Alamos Site Office

or

_____ Date: _____

Herman LeDoux,
Assistant Area Manager of
Environmental Projects
Department Of Energy/Los Alamos Site Office

Responses to NMED Comments on the Accelerated Corrective Action Work Plan for the Investigation and Remediation of Consolidated Solid Waste Management Unit 19-001-99 (Former TA-19/East Gate Laboratory)

This response follows the organization of the NMED's Request for Supplemental Information (RSI), with general and specific comments and responses to those comments. The NMED RSI comments are provided verbatim, with LANL's responses following each comment.

General Comments

NMED Comment

1. *The Permittees must clarify if PCB-containing oil was used in any equipment (e.g., hydraulic equipment, electrical equipment, vacuum pumps, X-ray machines) at the site and where the equipment may have been located.*

LANL Response

1. The background/historical information included in the Accelerated Corrective Action (ACA) Work Plan provides all information that is currently available for the site, based on archival searches of historical records. If additional information regarding on-site historical use and/or storage of electrical equipment with PCB-containing oils is obtained, it will be included in the ACA Completion Report. Electrical equipment used and stored on site was likely associated with the main laboratory and battery buildings. The approximate location of these buildings is included in revised Figure 5 (see Attachment A).

NMED Comment

2. *The Permittees did not analyze for PCBs during past sampling events at the 25 previous sample locations. Therefore, the Permittees must field screen all past sample locations for PCBs using the field screening method described in section 5.3.4 of the ACA Work Plan. At least 20% of these samples (based on field screening results) must be analyzed in an off-site laboratory. See also Specific Comment No. 8.*

LANL Response

2. Field screening and fixed analytical sampling for total PCBs will be conducted as recommended by NMED. The locations that were originally sampled during the voluntary corrective action (VCA) and the Resource Conservation and Recovery Act (RCRA) facility investigation (RFI) will be sampled to the soil/tuff interface and field screened for PCBs. Figure 7 shows the locations that were sampled during the VCA and RFI at Solid Waste Management Unit (SWMU) 19-001-99 (see Attachment A).

NMED Comment

3. *If PCBs are detected, the Permittees must follow the NMED position paper "Risk-based Remediation of Polychlorinated Biphenyls at RCRA Corrective Action Sites" which states that "PCB-contaminated soil/sediments should be remediated to either a default concentration of 1 mg/kg or parts per million (ppm) total PCBs (defined as the sum of congeners, Aroclors, or homologues) or a risk-based PCB concentration level established through performing a health risk*

evaluation." NMED recommends the removal of any hot spots of PCBs detected over 1 ppm during field screening.

LANL Response

3. Enzyme immunoassay test kits will be used to field screen both soil and tuff samples for total PCBs at a detection limit of 0.5 ppm, which is close to the proposed threshold value of 1 ppm (the residential soil action level). The field analytical method is designed to detect total PCBs predominantly as Aroclor-1254; however, matrix interference and reactivity with other contaminants could result in elevated detections and false positives above the remediation threshold.

   Because of the semi-quantitative nature of field screening technologies, recommendations for PCB-contaminated soil removal will be based on fixed-laboratory analytical (i.e., confirmation) sampling results, rather than relying exclusively on field screening results. At least 20% of the field screening locations will be selected for fixed-laboratory analysis of total PCBs (more if the field screening results indicate wide-spread PCBs at the site). In the event that no PCBs are detected during field screening, the selection of confirmation sample locations will be biased toward potential contaminant sources (e.g. locations below the former pipeline outfalls and any apparent drainage/runoff rivulets on the upper mesa slope).

NMED Comment

4. *The Permittees must provide the following information on PAH screening as described in section 5.3.4 of the Work Plan.*

   - *Information on whether or not this testing has been used at other LANL sites before and, if so, which sites.*
   - *Information on the field screening data's correlation to the laboratory analytical data.*

LANL Response

4. Bullet 1: Field screening for total polynuclear aromatic hydrocarbons (PAHs) with Strategic Diagnostics, Inc. Rapid Assay® enzyme immunoassay test kit has not been done previously at LANL.

   Bullet 2: A correlation between field screening data and laboratory data is included in Attachment B as a paper entitled "Determination of PAHs in Soil and Water by a Magnetic Particle-based Enzyme Immunoassay System."

Specific Comments

NMED Comment

1. ***Section 2.1 Operational History, p.2***

The Permittees must provide information explaining the processes involved in the scintillation, irradiation, and spontaneous fission experiments conducted at the site. Specifically, the Permittees must address the type of equipment used, procedures conducted, type and amount of waste generated from the experiments, how sources were stored and disposed of, and how these activities may have impacted the site.

LANL Response

1. The information included in the ACA Work Plan is all that is currently available. If additional information regarding the operational history and processes involved in the scintillation, irradiation, and spontaneous fission experiments conducted on site is obtained, it will be included in the ACA Completion Report. See also the response to General Comment 1.

NMED Comment

2. ***Section 2.3 Relationship to Other SWMUs and AOCs, p.3***

The permittees must provide an explanation why consolidated SWMU 73-001(b)-99, SWMUs associated with TA-26 D-Site activities, and AOC 00-018(b) are being addressed in this report as having potentially affected consolidated SWMU 19-001-99 given their locations. The Permittees must also submit information on if the wastes generated at the neighboring SWMUs and AOC were ever disposed of at SWMU 19-001-99.

LANL Response

2. Consolidated SWMU 73-001(b)-99 (the Airport Landfill), SWMUs associated with TA-26 D-Site activities, and Area of Concern (AOC) 00-018(b) (the Bayo Canyon Wastewater Treatment Plant) are the LANL environmental restoration sites in closest proximity to the ACA investigation area (SWMU 19-001-99). Information on proximal sites is provided per the general work plan format used by LANL to provide context for site investigations. There is no evidence of impact to SWMU 19-001-99 from the proximal sites. The nearest proximal site is over ½ mile away. There has not been any record or other evidence to indicate that any wastes generated at the proximal SWMUs and the AOC were ever disposed of at SWMU 19-001-99.

NMED Comment

3. ***Section 2.4 Contamination Transport Mechanisms and Potential Receptors, p. 4, paragraph 1***

Permittees Statement: *"The primary mechanisms of contaminant release at SWMU 19-001-99 are related to the historical laboratory operations at the site, specifically sanitation systems that served the site facilities and surface runoff at the site."*

NMED Comment: *This statement specifically addresses the sanitation systems as primary mechanisms of contaminant release. Because limited documentation of historical operations at the site is available, the Permittees must consider other mechanisms of contaminant release at the site (e.g., surface disposal (SWMU 19-002) and stormwater migration).*

LANL Response

3. Other mechanisms of contaminant release and transport at the site (e.g., surface disposal area SWMU 19-002 and stormwater migration) were considered in the ACA Work Plan. Proposed sampling will target eight locations in the depositional zones associated with main drainage channels present at the lower reaches of the mesa slopes in order to define a perimeter around the area of potential residual contamination at the site. Furthermore, additional characterization of the surface disposal area will be accomplished by revisiting the historical sampling locations at SWMU 19-002 (as recommended in NMED General Comment 2); see Figure 6 in the ACA Work Plan.

NMED Comment

4. ***Section 2.5 Waste Inventory, p. 5, paragraph 1:***

   Permittees Statement: *"Radioactive materials handled at the site were of three known types: (1) actinides used for spontaneous fission experiments in microgram quantities; (2) a cobalt-60, 300-curie source, used for irradiation as late as 1961 (cobalt-60 has a 5.27 year half-life); and (3) a radioactive lanthanum source used in irradiation experiments."*

   NMED Comment

   - *The Permittees must specify which actinides were used in the spontaneous fission experiments, identify where they were stored, and explain how they were used.*
   - *The Permittees must clarify what constitutes "microgram quantities" and how many times "microgram quantities" were used over the years.*
   - *The Permittees must specify the quantity of lanthanum-140 used in the irradiation experiments through time.*

LANL Response

4. Bullet 1: As stated previously, the background/historical information included in the ACA Work Plan contains all information that is currently available about the equipment, processes, experiments, and materials used at the former East Gate Laboratory.

   Bullet 2: The term "microgram quantities" is used to describe minute fractions of a gram. However, available historical information does not indicate the frequency in which experiments involving microgram quantities of actinides were conducted.

   Bullet 3: Based on available background information, the exact quantity of the lanthanum-140 irradiation source used at the site is unknown. As stated in the ACA Work Plan, this lanthanum-140 is derived from barium-140, and both of these radionuclides have very short half-lives (40 hours and 12 days, respectively); therefore, these isotopes would currently not be detected at the site, regardless of the quantity used during historical operations at the site.

