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PITT-07-0-086

July 28, 2000

Project Number 1549

Ms. Meghan Cassidy
Environmental Protection Agency
Region I (Mail Code: HBT)
1 Congress Street, Suite 1100
Boston, Massachusetts 02114-2023

Mr. Iver McLeod
Maine Department of Environmental Protection
State House Station 17
Augusta, Maine 04333-0017

Reference: Contract No. N62472-90-D-1298 (CLEAN)
Contract Task Order No. 166

Subject: Draft Revised OU2 Risk Assessment
Portsmouth Naval Shipyard (PNS), Kittery, Maine

Dear Ms. Cassidy/Mr. McLeod:

On behalf of the U.S. Navy, Tetra Tech NUS, Inc. is pleased to provide to the U.S. Environmental Protection Agency Region I (USEPA) and to the Maine Department of Environmental Protection (MEDEP) 4 copies each of the responses to SAPL comments dated June 15, 2000.

As per the project schedule, comments are requested by **August 7, 2000**.

If you have any comments or questions, or if additional information is required, please contact Mr. Fred Evans at 610-595-0567 x 159.

Sincerely,

Deborah Cohen, P.E.
Project Manager

DC/kf

Enclosure

NORTHDIV, (Code 1823/FE, F. Evans) (4 copies)
PNS (Code 106.3R, M. Raymond) (2 copies)
NOAA (K. Finkelstein)
ME Dept. of Marine Resources (D. Card)
Mr. Doug Bogen
Ms. Michele Dionne
Ms. Mary Marshall
Mr. Jack McKenna
Mr. Onil Roy
Dr. Roger Wells
PNS Code 100PAO (w/o enclosure)
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US Fish & Wildlife Service (K. Munney)
NH Fish & Game (C. McBane)
Mr. Jeff Clifford
Ms. Eileen Foley
Mr. Phil McCarthy
Ms. Mary Menconi
Ms. Johanna Lyons (SAPL)
Ms. Carolyn Lepage
COMSUBGRU TWO (R. Jones)
Agency for Toxic Substance and Disease
(Ms. Louise House)

RESPONSE TO SAPL COMMENTS DATED JUNE 15, 2000
DRAFT REVISED OU2 RISK ASSESSMENT
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

1. **Comment:** **Page ES-1, EXECUTIVE SUMMARY.** The reference for the updated risk assessment guidance mentioned in the second paragraph (and elsewhere in the text) should be cited and added to the reference list.

   Response: The updated risk guidance will be added to the text. Please see the Navy's June 22, 2000 response to EPA Specific Comment No. 1 on the draft Revised OU2 Risk Assessment for the specific text changes. The guidance documents are provided in the reference list.

2. **Comment:** **Page ES-1, EXECUTIVE SUMMARY.** The third paragraph should be amended to clarify that this risk assessment focuses on onshore areas, that human health risks in offshore areas were evaluated in the May 1994 *Final Human Health Risk Assessment Report for Off-shore Media*, and that potential offshore impacts are being monitored as part of the on-going OU4 monitoring program. This information should also be added to the discussion of the scope of this document on page 1-1.

   Response: The revised OU2 risk assessment characterizes potential risks to human receptors under current and future land use at OU2. The potential exposure to soils, groundwater, surface water, and sediment were considered. Because an exposure pathway from OU2 to surface water and sediment is not present (these media are inaccessible from OU2), human health risks for exposure to these media were not calculated.

   This document focuses on OU2 human health risks and does not address ecological risks or potential offshore impacts from OU2. Onshore ecological risks for sites at PNS are summarized in the "On-Shore Ecological Risk Assessment," McLaren/Hart, August 1992 and offshore ecological risks are summarized in the " Estuarine Ecological Risk Assessment for Portsmouth Naval Shipyard," NCCOSC, May 2000. Offshore human health risks are summarized in the "Final Human Health Risk Assessment for Offshore Media," McLaren/Hart, March, 1994. The FS for OU2 will address OU2 human health and ecological risks and offshore impacts from OU2, as necessary and the above listed documents will be used as part of the preparation of the OU2 FS, as appropriate.

   The following text revisions will be made to clarify that the document focuses on human health risks for receptors at OU2.

   - ES-1 and Section 1-1, first paragraph, first sentence: "human health" will be added before "risk assessment"
   - ES-1 and Section 1-1, second paragraph, first sentence: "receptors at" will be added before "OU2"
   - ES-1 and Section 1-1, second paragraph, last sentence: "human health" will be added before "risk assessment"
   - ES-1 third paragraph, Section 1-2 first paragraph, first sentence: "for human receptors at OU2" will be added to the end of the sentence

   In addition, the following sentence will be added to the last paragraph on Page ES-1 and the last paragraph on Page 1-1 (continued on the top of Page 1-2) to clarify that human health exposure was considered for surface water and sediment as part of the OU2 risk assessment.

   "Potential human health exposures to surface water and sediment are not evaluated for OU2 because these media are inaccessible from OU2."

3. **Comment: Page ES-2, EXECUTIVE SUMMARY.** The depth ranges for surface soil samples collected at the DRMO Impact Area are not presented consistently throughout the document. The first footnote on the table at the top of page ES-2 states that soil samples were evaluated for two depth ranges: 0 to 1 feet and 0 to 2 feet. The text on page 2-7 states that the maximum depth of soil samples collected at the DRMO Impact Area is 34 inches, while the text on page 2-10 states that surface soils of 0 to 12 inches were evaluated as part of the 1994 on-shore human health risk assessment. Tables 3-5 and 3-6, and the text on pages 3-9 and 3-10 present data for 0-1' and >1' intervals. Also, the bullet at the bottom of page ES-6 states that risks from surface and subsurface soils are within the USEPA target risk range. Additional information and/or editing is needed to prevent the reader from being confused.