   Any additional information regarding the operational history of the former East Gate Laboratory and the type of equipment, processes, experiments, and materials used on site will be included in the ACA Completion Report (see also the response to Specific Comment 1).

NMED Comment

5. ***Section 2.5 Waste Inventory p. 5, paragraph 2:***

Permittees Statement: *"A certification dated October 11, 1972, indicated that the septic tank for the guard house was free of HE and radioactive material (LANL 1997, 71468)."*

NMED Comment: *The Permittees must provide information on the type of investigation performed to obtain the certificate and the type/quantity of samples collected, if any, the analyses conducted, and the results of the screening and/or analyses.*

LANL Response

5. Historical information presenting the specific procedures associated with the septic system certification dated October 11, 1972, could not be located for review. However, more recent characterization of the septic system (SWMU 19-001) was conducted as part of the RFI in 1997.

Based on information from the RFI Report (LANL 1997, 71468) describing structure removal and subsurface sampling, the septic tank associated with the guard house (e.g., retreat building) was removed on July 17, 1997, and two subsurface samples were collected below this structure.

Subsurface soil and tuff samples associated with the septic tank were collected at the north and south ends of the excavation at a depth of 10 ft below ground surface (bgs). Additional samples were collected along the supply and discharge lines associated with the septic tank. These samples were collected at depths of approximately 3 ft. No soil or tuff staining or other visible evidence of contamination was observed during the removal of the septic system.

Soil and tuff samples were analyzed for metals, volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), and radionuclides. A total of seven samples were collected below the septic system, two below the septic tank, and five below the distribution lines. Metals, VOCs, and radionuclides were detected in most of these samples but at concentrations well below their respective screening action levels (SALs). SVOCs were detected in four of seven samples analyzed, where three polynuclear aromatic hydrocarbon (PAH) compounds [Benzo(b)fluoranthene, Benzo(a)pyrene, and Indeno(1,2,3-cd)pyrene] were detected at concentrations above their respective SALs.

NMED Comment

6. ***Section 2.7.1 1995 VCA, p. 6***

NMED Comment: *The historical samples collected at this SWMU are inadequate to determine nature and extent for the following reasons:*

- *The VCA Report for SWMU 19-002 only presents values above either background concentrations, or SALs. In the cases where the SALs exceed the background concentrations, only the values above the SALs are presented. The Permittees must present all of the data above background concentrations.*
- *All but three of the samples collected during the VCA were analyzed using a mobile laboratory. This may be adequate to help direct a field investigation (e.g., prioritizing sampling for lab analysis) but this data cannot be used to determine the extent of contamination at a site because of concerns regarding data quality (e.g., precision and*

accuracy) compared with fixed analytical labs. In addition, several metals were detected much above their respective background concentrations. For these reasons, the Permittees must resample the locations in the VCA Report (or close to them if the exact locations cannot be identified) and subsequent depths if contamination is found. The Permittees may use field screening to direct the sampling and to determine which samples will be sent to an off-site laboratory for analysis.

LANL Response

6. Bullet 1: Table 3 of the ACA Work Plan summarizes the analytical data from SWMU 19-002 that were collected during the 1995 VCA at the site. All analytical data acquired during the ACA investigation used for making decisions about soil removal, potential risk, and nature and extent of contamination at the site will be provided with the ACA Completion Report, including the results for all chemicals greater than background.

   Bullet 2: The sample locations proposed in the ACA Work Plan were based on possible migration of residual contamination downgradient from the site, including locations in the same drainages and general area of the historical sample locations. As requested by NMED, each of the VCA sample locations will be revisited, sampled, and screened for total PCBs, PAHs, and metals (see also the responses to General Comments 2, 3, and 4). The VCA sample locations are shown on Figure 7.

   Sampling protocol will follow the methodology described in the ACA Work Plan, but modified to include a greater number of samples analyzed at a fixed laboratory. At least 20% of the field screening samples will be submitted to an off-site, fixed laboratory for confirmation analysis. Field screening will enable the selection of confirmation samples based on the range of concentrations observed for total PCBs, PAHs, and metals. Samples at the upper limit of the concentration range (top 20%) will be submitted for confirmation analysis. However, because of the semi-quantitative nature of field screening data, it will not be used for making decisions about soil removal, potential risk, and nature and extent of contamination at the site. Only validated and qualified analytical data from confirmation samples submitted to a fixed laboratory will be used for these purposes.

NMED Comment

7. ***Section 5.3.3 Surface and Subsurface Sampling, p. 15, paragraph 2***

   Permittees Statement: "...and samples will be collected from two distinct horizons and depths: surface soils (0-0.5 ft [0.1m] and the soil/weathered tuff interface (3.5–4.0 ft [1.0m] or less, depending on auger refusal resulting from the presence of competent tuff)."

   NMED Comment: Sampling depths should be determined based on the presence (or absence) of contamination. The two sampling intervals 0–0.5 and 3.5–4.0 ft are good depths to begin with, but sampling should not be limited to those specific depths. If contamination is present at the 3.5- to 4.0-interval, sampling should continue to further depths in order to define the vertical extent of contamination.

LANL Response

7. Investigative sampling and field screening will be conducted to determine the nature and lateral and vertical extent of contamination at SWMU 19-001-99. Based on site conditions, the sampling depths at some locations may be either less than or greater than 4 ft bgs depending on where the soil/tuff interface is encountered.

NMED Comment

8. ***Section 5.3.5, Fixed Laboratory Analytical Methods, p. 16, paragraph 1:***

Permittees Statement: *"Approximately 10% of the surface and subsurface soil or tuff samples collected from the 31 grid points inside AOC C-19-001 and all the samples collected from the mesa slopes will be sent to an off-site contract laboratory for confirmation analysis. The confirmation samples will be selected based on the range of concentrations observed during field screening for specific constituents (total PAHs, PCBs, and metals). Samples at the upper limit of the concentrations range (top 10%) will be submitted for confirmation analysis."*

NMED Comment:

- *The Permittees must send at least 20% of the 62 field screening samples collected from inside AOC C-19-001 for off-site fixed laboratory analysis instead of the proposed 10%.*
- *The Permittees must collect for laboratory analysis the samples with the greatest apparent contamination to use as part of the risk assessment. The Permittees must collect for laboratory analysis the samples with the least amount of apparent contamination to show extent of contamination.*
- *The Permittees must explain if all samples will be field screened for PCBs, PAHs, and metals.*
- *The Permittees must include all field screening data and the correlation between the field screening data and off-site laboratory analyses in the investigation report (field screening are data not to be used as part of any risk assessments).*

LANL Response

8. Please see the LANL responses to NMED General Comment 2 and Specific Comment 6. Additional clarification is provided below:

Bullet 1: At least 20% of the 62 field screening samples collected from AOC C-19-001 will be submitted to an off-site laboratory for confirmation analysis. In addition, 20% of the original 23 VCA sample locations will also be submitted for confirmation analysis.

Bullet 2: Field screening results indicating the highest apparent contamination will be used to select confirmation samples to be submitted to an off-site laboratory for confirmation analysis, and the confirmation sampling results will be used for risk assessment. Assuming there is a wide distribution of contaminant concentrations on site, both field screening and confirmation sampling results will be used to characterize AOC C-19-001. Locating the sample points using a systematic grid (with a random start) ensures adequate spatial coverage to define the lateral and vertical extent of contamination within the AOC.

Bullet 3: Field screening of all proposed ACA sample locations and historical VCA sample locations will be conducted for total PCBs, total PAHs, and metals. However, the historical RFI sampling locations will only be field screened for total PCBs since these samples were previously analyzed for SVOCs (including PAHs) and total metals via an off-site laboratory. See also responses to General Comments 2, 3, and 4.

Bullet 4: All field screening data, qualified fixed-laboratory analytical data, and historical data will be summarized in the ACA completion report, including the correlation between the field screening and fixed laboratory analytical techniques. Field screening data will not be used as part of the risk assessment data set. See also the response to General Comment 4 and Specific Comment 6.

NMED Comment

9. ***Figure 5 Proposed sampling locations for the mesa top at SWMU 19-001-99, p. 24:***

The Permittees must provide a figure that depicts the proposed sampling locations with the former building locations. Because at least one of the former building locations is known, the Permittees must provide a justification for proposing random grid sampling instead of judgmental sampling.

LANL Response

9. Figure 5 was revised to depict the proposed new soil and tuff sampling locations in relation to the approximate locations of the former buildings at the site.

The justification for the proposed sample design is described in the remainder of this response. In summary, the non-parametric (random start point) systematic grid sample design was developed for complete characterization of AOC C-19-001, amplified by the removal of areas from the design where sampling cannot occur (e.g., rock outcrops and mature tree trunks). The random grid sampling is adequate for characterizing the extent of contamination at the AOC, as detailed below:

A non-parametric systematic sampling grid (based on a random starting point) was developed using Visual Sample Plan version 2.2 to enable statistically-based environmental decision-making for AOC C-19-001 as a whole. The non-parametric systematic design requires fewer assumptions and allows for more uncertainty about the statistical distribution of contaminant concentration values at the site. Locating the sample points over a systematic grid with a random start ensures adequate spatial coverage of the site. A judgmental sampling scheme focused toward the buildings and/or other potential contaminant sources allows only for decision-making at the specific sampling point(s) and would not be valid for risk assessment and remediation decisions concerning the entire AOC.

NMED Comment

10. ***Figure 6 Proposed sampling locations for the mesa slopes at SWMU 19-001-99, p.25***

The drainages on the figure are not well defined. The Permittees must explain how the drainages and sampling locations will be identified. The Permittees must identify and sample any areas of sediment accumulation.

LANL Response

10. The drainages depicted in Figure 6 were inferred from a topographic map of the site developed using a GIS database. Initial field reconnaissance was conducted as part of the planning and development of the ACA Work Plan to identify erosional features and depositional areas on the mesa slopes. The eight proposed sampling locations (shown in Figure 6) are designed to target the depositional areas associated with drainage channels on the lower reaches of the mesa slopes and capture contaminant migration via runoff from the AOC and SWMUs situated on the top and upper slopes of the mesa.

NMED Comment

11. ***Section D-2.1 Optimal Sample Design for SWMU 19-001-99, p. D-5, paragraph 2***

Permittees Statement: *"Sample locations were derived using the Wilcoxon Signed-Rank (One-Sample) Test statistical method (Gilbert 1987, 56179)."*

NMED Comment: *Sample locations cannot be derived based on the Wilcoxon Signed-Rank Test method because this statistical test is used for analytical data, and not used to identify sample locations. The Permittees must clarify this statement.*

LANL Response

11. The Wilcoxon Signed-Rank test method was applied to the historical data for lead at SWMU 19-001-99 to determine the appropriate number of samples needed to adequately characterize AOC C-19-001. Assuming that a wide distribution of contaminant concentrations may be found on site, a non-parametric systematic sampling grid was developed using Visual Sample Plan version 2.2 to determine the optimal sampling design and spatial distribution of sampling points to characterize the AOC (see Figure 5).

NMED Comment

12. ***Section D-2.1 Optimal Sample Design for SWMU 19-001-99, p. D-5, paragraph 4***

Permittees Statement: *"SWMU 19-001-99 Lower Mesa Slopes: Seven sampling locations at the down gradient extent of..."*

NMED Comment: *The Permittees must clarify if seven or eight samples will be collected in this area. Section 5.3.3 states "...and from eight locations on the mesa slope..."*

LANL Response

12. Proposed field activities at SWMU 19-001-99 will target eight sampling locations in the depositional areas associated with main drainage channels present at the lower reaches of the mesa slopes in order to define a perimeter around the area of residual contamination.

NMED Comment

13. Section D-3.3 Total Number of Samples: Equation and Parameters, p. D-6, paragraph 2

LANL Statement: *"The equation used to calculate the number of samples is based on a Wilcoxon Signed-Ranks test (Gilbert 1987, 56179)."*

NMED Comment: *NMED was unable to find the referenced equation used to calculate the number of samples. However, the equation is consistent with similar formulas used for calculating the number of samples. The Permittees must provide the page number for the equation in the reference and indicate the values of each parameter used in the formula presented in section D-3.3, D-6.*

LANL Response

13. The number of samples is determined using the Wilcoxon Signed-Ranks (one-sample) test by applying the equation referenced in "Version 2.0 Visual Sample Plan (VSP) Models and Code

Verification" (Gilbert et al. 2002, 85930). The values associated with each parameter used in the equation are shown in parentheses next to the definition of these parameters (below the equation presented in Section D-3.3 of the Work Plan).

NMED Comment

14. ***Section D-3.5 Recommended Data Analysis, p. D-7, paragraph 3***

Permittees Statement: *"Assuming the data are adequate, at least one statistical test will be performed to compare the data collected with the threshold of interest."*

NMED Comment: *LANL must specify which statistical test(s) will be performed to compare the data with the threshold and how they will be used.*

LANL Response

14. A statistical software program developed by the U.S. Environmental Protection Agency, ProUCL version 3.0(available at www.epa.gov/nerlesd1/tsc/software.htm), will be used to evaluate the data distribution and calculate the upper confidence limit (UCL) of the data set, and will be used for comparison to risk thresholds for human and ecological receptors (e.g., SALs).

REFERENCES

The following list includes all documents cited in this document. Parenthetical information following each reference provides the author, publication date, and ER ID number. This information is also included in text citations. ER ID numbers are assigned by the RRES-RS Records Processing Facility (RPF) and are used to locate the document at the RPF.

Gilbert, R. O., 1987. *Statistical Methods for Environmental Pollution Monitoring*, Van Nostrand Reinhold, New York. (Gilbert 1987, 56179)

Gilbert, R. O., J. E. Wilson, R. F. O'Brien, D. K. Carlson, D. J. Bates, B. A. Pulsipher, and C. A. McKinstry, 2002. "Version 2.0 Visual Sample Plan (VSP): Models and Code Verification," U.S. Environmental Protection Agency report, Pacific Northwest National Laboratory, Richland, Washington. (Gilbert et al. 2002, 85930)

LANL (Los Alamos National Laboratory), September 1997. "RFI Report for TA-19, PRSs 19-001, 19-003, and C-19-001, Field Unit 1," Los Alamos National Laboratory document LA-UR-97-3791, Los Alamos, New Mexico. (LANL 1997, 71468)

Attachment A

Revised Figures

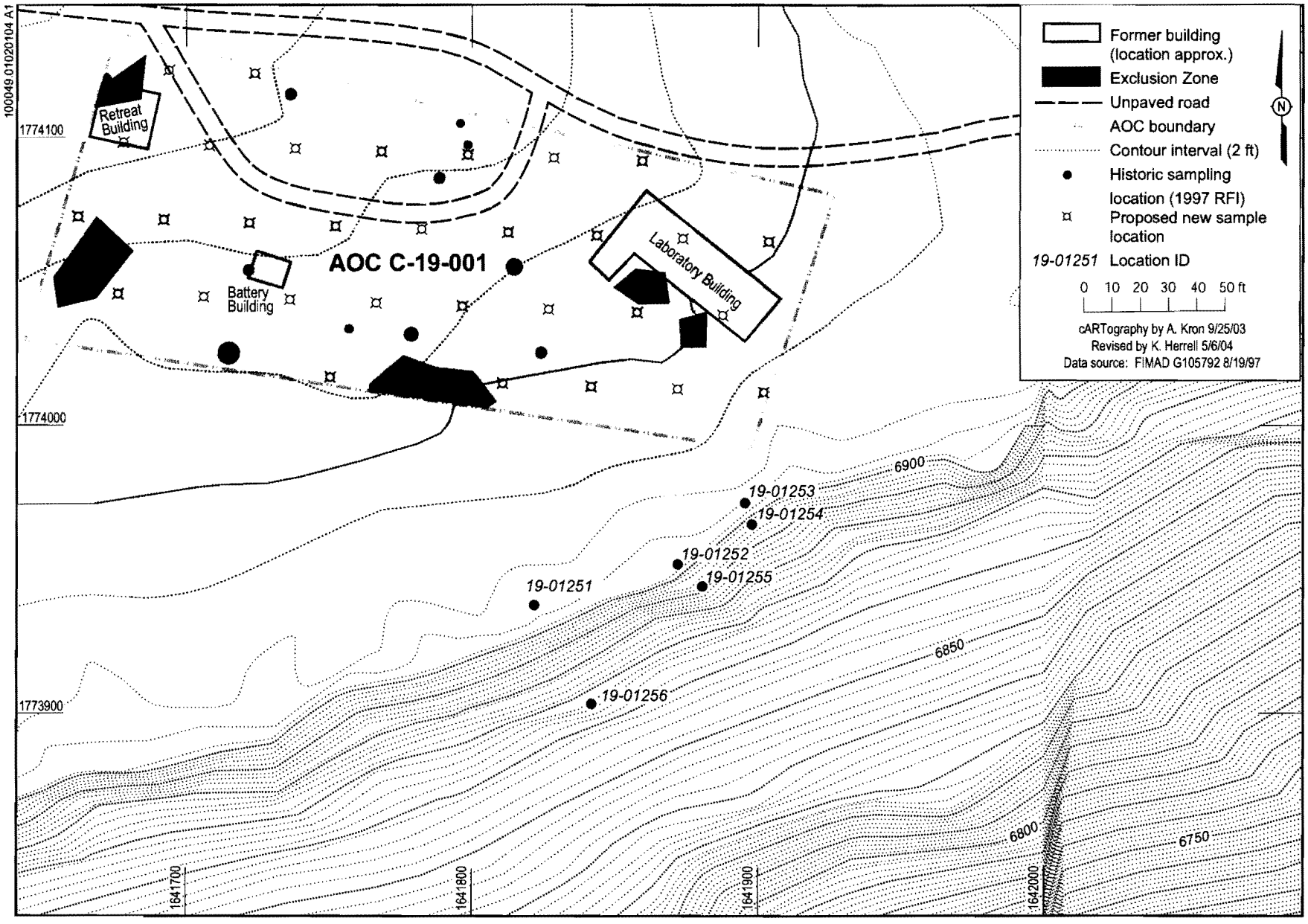

Figure 5. **Proposed New Soil and Tuff Sampling Locations in Relation to Former Buildings on Site at Consolidated Solid Waste Management Unit 19-001-99.**