   Response: The depth ranges for evaluation of risks for the DRMO Impact Area for the revised OU2 risk assessment were consistently 0 to 1 feet and 0 to 2 feet, in accordance with the Technical Memorandum for the OU2 risk assessment. The text on Pages ES-6, ES-7, and 6-7 related to the DRMO Impact Area will be corrected to remove "subsurface soil" from the text. The last paragraph on Page 5-53 will be revised to clarify that the eight subsurface soils (2 to 3 feet bgs) were not used in the risk assessment but, were evaluated qualitatively to assure that risk estimates would not be underestimated if these samples were not included in the quantitative risk assessment.

   The text on Page 2-7and Pages 3-8 through 3-10 discusses the available data for the DRMO Impact Area. The text in Section 2.2.3 (Page 2-7) and the first paragraph of Section 3.3 (Page 3-8) will be revised to indicate that "During Phase IV of the RFI, 11 soil and 1 duplicate samples were collected..."

   The text on Page 2-10 is part of Section 2.2.5, Previous Human Health Risk Assessment Summary, and provides the depth interval used in the previous human health risk assessment for the DRMO Impact Area.

4. **Comment: Page ES-5, Site 29.** As we stated in our comment letter dated May 10, 2000 regarding the responses to comments on the *Draft Final Field Investigation Report for Site 10 and Site 29*, we do not believe that the vertical and horizontal extent of contamination at Site 29 have been adequately defined. The range of contaminant concentrations, particularly maximum values, also needs to be refined. Without additional investigation to adequately characterize the site, it is likely that risks are being underestimated at Site 29.

   Response: The Navy does not believe that additional investigation is needed at this time to adequately characterize the risks for OU2. Based on the available information for Site 29, the horizontal and vertical extent of contamination have been adequately defined for the risk assessment. In particular, at the time of disposal, the ash was spread throughout the disposal area, which in some areas was up to 25 feet in depth, while in other areas is only a couple feet in depth. Chemical concentrations in the ash would vary depending on what is burned and will vary randomly throughout the disposal area. Therefore a range of chemical concentrations would be expected throughout the entire disposal area and not in any particular localized area. At least 20 samples were collected within the ash disposal area in accordance with the final work plan. These samples are considered representative of the ash disposal area and the analytical data for these samples adequate to calculate representative concentrations. Therefore, it is unlikely that additional sampling to refine the horizontal and vertical extent of contamination would significantly impact the representative concentration.

   As with any sampling program, it is impossible to sample every piece of soil, so assumptions must be made and representative samples collected. It is also impossible to know the "true" concentration, because an infinite number of samples would be necessary. In risk assessments, representative concentrations are calculated based on the data from the representative samples, to characterize the baseline risks for a site.

5. **Comment: Page ES-5, Site 29.** What is the basis for the statement near the bottom of the page that risk estimates for military residents located in the general vicinity of Site 29 are anticipated not to exceed the USEPA target risk range? What about the State of Maine risk guideline?

   Response: It is anticipated that the risk estimate for military residents located near Site 29 or the hypothetical future military resident at Site 29 would not exceed the USEPA target risk range. This statement is based on the cancer risk estimate developed for the hypothetical future on-site resident (anticipated to be exposed for a longer duration) does not exceed the USEPA target risk range ($1x10^{-6}$ to $1x10^{-4}$). For the hypothetical future military resident at Site 29, cancer risks were estimated and are included in Attachment A to these responses. These risk calculations will be included in the OU2 risk assessment appendix and the results summarized in the OU2 risk assessment text. The following summarizes the results of the risk estimation for the hypothetical future military resident at Site 29:

   - For a future hypothetical military adult resident, the estimated cancer risks would be approximately $3.2x10^{-6}$.
   - For the future hypothetical military child resident, the estimated cancer risks would be approximately $2.8x10^{-5}$.

   Therefore, the future hypothetical military child resident cancer risk exceeds the State of Maine risk guidelines, whereas the future hypothetical military adult resident cancer risk is below the State of Maine risk guidelines.

6. **Comment: Page ES-6, Site 29.** The risk assessment document contains numerous references to and comparisons with facility background data. As we have stated in a number of previous comment letters (see our April 26, 2000 letter regarding the *Draft Final Facility Background Development*, for example), the issue of what constitutes representative background conditions for the Shipyard as a whole and for individual sites is still unresolved and we continue to have concerns with the interpretation and application of background values. We do not believe that the Navy is able to differentiate "background" contamination from site-related contamination. As the MEDEP points out in their comment letter dated May 15, 2000, "facility background" should not be considered the same as "local anthropogenic background" contaminant conditions without confirmatory data, particularly for substances such as DDT that are not naturally-occurring. In our November 19, 1999, letter on the *Technical Memorandum for the Human Health Risk Assessment Protocol for OU2*, we commented on the Navy's proposal to eliminate inorganic compounds on the basis of background levels, even though the most recent USEPA guidance states that background levels should not be used to eliminate any COPC from the evaluation process. As the USEPA stated in their May 9, 2000, comment letter, if chemicals are eliminated based on background studies, the total site risk will be underestimated by the risk assessment, and that uncertainty associated with the background study should be discussed.

   Response: Please refer to EPA General Comment No 2 dated November 29, 1999 on the Draft Technical Memorandum for the OU2 risk assessment that indicates use of facility background in the COPC screening is acceptable for the OU2 risk assessment. Also, as provided in the Navy's June 22, 2000 response to EPA Specific Comment 14 (the EPA comment to which SAPL's comment refers to), no chemicals were eliminated from the OU2 risk assessment solely on the basis of background.