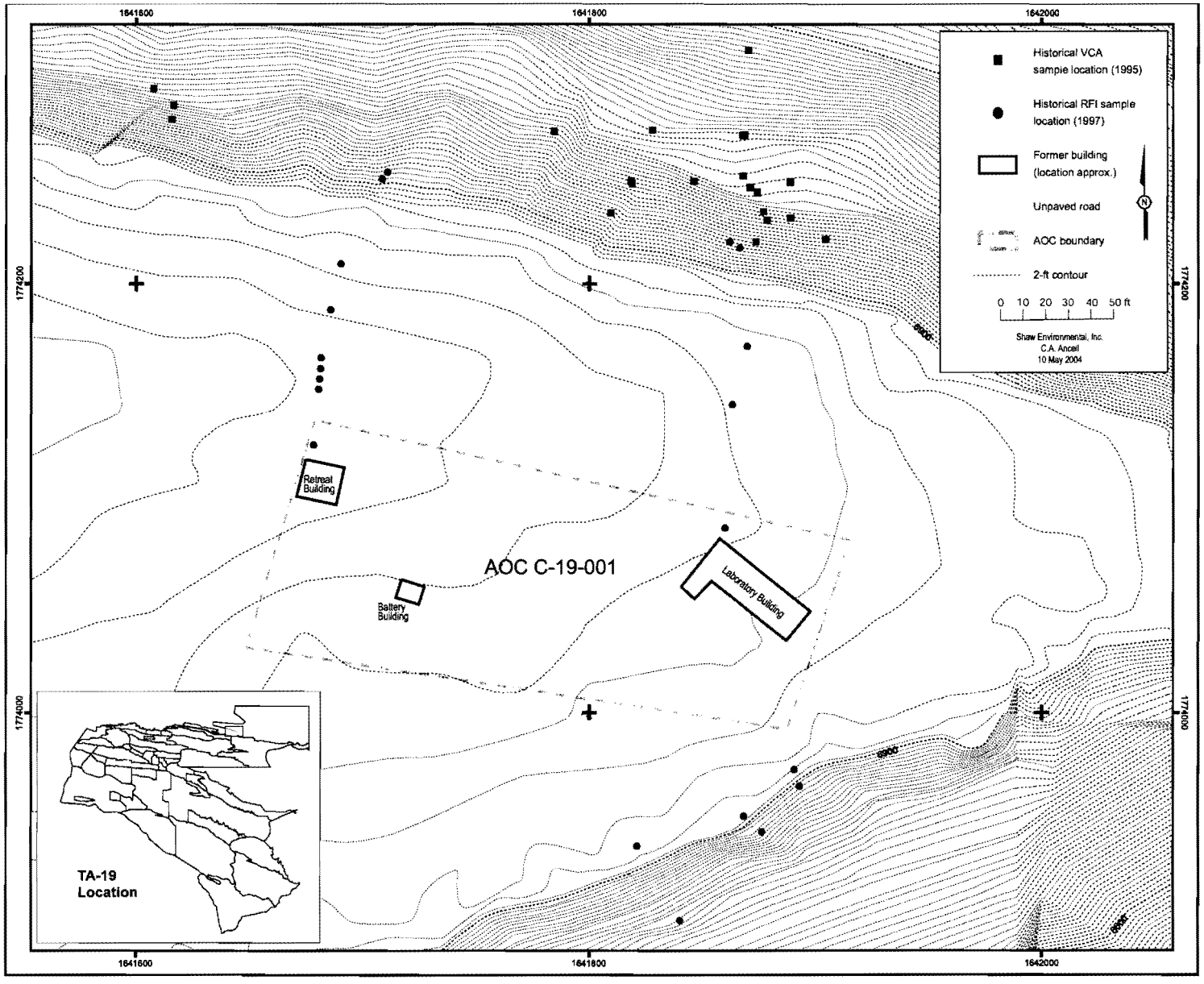

Figure 7. VCA sample locations to be revisited, sampled, and screened for total PCBs, PAHs, and metals at consolidated SWMU 19-001-99

Attachment B

Information on PAH Field Screening Test

DETERMINATION OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN SOIL AND WATER BY A MAGNETIC PARTICLE-BASED ENZYME IMMUNOASSAY SYSTEM.

Fernando M. Rubio, Timothy S. Lawruk, Charles E. Lachman and David P. Herzog, Ohmicron Environmental Diagnostics, 375 Pheasant Run, Newtown, Pennsylvania 18940; James R. Fleeker, North Dakota State University, P.O. Box 5516, Fargo, North Dakota 58105

Presented at the Fourth International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Tropicana Hotel, Las Vegas, Nevada, February 22-24, 1995.

ABSTRACT

Use of immunoassays as field-screening methods to detect environmental contaminants has increased dramatically in recent years. Immunochemical assays are sensitive, rapid, reliable, cost-effective and can be used for lab or field analysis. A magnetic particle-based immunoassay system has been developed for the quantitation of Polynuclear Aromatic Hydrocarbons (PAHs) in soil and water. Paramagnetic particles used as the solid-phase allow for the precise addition of antibody and non-diffusion limited reaction kinetics. The magnetic particle-based immunoassay is ideally suited for on-site investigation and remediation processes to delineate PAH contamination. This system includes easy-to-use materials for collection, extraction, filtration and dilution of soil samples prior to analysis by immunoassay. When analyzing water samples, a simple dilution of the sample with methanol is performed during sample collection. The method detects PAHs, including anthracene, chrysene, fluoranthene, phenanthrene, pyrene and benzo[a]pyrene, at sub-parts-per-million levels in soil and at less than 1 ppb in water. The typical precision of the assay (within assay) in soil and water is less than 15% and 12%, respectively. Recovery studies (based on phenanthrene) from soil averaged 108%, and 107% from water. The analysis of soil samples by this ELISA correlate well with Method 8310, yielding a correlation coefficient (r) of 0.963; when water samples were compared to method 8270, a correlation (r) of 0.987 was obtained. The application of this ELISA method permits the cost-effective evaluation of samples with minimal solvent disposal and can result in savings of time and money. The system's flexibility allows the analysis of PAHs in many other sample matrices with minimum sample preparation.

INTRODUCTION

Polycyclic or polynuclear aromatic hydrocarbons (PAHs) are a group of compounds composed of two or more fused aromatic rings. The U.S. EPA has selected 16 unsubstituted PAHs as Consent Decree priority pollutants for regulatory purposes. Some of the four, five and six-ring PAHs such as chrysene, benzo[a]pyrene and indeno[1,2,3-cd]pyrene are considered to be possible or probable human carcinogens (U.S. EPA, 1985). The two and three-ring PAHs such as naphthalene, anthracene, and phenanthrene are considered non-carcinogenic and found as a component of certain grades of fossil fuels.

PAHs are introduced into the environment as a product of natural and fossil fuel combustion. Volcanic eruptions and forest fires are among the major sources of naturally produced PAHs. However, activities attributed to fossil fuel combustion sources, such as automobiles, coking plants, asphalt production, and manufacturing facilities that use fossil fuels, have dramatically increased the quantity of PAHs in the environment. Wood preserving sites that use creosote as a preservative, petrochemical

waste disposal sites, and leaking underground fuel storage tanks, have also contributed to the widespread contamination of PAHs in the environment.