7. **Comment: Page ES-7, DRMO Impact Area.** The final paragraph on the page summarizes risks associated with the DRMO Impact Area. Do the risks presented consider the additional potential risks should the soils, including subsurface soils, at the DRMO be disturbed?

   Response: The DRMO Impact Area was investigated as a potential depositional area for airborne soil particulates from the DRMO (RCRA Facility Investigation [RFI], McLaren/Hart, July 1992). Consequently surface soil and shallow subsurface soil (up to 3 feet bgs) were collected during the site investigation. Deeper soil samples were not collected because of the nature of the source. The soil data for the DRMO

Impact Area indicate that although the concentrations in the 0 to 1 foot and 0 to 2 foot intervals are similar, the concentrations below 2 feet are less than the 0 to 2 feet concentrations. Therefore, risk estimates would not increase if the deeper soils were disturbed.

8. **Comment: Page 2-5, Section 2.2.1 Site 6 - DRMO.** The last paragraph in the section should be revised to include information regarding the sampling the Navy conducted in 1999 after discovering the soil erosion problem along the DRMO shoreline. The reference for the 1999 sampling results should also be added to the reference list. In addition, the text should state that potential offshore impacts have been evaluated as part of previous risk assessment efforts (with the appropriate documents cited) and will continue be evaluated as part of the on-going OU4 monitoring.

   Response: The following text will be added to the last paragraph of Section 2.2.1 (on Page 2-5): "In July 1999 the Navy collected 8 surface soil samples of the eroding soil. The samples were analyzed for TCL inorganics. The sampling results are provided in Appendix A of the revised OU2 risk assessment.

   The text in Section 2.2 provides a description and history of activities at OU2 sites and therefore no revision will be made to discuss the offshore (OU4) risk assessment or OU4 monitoring.

9. **Comment: Page 2-7, Section 2.2.3 DRMO Impact Area - Quarters S, N, and 68.** The first paragraph in the section states that the DRMO Impact Area was identified as potentially being impacted by wind dispersion of contaminants from the DRMO. The reference that supplies the basis for this statement should be cited in the text and should be added to the reference list.

   Response: Although provided in various documents related to the DRMO Impact Area, the identification and evaluation of the DRMO Impact Area as potentially impacted by wind dispersion from the DRMO dates back to the RFI investigation. A reference to the RFI (McLaren/Hart, 1992) will be added to the sentence. The RFI is provided in the reference list.

10. **Comment: Page 2-8, Section 2.2.4 OU2 Physical Characteristics.** The last sentence in the second paragraph on the page states that historical photographs of the site indicate a retaining wall separates the fill material along the shoreline from the river. The text should be revised to clarify what is being separated by the retaining wall. In addition, what is the (approximate) timeframe for the installation of the retaining wall?

    Response: Fill material along the shoreline is being separated from the river by the retaining wall. The Navy does not have any information on the (approximate) timeframe for the installation of the retaining wall. However, a cement retaining wall behind building 298 is first shown on a Shipyard map in 1955.

11. **Comment: Page 2-10, Section 2.251 Previous Human Health Risk Assessment Summary.** The last paragraph on the page should also address how cumulative carcinogenic risks compared with the State of Maine risk guidelines.

    Response: As indicated in Navy's June 22, 2000 response to MEDEP Specific Comment No. 4, Section 2.2.5 summarizes the results of the previous risk assessment (PHERE). The exceedances of the Maine risk guideline are pointed out in the document based on the revised OU2 risk assessment results.

12. **Comment: Page 2-11, Section 2.251 Previous Human Health Risk Assessment Summary.** The discussion of risks posed by dioxins/furans at Site 29 should state how risks compared with State of Maine risk guidelines. In addition, the DRMO is located immediately adjacent to the Teepee Incinerator

(Site 29), and the DRMO Impact Area is located nearby. Have the potential risks posed by windblown deposition from Site 29 been evaluated at the other two sites?

Response: The following sentence will be added to the referenced text: "However, dioxin/furans cancer risk estimates developed for the construction worker and the hypothetical future adult ($1.2x10^{-5}$) marginally exceeded the State of Maine risk guidelines of $1x10^{-5}$ when the Reasonable Maximum Exposure (RME) case was evaluated." Also, please see Section 5.0 of the Revised OU2 Risk Assessment for the discussion of risks for Site 29 in comparison with the Maine risk guidelines (e.g., first paragraph on Page 5-50).

Dioxin samples were not collected at Site 6 or the DRMO Impact Area. However, regarding the potential for "windblown deposition from Site 29", please note that the maximum dioxin concentration (in terms of toxic equivalent concentrations [TEQs]) in the surface soils at Site 29 is 0.12 ug/kg. This concentration is an order of magnitude less than the EPA residential action level of 1 ug/kg (assuming residential land use scenario). The magnitude of the dioxin concentrations detected in the surface soils at Site 29 and fact that Site 29 source area is relatively small indicates that the potential for windblown dispersion of dioxin to the adjoining areas would not be significant.

13. **Comment: Page 3-1, Section 3.1 SITE 6 - DEFENSE REUTILIZATION AND MARKETING OFFICE (DRMO).** The last sentence states that the locations of surface soil samples collected in 1999 are shown on Figure 2-3. The text should refer to Figure 2-4 instead. However, it is not clear which of the soil sampling locations shown on Figure 2-4 are the 1999 sampling locations. The sampling designation for the 1999 soil samples should be added to the text in this section, and the legend on Figure 2-4 should be amended to indicate the 1999 surface soil sampling locations (as opposed to the soil boring symbol). In addition, the term "decaying cap" requires additional explanation. Earlier text describes the shoreline erosion problems and emergency remedial action. Does "decaying cap" mean that inland portions of the cap are also deteriorating?