The large number of sites contaminated with PAHs in soil and groundwater and the reenactment of key environmental legislation (Safe Drinking Water Act, Superfund Amendment Reauthorization Act) has led federal and state agencies to mandate clean-up. Federal and state agencies have set various regulatory levels for PAHs in soil; however, the usual concentrations of interest are 1 ppm and 10 ppm. In groundwater, the levels of interest are usually below 100 ppb. The analysis of PAH contamination in environmental samples is typically performed by GC/MS or HPLC methods, which are accurate and precise but can be time-consuming and expensive. This poster describes a magnetic-particle solid-phase immunoassay method for the analysis of PAHs in soil and water samples. Immunoassays have the advantage of being rapid and less expensive than GC/MS or HPLC, as well as field-portable.

The principles of enzyme linked immunosorbent assays (ELISA) have been described (Hammock and Mumma, 1980). Magnetic particle-based ELISAs have previously been described and applied to the detection of pesticide residues (Itak et al, 1993; Lawruk et al, 1993; Itak et al, 1992; Lawruk et al, 1992; Rubio et al, 1991). These ELISAs eliminate the imprecision problems that may be associated with antibody coated plates and tubes (Harrison et al, 1989; Engvall, 1980) through the covalent coupling of antibody to the magnetic particle solid-phase. The uniform dispersion of particles throughout the reaction mixture allows for rapid reaction kinetics and precise addition of antibody. The PAH magnetic-based ELISA described in this paper combines antibodies specific for PAHs with enzyme labeled PAHs. The presence of PAHs in a sample is visualized through a colorimetric enzymatic reaction and results are obtained by comparing the color in sample tubes to those of calibrators.

MATERIALS AND METHODS

Amine terminated superparamagnetic particles of approximately 1 um diameter were obtained from Perseptive Diagnostics, Inc. (Cambridge, MA). Glutaraldehyde (Sigma Chemical, St. Louis, MO). Rabbit anti-PAHs serum and PAH-HRP conjugate (Ohmicron, Newtown, PA). Hydrogen peroxide and TMB (Kirkegaard & Perry Labs, Gaithersburg, MD). PAHs and related compounds, as well as non-related cross-reactants (Chem Service, West Chester, PA).

The anti-PAH coupled magnetic particles were prepared by glutaraldehyde activation (Rubio et al, 1991). The unbound glutaraldehyde was removed from the particles by magnetic separation and washing four times with 2-(N-morpholino) ethane sulfonic acid (MES) buffer. The PAH antiserum and the activated particles were incubated overnight at room temperature with agitation. The unreacted glutaraldehyde was quenched with glycine buffer and the covalently coupled anti-PAH particles were washed and diluted with a Tris-saline/gel preserved buffer.

The various PAH compounds used during cross-reactivity studies were diluted in DMF to obtain a stock concentration of 1 mg/mL. The stock was further diluted in PAH diluent to obtain concentrations of 10 , 1, 0.1, 0.01, 0.001, and 0.0001 ppm. The creosote sample was diluted in methanol to obtain a stock concentration of 1 mg/mL; the stock was further diluted as described previously. After dilution, the diluted compounds were analyzed as samples in the assay.

When analyzing soil samples, a simple extraction was performed prior to analysis: 10 g of soil and 20 mL of a methanolic solution are added to a soil collector (Figure 1). The collector was shaken vigorously for 1 minute and the mixture allowed to sit at least five minutes. The cap of the soil collector was then replaced with a filter cap and the extract collected in a small glass vial. The filtered extract was then diluted 1:50 in PAH zero standard and assayed.

Water samples were collected in glass vessels with teflon lined caps. Immediately upon collection, samples were diluted with methanol 1:3 (1 part methanol:3 parts sample) to prevent adsorptive losses to the glass containers.

Diluted soil extract or water samples (250 uL) and horseradish peroxidase (HRP) labeled PAH (250 uL) were incubated for 30 minutes with the antibody coupled solid-phase (500 uL). A magnetic

field was applied to the magnetic solid-phase to facilitate washing and removal of unbound PAH-HRP and eliminate any potential interfering substances. The enzyme substrate (hydrogen peroxide) and TMB chromogen (3,3',5,5'-tetramethyl benzidine) were then added and incubated for 20 minutes. The reaction was stopped with the addition of acid and the final colored product was analyzed using the RPA-I RaPID Analyzer™ by determining the absorbance at 450 nm. The observed absorbance results were compared to a linear regression line using a log-logit standard curve prepared from calibrators containing 0, 2, 10, and 50 ppb of phenanthrene. If the assay is performed in the field (on-site), a battery powered photometer such as the RPA-III™ can be used.

RESULTS AND DISCUSSION

Figure 2 illustrates the mean standard curve for the PAH calibrators collected over 30 runs; error bars represent two standard deviations (SD). This figure shows the typical response of the assay and the reproducibility of the standard curve from run-to-run. The displacement at the 2 ppb level is significant (81.3% B/Bo, where B/Bo is the absorbance at 450 nm observed for a sample or standard divided by the absorbance at the zero standard). The assay sensitivity in diluent based on 90% B/Bo (Midgley et al, 1969) is 0.7 ppb. When analyzing water samples, the assay has a range of 0.9 to 67 ppb. The assay range when analyzing soils in conjuction with the PAHs Sample Extraction Kit is 0.2 to 5 ppm as a result of sample dilution.

A precision study was conducted using four surface and groundwater samples fortified with phenanthrene at four concentrations. The samples were diluted 1:3 with methanol and assayed 5 times in singlicate per assay on five different days. The results are shown in Table 1. Coefficients of variation (%CV) within and between day (Bookbinder and Panosian, 1986) were less than 12% and 10% respectively.

In another precision study, ten samples of two soils were weighed on a balance or measured by packed volume in the soil collector. The samples were then extracted and diluted (as described in the Methods Section), followed by assaying in duplicate in one assay. Results are shown in Table 2. The overall coefficient of variation for PAHs measurement using components of the Soil Collection and the PAHs Soil Extraction Kit with analysis by the PAHs RaPID Assay® was determined to be less than 18% in both cases.

Table 3 and Figure 3 summarize the cross-reactivity data of the PAHs RaPID Assay for various polynuclear aromatic hydrocarbons and petroleum products. The percent cross-reactivity was determined as the amount of analog required to achieve 50% B/Bo. The broad specificity of the antibody used, allows for the detection of a majority of the PAHs. Many non-structurally related organic compounds demonstrated no reactivity at concentrations up to 10,000 ppb (data not shown).

Table 4 summarize the accuracy of the PAHs RaPID Assay in soil samples. Thirteen different soil types were fortified with phenanthrene at 1 ppm. The samples were extracted and diluted as described above, followed by analysis in the immunoassay. The average recovery of phenanthrene in the samples was 108% with one sample (Alkali Lake) giving higher recoveries. The reason for the higher recovery on that sample is currently under investigation. To demonstrate the detection of other PAHs in soil, anthracene, benzo[a]pyrene, chrysene, fluoranthene, and pyrene, were spiked into four soils at 1 ppm; recoveries of those PAHs (data not shown) agreed closely with the predicted response based on the previously reported cross-reactivity data for the assay.

Table 5 summarizes the accuracy of the PAH ELISA in water. Four ground water samples were spiked with phenanthrene at the following levels: 5.0, 7.5, 20, and 40 ppb. Phenanthrene in the samples were recovered correctly in all cases with an average assay recovery of 107%.

Correlation of twenty-five samples, including both field contaminated soils and analytically spiked soils, analyzed by the ELISA method (y) and HPLC EPA Method 8310 (x) is illustrated in Figure 4. The regression analysis yields a correlation of 0.931 and a slope of 2.02 between methods. The lower values obtained with Method 8310 could be due to lower recoveries during the soxhlet extraction or to higher

values obtained by the ELISA to >100% cross-reactivity of some of PAHs in the ELISA system. Figure 5 illustrates the correlation of HPLC Method 8310 (y) versus the phenanthrene spike concentration (x) on 15 of the above soils; the regression analysis obtained was 0.991 with a slope of 0.49, indicating a bias with the HPLC method.

Figure 6 illustrates the correlation of 30 water samples between the ELISA (y) and Method 8270 (x). The regression analysis yields a correlation of 0.987 and a slope of 1.10 between methods.

SUMMARY

This work describes a magnetic particle-based ELISA for the detection of PAHs and its performance characteristics in soil and water samples. The assay compares favorably to HPLC or GC/MS determinations, is faster, and eliminates the need for expensive instrumentation and solvent disposal. The ELISA exhibits good precision and accuracy which can provide consistent monitoring of environmental samples. Using this ELISA, forty (40) results from soil samples can be obtained in less than two hours without the variability encountered with antibody coated tubes and microtiter plates (e.g. coating variability, antibody leaching, etc.). This system is ideally suited for adaptation to on-site monitoring of PAHs in water, soil, and solid waste samples.