    Response: The text will be revised to refer to Figure 2-4 (and not Figure 2-3). In addition, the text will be revised to indicate that the location of the RFI sample locations are shown on Figure 2-4. The 1999 soil sample locations were not surveyed and were collected along the shoreline to further characterize the eroding soils near the capped portion of the site. This will be added to the text and as a note to Figure 2-4. The cap is not decaying and the text will be deleted.

14. **Comment: Page 3-1, Section 3.1.1 Surface Soils at Site 6.** The text states that acetone and methylene chloride are common laboratory contaminants and are not likely to be site-related. Do the laboratory blanks demonstrate that this is indeed the case? If so, this information should be added to the text. If not, it is not appropriate to dismiss the contaminants in this manner. This comment also applies to other parts of the text (see pages 3-5, 3-6, 3-11 and 4-1, for example) where compounds are identified as common laboratory contaminants, and, therefore, not site-related.

    Response: The text on Pages 3-1, 3-5, and 3-11 will be revised by deleting the statement that the chemicals may not be site related. Please see the Navy's June 22, 2000 response to EPA Specific Comment No. 4 for an example of the text change. No change is necessary for Page 4-1.

15. **Comment: Page 3-2, Section 3.1.1 Surface Soils at Site 6.** *"One surface soil sample, SS-02, had a lead concentration of 12,100 mg/kg. However, Building 348 has since been built at or near this sample location."* What is the significance of Building 348 being built at or near the location of the elevated lead concentration? Was the contaminated soil covered over, removed, or disturbed? If the soil was disturbed, what is the potential impact for contaminant migration at this and nearby sites? If the soil was removed, where was the soil disposed?

Response: The referenced text is presenting a current picture of the site. The fact that the building may now cover the sampling location would limit the potential for exposure under current conditions. However, the risk assessment included this data point, conservatively assuming the sampling location was exposed. Building 348 was constructed in 1991-1992, prior to the Navy setting up a review process to minimize impacts from construction on current Installation Restoration Program sites. The Navy has been unable to locate any records regarding the disposition of soil during the construction of Building 348.

16. **Comment: Pages 3-4 & 3-5, Section 3.2 SITE 29 - TEEPEE INCINERATOR.** The text on page 3-4 states that soil boring TPI-SB03 is outside the ash disposal area, while the text on page 3-5 states that analytical data indicate that the ash disposal area extends at least to this soil boring location. The text must be revised to clear up this confusion.

    Response: The fourth sentence of the last paragraph on Page 3-4 will be revised to read "Subsurface soil samples from soil borings assumed to be outside the ash disposal area...." The fifth sentence will be revised to read "Subsurface soil samples from the four soil borings drilled within the area assumed to be the ash disposal area....."

17. **Comment: Page 3-9, Section 3.3.1 DRMO Impact Area - 0 to 1 Foot bgs.** As the Maine Department of Environmental Protection points out in their comment number 6 (dated 5/15/00), the extent of contamination by DDT and its metabolites DDE and DDD should be described for the individual compounds and collectively, as the sum of concentrations.

    Response: Please see the Navy's June 22, 2000 response to MEDEP Specific Comment No. 6.

18. **Comment: Pages 5-3 & 5-4, Section 5.1.1.1 Data Usability.** We have noted in our comments on previous documents (the *Interim Offshore Monitoring Plan* and the *Site Screening Report for Sites 30, 31, and 32*, for example), that the frequency of detection for a compound may be underestimated if numerical detection limits are elevated. This would lead to the potential underestimation of the number of times action levels or other criteria are exceeded, and result in underestimation of risk. Therefore, we appreciate the Navy evaluating analytical detection limits by comparing detection limits to the screening criteria, as stated at the bottom of page 5-3. The text at the top of page 5-4 implies that detection limits for PAHs were the only ones to exceed screening criteria. How did detection limits for other compounds compare with screening criteria?

    Response: A Data Quality/Data Usability evaluation was conducted as suggested by EPA Guidance (Risk Assessment Guidance for Superfund (RAGS), Supplemental Guidance, Dermal Risk Assessment Interim Guidance, November 1998 – Part D) and is provided in Appendix E. The evaluation includes an evaluation of analytical detection limits by comparing the detection limits to the screening criteria presented in the COPC selection tables provided in Appendix B. The evaluation indicates that generally the detection limits were lower than screening criteria and notes that besides PAHs, detection limits for antimony and arsenic in some samples exceeded criteria.

19. **Comment: Page 5-14, Section 5.1.2.5 Exposure Point Concentrations.** The text states that duplicates were averaged for purposes of calculating the EPC (exposure point concentration) for groundwater and soil. Why weren't the greater of the duplicate results used?

    Response: The approach of averaging the duplicates produces an EPC that is more representative of site contamination and potential for exposure. This approach is consistent with EPA guidelines as discussed in the Technical Memorandum for the OU2 risk assessment.

20. **Comment: Page 5-17, Section 5.1.2.6.1 Incidental Ingestion of Soil.** The scenario described in this section and the following section should also take into account disturbance of subsurface soils (such as with the construction of a foundation) that would bring these soils to the surface, allowing receptors other than construction workers to be potentially exposed.

    Response: Exposure to combined surface/subsurface soil by receptors other than construction workers are included in Appendix B.5 of the OU2 risk assessment for informational purposes in accordance with the Technical Memorandum for OU2. As noted in the last sentence of the first paragraph in both Sections 5.1.2.6.1 and 5.1.2.6.2.

21. **Comment: Pages 5-25 through 5-34, Section 5.1.5. Uncertainty Analysis.** We appreciate the discussion of the uncertainties affecting the OU2 risk assessment. As we pointed out in comment 4, above, we believe additional investigation is necessary to adequately characterize Site 29. In the meantime, the uncertainty regarding the extent of contamination at Site 29 and the resulting impact on the assessment of site risks should be added to the discussion in this section. This comment also applies to Section 5.3.4, which discusses the uncertainties specific to the risk assessment for Site 29.