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Table 1

Precision of PAHs Measurement in Water

Pool Number	Pool 1	Pool 2	Pool 3	Pool 4
Replicates	5	5	5	5
Days	5	5	5	5
N	25	25	25	25
Mean (ppb)	5.9	8.9	24.4	44.1
% CV (within)	9.1	3.7	5.7	2.9
% CV (between)	13.8	11.5	8.8	8.1

Table 2

Precision of PAHs Measurement in Soil

Soil:	**Wisconsin**		**Joshua Tree**	
Sample Collection Method	weight	volume	weight	volume
Replicates	10	10	10	10
Mean (ppm)	1.57	1.18	1.43	1.26
% CV (total)	17.6	17.8	14.3	14.4

Table 3

Specificity (Cross-Reactivity)

Compound	90% B/Bo LDD (ppb)	50% B/Bo ED50 (ppb)	% Cross Reactivity
Phenanthrene	0.70	16.5	100
Anthracene	0.54	12.5	132
Fluoranthene	0.32	4.7	351
Chrysene	0.40	7.8	212
Pyrene	0.70	15.1	214
Benzo(a)Pyrene	0.50	6.9	239
Fluorene	1.65	35.2	47
Benzo(b)fluoranthene	0.91	54.2	30
Benzo(k)fluoranthene	0.77	524	3
1,12 Benzoperylene	14.7	>1000	<2
1,2:5,6 Dibenzanthracene	25.7	>1000	<2
Indeno (1,2,3-c,d)pyrene	0.78	27.2	61
Naphthalene	65	>1000	<2
Acenaphthalene	12.9	688	2
Acenaphthylene	10	447	4
1.2 Benzanthracene	0.77	28.4	58
1-Methylnaphthalene	28.2	1330	1.2
2-Methylnaphthalene	28.2	802	2.1
Aroclor 1242	37.5	1450	1.8
Aroclor 1248	41.0	5330	0.4
Aroclor 1254	>10000	>10000	<0.2
Aroclor 1260	>10000	>10000	<0.2
Benzene	>10000	>10000	<0.2
Toluene	>10000	>10000	<0.2
Phthalate	>10000	>10000	<0.2
Pentachlorophenol	340	>10000	<0.2
Biphenyl	15.9	703	2.8
CCA	>10000	>10000	<0.2
Creosote	1.1	16.6	117
Fuel Oil #6	5	53.7	31
Gulf Diesel Fuel	19.6	497	3
Sunoco Home Heating Fuel	12.8	292	6
Kerosine	1250	>10000	<0.1
Jet A Fuel	>10000	>10000	<0.1
Regular Gasoline	1000	>10000	<0.1
Premium Gasoline	597	>10000	<0.1

B/Bo = Absorbance at 450 nm observed for a sample or standard divided by the absorbance at the zero standard.

% Cross Reactivity = Concentration of phenanthrene exhibiting 50% inhibition (16.5 ppb) divided by the 50% inhibition of a compound x 100.

Table 4

Phenanthrene Recovery From Different Soil Types

Soil Sample	Neat (ppm)	Total (ppm)	Recovered (ppm)	Recovery (%)	Soil Type
Alkali Lake	0.50	2.19	1.69	169	loamy sand
Beardon	0.42	1.45	1.03	103	clay loam
Holland	2.30	3.22	0.92	92	silt loam
Joshua Tree	0.07	1.28	1.21	121	sand
Levittown	4.70	5.82	1.12	112	silt loam
Muck	2.90	3.94	1.04	104	organic potting
Munin	0.17	1.23	1.06	106	clay loam
Piscataway	2.69	3.67	0.98	98	sandy loam
Sagamore	4.40	5.56	1.16	116	silty clay loam
Sharkey	0.68	1.92	1.24	124	clay loam
Tennessee	0.30	1.29	0.99	99	sandy loam
Wiscosin	0.72	1.80	1.08	108	loam
Virginia	1.54	2.64	1.10	110	loamy sand
Mean			1.12	108	
SD			0.19		
%CV			17.1		

Neat = background concentration of a sample
Total = Observed concentration after fortification with 1 ppm phenanthrene
Recovered = Total - Neat

Table 5

Phenanthrene Recovery In Water

Added (ppm)	Observed (ppm)	SD (ppm)	Recovery (%)
+ 5.0	5.4	0.49	109
+ 7.5	8.2	0.74	109
+ 20	22.3	2.12	112
+ 40	39.9	3.06	100
Average			107

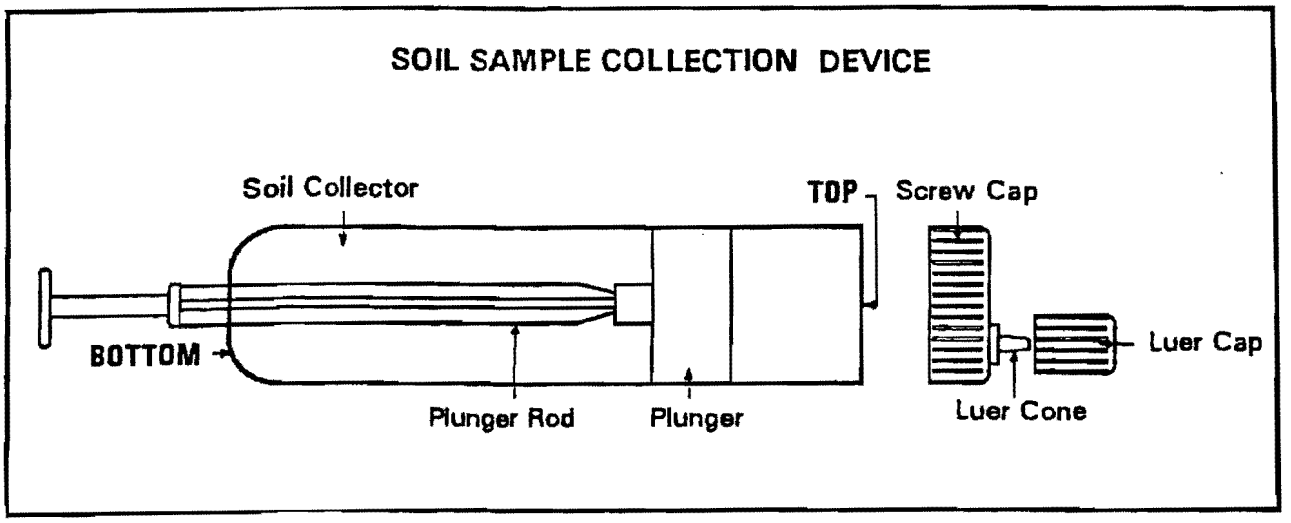

Figure 1. Diagram of soil collector used to collect and extract soil samples.