    Response: As provided in the Navy's response to SAPL Comment No. 4, the data collected for Site 29 are adequate to characterize the risks for Site 29.

22. **Comment: Page 5-28, Section 5.1.5.1 Uncertainty in Selection of COPCs.** We agree with the USEPA's comment number 14 (dated 5/9/00) that if chemicals are eliminated based on background data, then the risk assessment will underestimate the total site risk. Discussion of the uncertainty associated with the background study and the application of background data should be added to the report.

    Response: Please see Navy's June 22, 2000 response to EPA Specific Comment No. 14. No chemicals were eliminated as COPCs solely on the basis of background.

23. **Comment: Page 5-41, Section 5.2.3.1 Quantitative Risk Estimates - RME Evaluation - Sit 6.** We note that "acceptable" risk range should be changed to "target" risk range here and elsewhere in the text, based on the USEPA's comment number 20 (dated 5/9/00).

    Response: Please see the Navy's June 22, 2000 response to EPA Specific Comment No. 20 (note that based on this comment the Navy has identified that revisions are necessary on Pages 5-41, 5-50, 5-57, and 5-58).

22. **Comment: Page 6-1, Section 6.1.1 Revised Human Health Risk Assessment.** We agree that potential risks associated with inhalation exposures under the current land use are likely to be minimal. However, if soils are disturbed, the potential risks could be significantly greater.

    Response: Please see the Navy's June 22, 2000 response to MEDEP Comment No. 21 for the text revisions based on this comment.

23. **Comment: Page 6-3, Section 6.1.1 Revised Human Health Risk Assessment.** Given the proximity of Site 29, another potential source of PAHs found at Site 6 is the Teepee Incinerator.

    Response: Please see the Navy's June 22, 2000 response to MEDEP Comment No. 22 for text revisions related to Site 29 as a potential source of PAHs.

Dr. Brown's Comments and Questions

1. **Comment:** There are contaminates at the sites with both acute and chronic toxic actions but the limited opportunity for exposures reduces the potential for exposures. This appears to be a condition unique to the Shipyard site. In the interpretation of the risk assessment should include discussion of the mercury and other metals over the SSL.

   Response: The risk assessment was conducted in accordance with CERCLA guidance and is not unique to PNS.

   The revised OU2 risk assessment discusses the exceedances of SSLs. However, for Site 6, the exceedance of the inhalation SSL for mercury was not noted in the text. However, the risk assessment did not quantitatively evaluate exposure to mercury via the inhalation pathway. The following explains the rationale. The text will be revised to indicate that the inhalation SSL for mercury was exceeded, but not quantitatively evaluated for the inhalation pathway.

   A follow-up Phase II Air Monitoring and Meteorological Monitoring study was conducted in 1994 "to confirm the presence and ambient concentration groups" (including volatile mercury). The following conclusions are presented in the Phase II report:

   "The strong influence of offshore sources of volatile mercury along with the potential of false positives being reported indicates that PNS SWMUs were not significant sources of volatile mercury. Also, the two "true occurrences" could not be attributed to a given SWMU; therefore, corrective action is not warranted." (A complete copy of the referenced report will be forwarded to the reviewer at his request.)

   The evaluation of the inhalation pathway presented in the 1994 risk assessment was based on an air monitoring study (actual air monitoring data) conducted in 1991 (Revised Ambient Air Quality Study Report, dated April 9, 1992) and reported in the 1994 assessment on pages 2-12 and 2-13. The hazard index for mercury exceeds 1 for receptors at Site 6 and the DRMO Impact Area (Quarters S, N, and 68) when **maximum** mercury concentrations are evaluated. However, the hazard index did not exceed 1 when average mercury concentrations are evaluated. Also, the evaluation of the maximum mercury concentration will over-predict the estimated risks. Current USEPA risk assessment guidance advocates the use of the 95 percent upper percent confidence limit (UCL) on the arithmetic mean as the exposure point concentration. Based on the 95 percent UCL, the hazard index would be less than 1.

   The March 2000 risk assessment did not re-evaluate the monitoring data collected in 1991 or 1994. Rather, the assessment evaluated the potential for source area soils **to contribute to** an air quality problem. The maximum soil concentrations were compared to the EPA SSLs for the migration of contaminants from soil to air and the maximum concentration of mercury at Site 6 (20 mg/kg) exceeded the SSL (10 mg/kg). Typically and if no air monitoring data were available, an exceedance of the SSL would be indicative of the need to quantitatively evaluate the air pathway. However, only 2 of the 28 soil samples were detected at concentrations exceeding the SSL. Additionally, the SSL presented for mercury in the EPA guidance (EPA/540/R-95/128) assumes that all the mercury present is volatile, elemental mercury. (Inhalation reference concentrations are not available for other forms of mercury.) In reality, it is unlikely that all the mercury detected at Site 6 is volatile mercury and that volatile mercury is present in sufficient mass to create an air quality problem. (However, no speciation was conducted for soil samples analyzed for mercury.) This fact and, more importantly, the results/conclusions of the Phase II monitoring indicate that OU2 is not a significant source of volatile mercury in the air. Consequently, the March 2000 risk assessment did not quantitatively evaluate exposure to mercury via the inhalation pathway.

   The following chemicals were also detected at maximum concentrations exceeding the SSL for migration of chemicals from soil to air and were discussed in the text:

   Site 6 (DRMO) Chromium (page 5-36 of draft)

Site 29 Dioxins/furans and chromium (page 5-46 of draft)

Risk estimates for these parameters were presented in the Appendix B tables and summarized in the Section 5 cumulative risk summary tables.

2. **Comment:** Page 6-3 paragraph 5 cites work by Jones et al. 1998. Is it proposed that the contaminates at site 6 are due to background and thus not site related?

   Response: Organic chemicals (such as the PAHs) were not eliminated as chemicals of concern on the basis of background. The referenced text on page 6-3 is providing the reader with information regarding **one** of the major sources of PAHs in environmental media.

3. **Comment:** The IUBK model for lead is designed to identify public health actions needed when children are exposed to a contaminated environment. While IUBK can be used as an indicator of a problem with lead, it should not be interpreted as a safe level of lead at a contaminated site when 5% of exposed can have an elevated lead level.

   Response: The Integrated Exposure Uptake Biokinetic (IEUBK) Model is used for the evaluation of risks associated with environmental lead exposure assuming a residential land use scenario as per USEPA guidance. The IEUBK Model allows the user to estimate, for a hypothetical child or population of children, a plausible distribution of blood lead concentrations centered on the geometric mean blood lead concentration predicted by the model from available information about children's exposure to lead. The IEUBK does not identify an absolute threshold below which adverse affects are not possible (i.e., zero risk [zero percent chance exceeding 10 ug/dL] does not exist). However, this blood lead level is below a level that would trigger medical intervention.

4. **Comment:** State of Maine criteria for cancer should direct the remediation considerations even when the EPA criteria are not exceeded.

   Response: The State of Maine risk guidelines are considered in remedial actions, but are not requirements that direct remedial actions. The discussion of the regulatory requirements that remedial actions must meet is generally conducted as part of the feasibility study for a site. The risk assessment provides information to assist the risk managers in identifying and selecting the appropriate action for a site.

5. **Comment:** There is a question of the extent of the contamination at the former Teepee incinerator area. How did the extent of the contamination affect the interpretation of the dioxin/furan risks? Would this be characterized a low level of hazard?

   Response: Please see the Navy's response to SAPL Comment No. 4 related to the understanding of the extent of contamination.

   Specifically related to dioxins/furans, the Navy believes that the nature and extent of dioxin/furan contamination has been defined sufficiently to complete human health risk assessment and make risk management decisions for Site 29. Additional site characterization may be conducted in the future to define/refine contamination limits, if necessary, if dioxin/furans are selected as chemicals of concern (i.e., contaminants to be addressed in a feasibility study). As provided in the Revised OU2 Risk Assessment, the chemical-specific cancer risks for dioxins are within the USEPA target risk range ($1x10^{-6}$ to $1x10^{-4}$), generally less than the State of Maine risk guidelines ($1x10^{-5}$), and identified as risk drivers for Site 29 risks.

6. **Comment:** What are the durations of exposure used for calculation of the HIs at site 29? What are the durations of exposure used to calculate the cancer risks, 1 year or 70 years?

   Response: All exposure assumptions for the risk assessment are presented in Section 5.0 of the revised OU2 risk assessment in Tables 5-6 through 5-18. The exposure durations range from 1 year for a construction worker, to 25 years for a typical industrial worker, to 30 years for a hypothetical future resident, etc, for the reasonable maximum exposure case. These assumptions are in basic agreement with published EPA guidelines and were also provided in the Technical Memorandum for Recommended Human Health Risk Assessment Protocol for Operable Unit 2 (December 1999).

7. **Comment:** The toxicological profiles are only referenced as to bibliographic source not with respect to each chemical. How did these profiles affect the interpretation of the risk?

   Response: The toxicity criteria are based on the toxicological information such as that presented in the toxicity profile. Quantitative risk estimates and interpretations are based on the toxicity criteria (reference doses and cancer slope factors) available for the chemicals of potential concern (COPCs). Also, the profiles present qualitative discussions of potential human and animal health effects from the COPCs and compliment and support the COPC selection. Please see the toxicological profiles provided in Appendix C, which provide the reader with basic background information regarding the toxicological properties of the COPC.

8. **Comment:** It is noted that the mercury risks are not highlighted in the risk assessment but mercury has been a problem at the site. Is there a change in the status of the mercury exposures?

   Response: Please see the Navy's response to Dr. Brown's Comment No. 1.

9. **Comment:** Although the exposures and risks tend to be characterized as low and justified by the comparison with background in an industrial area, it is noted that there are human health risks from these exposures? Such risks should be addresses by remediation activities

   Response: A baseline risk assessment is conducted to provide cancer and non-cancer risk estimates for receptors for concern under current and future land use scenarios. An evaluation of the need for remedial action will be presented in the OU2 Feasibility Study.

10. **Comment:** In the current form the risk assessment presents a complex discussion of risks and the potential for human health impacts. It requires a concise summary which is understood by the typical reader. This should clearly explain the limitations of the risk assessment and the fact that risks off of the site are not considered.

    Response: The Executive Summary of the report is provided to give a concise understanding of the results of the risk assessment, including a discussion of the purpose and scope of the document. Please also refer to the Navy's response to SAPL Comment 2.

ATTACHMENT A

CLIENT: OU2 - PNS	JOB NUMBER: 1549	
SUBJECT: ESTIMATE OF RISKS FOR HYPOTHETICAL FUTURE MILITARY RESIDENTS AT SITE 29		
BASED ON: USEPA, DEC. 1989		
BY: T. Jackman		DATE: 7/19/00

PURPOSE: To estimate carcinogenic risks for hypothetical future military residents assumed to reside on Site 29 for the reasonable maximum exposure (RME).