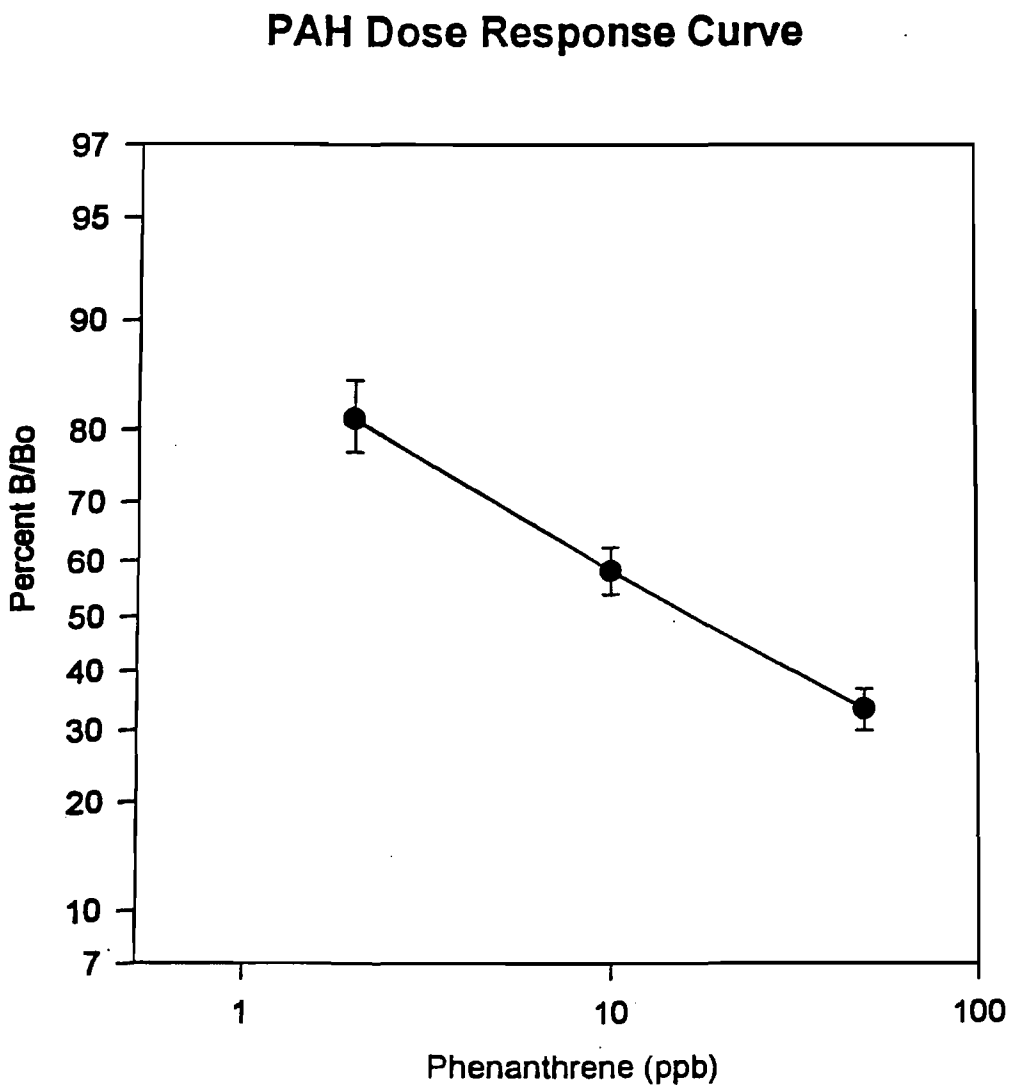

Figure 2. PAHs RaPID Assay dose response curve. Each point represents the mean of 30 determinations. Vertical bars indicate +/- 2 SD about the mean.

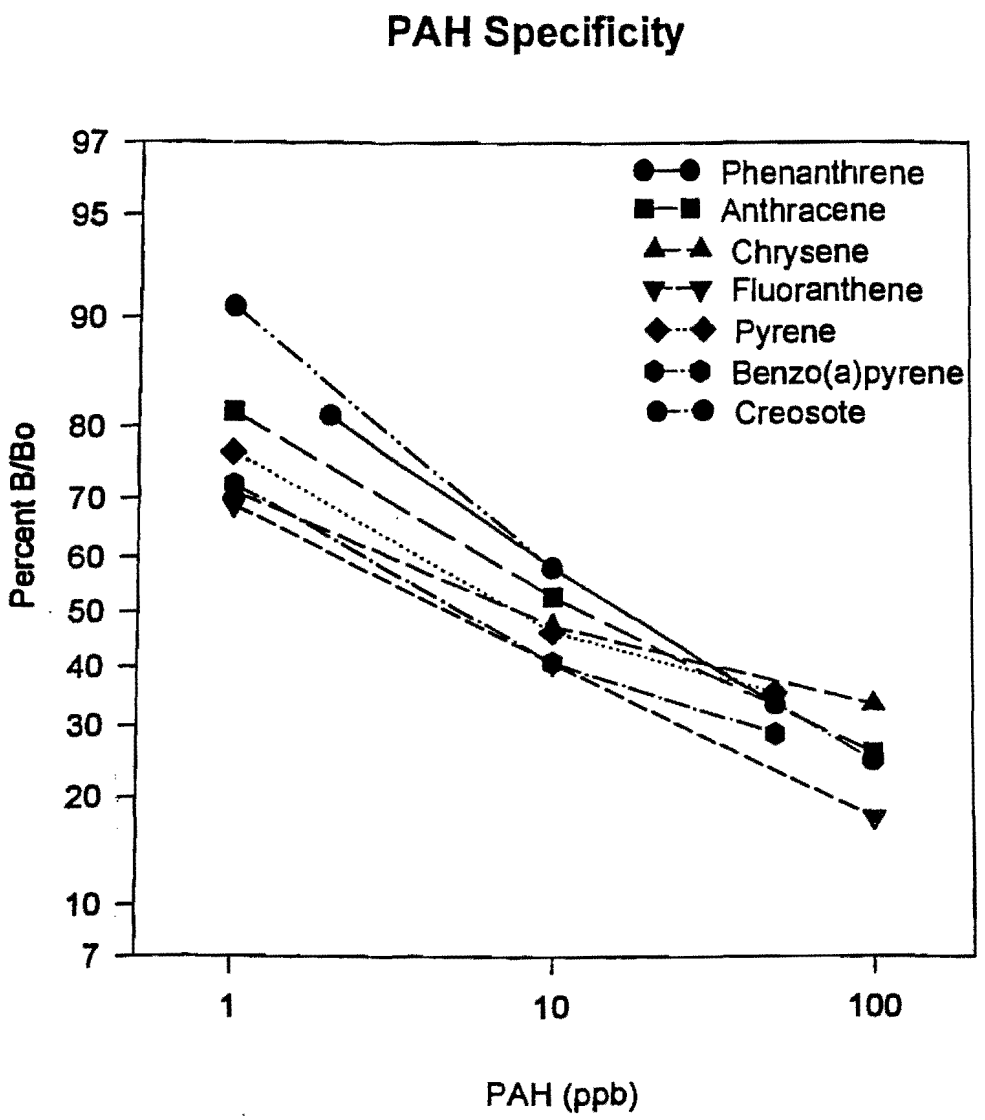

Figure 3. Specificity of the PAHs RaPID Assay against selected polynuclear aromatic hydrocarbons and creosote.

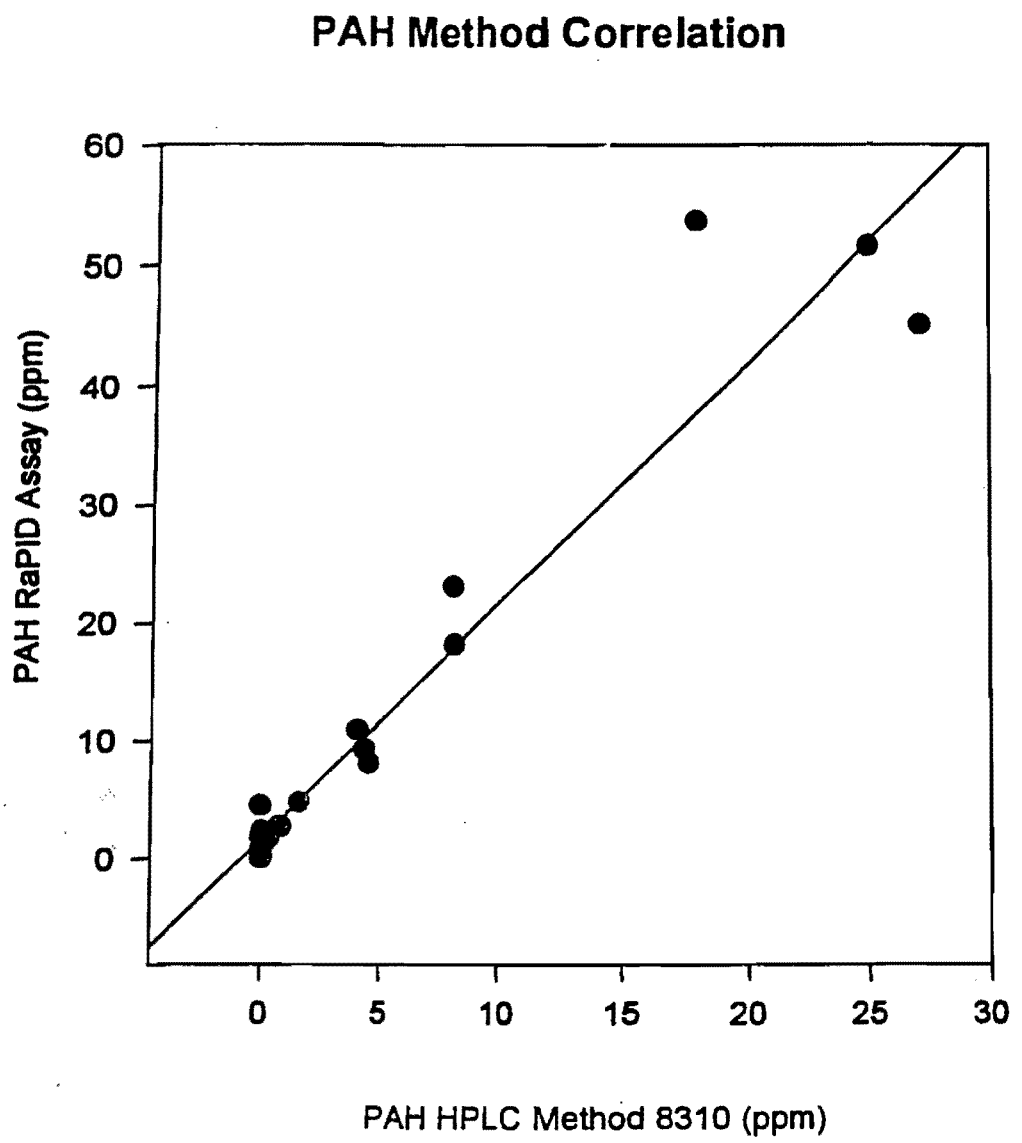

Figure 4. Correlation between PAHs concentrations as determined by the ELISA and HPLC Method 8310 in soil samples. $n = 25$, $r = 0.931$, $y = 2.02x + 1.55$.

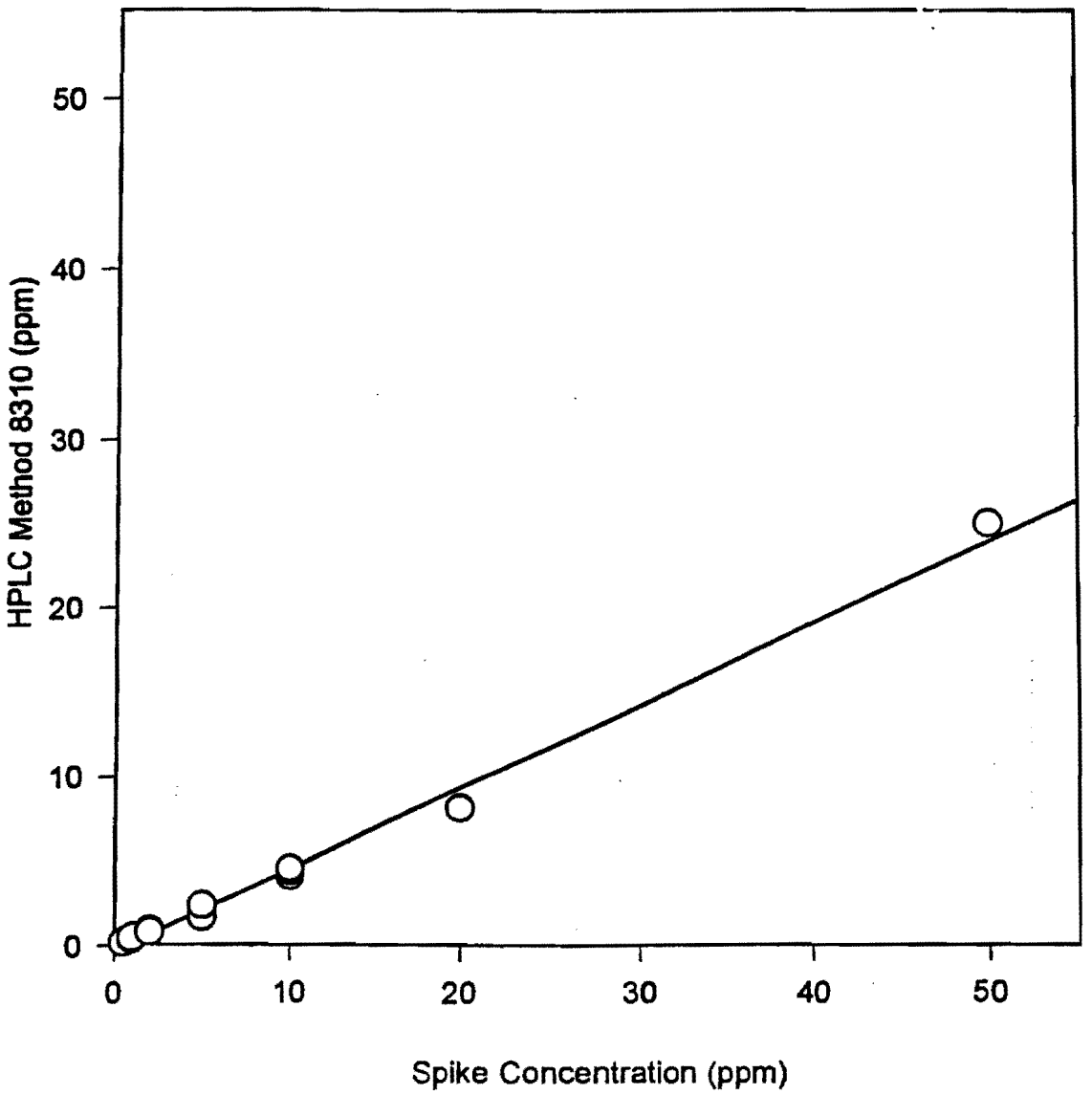

Figure 5. Correlation between PAHs concentrations as determined by HPLC Method 8310 vs. phenanthrene spiked concentration in soil samples. $n = 15$, $r = 0.991$, $y = 0.49x - 0.42$.

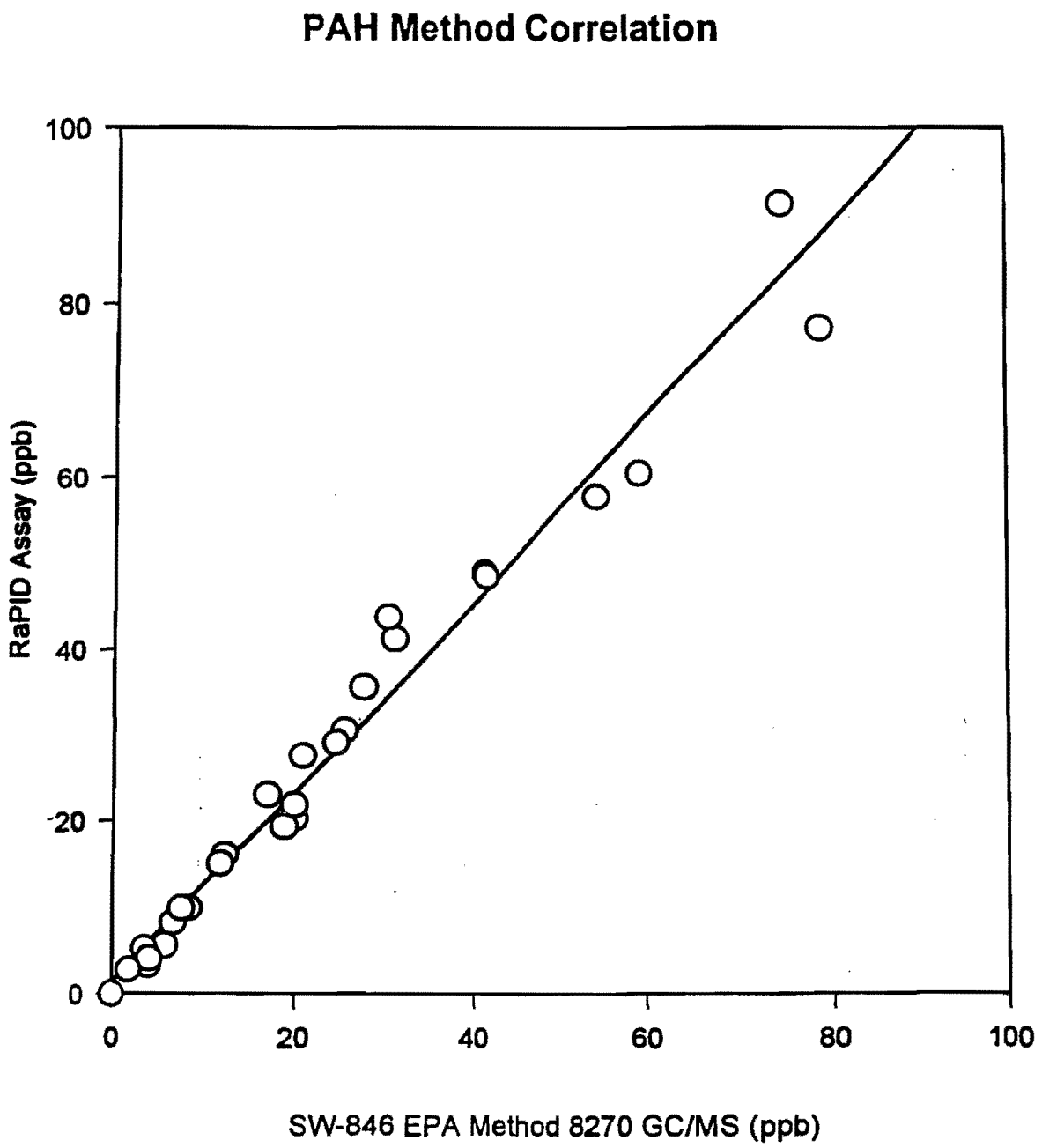

Figure 6. Correlation between PAH's concentrations as determined by the ELISA and GC/MS Method 8270 in water samples. n = 30, r = 0.987, y = 1.10x + 1.34.