ASSUMPTIONS:

Soil ingestion rate = 100 mg/day for adults and 200 mg/day for children

Exposure frequency = 350 days/year

Exposure duration = 4 years

Fraction ingested (FI) from contaminated source (unitless) = 1

Body weight = 15 kg for children and 70 kg for adults

Note that all exposure factors for the military resident are the same as those for the future residents evaluated in the OU2 risk assessment, with the exception of exposure duration. In the OU2 risk assessment, adult residents were assumed to be exposed for 24 years and child residents for 6 years. Child and adult military residents are assumed to be exposed for 4 years. Because exposure duration is the only factor that differs for military and non-military residents, risks for military residents can be estimated by multiplying the residential risks calculated in the OU2 risk assessment by a ratio of 4/24 for adults and 4/6 for children, as shown on page 2.

TETRA TECH NUS, INC. **CALCULATION WORKSHEET**

CLIENT OU2	JOB NUMBER
SUBJECT MILITARY RISKS FOR SITE 79	
BASED ON	DRAWING NUMBER
BY T. JACKMAN / CHECKED BY R. Lupini	APPROVED BY / DATE 7/19/2000

Hypothetical Future Risks:

ADULT

CANCER RISK FOR RESIDENT FROM RISK ASSESSMENT =

1.9×10^{-5} FOR 24 YEAR EXPOSURE

MILITARY EXPOSURE = 4 YEARS

ADULT MILITARY RISK = $1.9 \times 10^{-5} \times \frac{4}{24} = \underline{3.2 \times 10^{-6}}$ ✓

CHILD

CANCER RISK FOR CHILD RESIDENT FROM RISK ASSESSMENT

$= 4.2 \times 10^{-5}$ FOR 6 YEAR EXPOSURE

CHILD MILITARY EXPOSURE = 4 YEARS

CHILD MILITARY RISK = $4.2 \times 10^{-5} \times \frac{4}{6}$

$= \underline{2.8 \times 10^{-5}}$ ✓

4-1 to 4-10
plus cover
sheet.

United States
Environmental Protection
Agency

Office of Emergency and
Remedial Response
Washington DC 20460

Superfund

Risk Assessment Guidance for Superfund Volume I Human Health Evaluation Manual (Part A)

Interim Final

Compendium

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CHAPTER 4

DATA COLLECTION

This chapter discusses procedures for acquiring reliable chemical release and exposure data for quantitative human health risk assessment at hazardous waste sites.[1] The chapter is intended to be a limited discussion of important sampling considerations with respect to risk assessment; it is not intended to be a complete guide on how to collect data or design sampling plans.

Following a general background section (Section 4.1), this chapter addresses the following eight important areas:

(1) review of available site information (Section 4.2);

(2) consideration of modeling parameter needs (Section 4.3);

(3) definition of background sampling needs (Section 4.4);

(4) preliminary identification of potential human exposure (Section 4.5);

(5) development of an overall strategy for sample collection (Section 4.6);

(6) definition of required QA/QC measures (Section 4.7);

(7) evaluation of the need for Special Analytical Services (Section 4.8); and

(8) activities during workplan development and data collection (Section 4.9).

4.1 BACKGROUND INFORMATION USEFUL FOR DATA COLLECTION

This section provides background information on the types of data needed for risk assessment, overall data needs of the RI/FS, reasons and steps for identifying risk assessment data needs early, use of the *Data Quality Objectives for Remedial Response Activities* (EPA 1987a,b, hereafter referred to as the DQO guidance), and other data concerns.

4.1.1 TYPES OF DATA

In general, the types of site data needed for a baseline risk assessment include the following:

- contaminant identities;

ACRONYMS FOR CHAPTER 4

CLP = Contract Laboratory Program
DQO = Data Quality Objectives
FIT = Field Investigation Team
FSP = Field Sampling Plan
HRS = Hazard Ranking System
IDL = Instrument Detection Limit
MDL = Method Detection Limit
PA/SI = Preliminary Assessment/Site Inspection
QA/QC = Quality Assurance/Quality Control
QAPjP = Quality Assurance Project Plan
RAS = Routine Analytical Services
RI/FS = Remedial Investigation/Feasibility Study
SAP = Sampling and Analysis Plan
SAS = Special Analytical Services
SMO = Sample Management Office
SOW = Statement of Work
TAL = Target Analyte List
TCL = Target Compound List
TIC = Tentatively Identified Compound

DEFINITIONS FOR CHAPTER 4

Analytes. The chemicals for which a sample is analyzed.

Anthropogenic Background Levels. Concentrations of chemicals that are present in the environment due to human-made, non-site sources (e.g., industry, automobiles).

Contract Laboratory Program (CLP). Analytical program developed for Superfund waste site samples to fill the need for legally defensible analytical results supported by a high level of quality assurance and documentation.

Data Quality Objectives (DQOs). Qualitative and quantitative statements to ensure that data of known and documented quality are obtained during an RI/FS to support an Agency decision.

Field Sampling Plan (FSP). Provides guidance for all field work by defining in detail the sampling and data gathering methods to be used on a project.

Naturally Occurring Background Levels. Ambient concentrations of chemicals that are present in the environment and have not been influenced by humans (e.g., aluminum, manganese).

Quality Assurance Project Plan (QAPjP). Describes the policy, organization, functional activities, and quality assurance and quality control protocols necessary to achieve DQOs dictated by the intended use of the data (RI/FS Guidance).

Routine Analytical Services (RAS). The set of CLP analytical protocols that are used to analyze most Superfund site samples. These protocols are provided in the EPA Statements of Work for the CLP (SOW for Inorganics, SOW for Organics) and must be followed by every CLP laboratory.

Sampling and Analysis Plan (SAP). Consists of a Quality Assurance Project Plan (QAPjP) and a Field Sampling Plan (FSP).

Sample Management Office (SMO). EPA contractor providing management, operational, and administrative support to the CLP to facilitate optimal use of the program.

Special Analytical Services (SAS). Non-standardized analyses conducted under the CLP to meet user requirements that cannot be met using RAS, such as shorter analytical turnaround time, lower detection limits, and analysis of non-standard matrices or non-TCL compounds.

Statement of Work (SOW) for the CLP. A document that specifies the instrumentation, sample handling procedures, analytical parameters and procedures, required quantitation limits, quality control requirements, and report format to be used by CLP laboratories. The SOW also contains the TAL and TCL.

Target Analyte List (TAL). Developed by EPA for Superfund site sample analyses. The TAL is a list of 23 metals plus total cyanide routinely analyzed using RAS.

Target Compound List (TCL). Developed by EPA for Superfund site sample analyses. The TCL is a list of analytes (34 volatile organic chemicals, 65 semivolatile organic chemicals, 19 pesticides, 7 polychlorinated biphenyls, 23 metals, and total cyanide) routinely analyzed using RAS.

- contaminant concentrations in the key sources and media of interest;[2]
- characteristics of sources, especially information related to release potential; and
- characteristics of the environmental setting that may affect the fate, transport, and persistence of the contaminants.

Most of these data are obtained during the course of a remedial investigation/feasibility study (RI/FS). Other sources of information, such as preliminary assessment/site inspection (PA/SI) reports, also may be available.

4.1.2 DATA NEEDS AND THE RI/FS

The RI/FS has four primary data collection components:

(1) characterization of site conditions;

(2) determination of the nature of the wastes;

(3) risk assessment; and

(4) treatability testing.

The site and waste characterization components of the RI/FS are intended to determine characteristics of the site (e.g., ground-water movement, surface water and soil characteristics) and the nature and extent of contamination through sampling and analysis of sources and potentially contaminated media. Quantitative risk assessment, like site characterization, requires data on concentrations of contaminants in each of the source areas and media of concern. Risk assessment also requires information on other variables necessary for evaluating the fate, transport, and persistence of contaminants and estimating current and potential human exposure to these contaminants. Additional data might be required for environmental risk assessments (see EPA 1989a).

Data also are collected during the RI/FS to support the design of remedial alternatives. As discussed in the DQO guidance (EPA 1987a,b), such data include results of analyses of contaminated media "before and after" bench-scale treatability tests. This information usually is not appropriate for use in a baseline risk assessment because these media typically are assessed only for a few individual parameters potentially affected by the treatment being tested. Also, initial treatability testing may involve only a screening analysis that generally is not sensitive enough and does not have sufficient quality assurance/quality control (QA/QC) procedures for use in quantitative risk assessment.

4.1.3 EARLY IDENTIFICATION OF DATA NEEDS

Because the RI/FS and other site studies serve a number of different purposes (e.g., site and waste characterization, design of remedial alternatives), only a subset of this information generally is useful for risk assessment. To ensure that all risk assessment data needs will be met, it is important to identify those needs early in the RI/FS planning for a site. The earlier the requirements are identified, the better the chances are of developing an RI/FS that meets the risk assessment data collection needs.

One of the earliest stages of the RI/FS at which risk assessment data needs can be addressed is the site scoping meeting. As discussed in the *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA* (EPA 1988a, hereafter referred to as RI/FS guidance), the scoping meeting is part of the initial planning phase of site remediation. It is at this meeting that the data needs of each of the RI/FS components (e.g., site and waste characterization) are addressed together. Scoping meeting attendees include the RPM, contractors conducting the RI/FS (including the baseline risk assessment), onsite personnel (e.g., for construction), and natural resource trustees (e.g., Department of Interior). The scoping meeting allows development of a comprehensive sampling and analysis plan (SAP) that will satisfy the needs of each RI/FS component while helping to ensure that time and budget constraints are met. Thus, in addition to aiding the effort to meet the risk assessment data needs, this meeting can help integrate these needs with other objectives of the RI/FS and thereby help make maximum use of available resources and avoid duplication of effort.

During scoping activities, the risk assessor should identify, at least in preliminary fashion, the type and duration of possible exposures (e.g., chronic, intermittent), potential exposure routes (e.g., ingestion of fish, ingestion of drinking water, inhalation of dust), and key exposure points (e.g., municipal wells, recreation areas) for each medium. The relative importance of the potential exposure routes and exposure points in determining risks should be discussed, as should the consequences of not studying them adequately. Section 4.5 and Chapter 6 provide guidance for identifying exposure pathways that may exist at hazardous waste sites. If potential exposure pathways are identified early in the RI/FS process, it will be easier to reach a decision on the number, type, and location of samples needed to assess exposure.

During the planning stages of the RI/FS, the risk assessor also should determine if non-routine (i.e., lower) quantitation limits are needed to adequately characterize risks at a site. Special Analytical Services (SAS) of the EPA Contract

Laboratory Program (CLP) may be needed to achieve such lower quantitation limits. (See Section 4.8 for additional information concerning quantitation limits.)

4.1.4 USE OF THE DATA QUALITY OBJECTIVES (DQO) GUIDANCE

The DQO guidance (EPA 1987a,b) provides information on the review of site data and the determination of data quality needs for sampling (see the box below).

OVERVIEW OF DQO GUIDANCE

According to the DQO guidance (EPA 1987a and b), DQO are qualitative and quantitative statements established prior to data collection, which specify the quality of the data required to support Agency decisions during remedial response activities. The DQO for a particular site vary according to the end use of the data (i.e., whether the data are collected to support preliminary assessments/site inspections, remedial investigations/feasibility studies, remedial designs, or remedial actions).

The DQO process consists of three stages. In Stage 1 (Identify Decision Types), all available site information is compiled and analyzed in order to develop a conceptual model of the site that describes suspected sources, contaminant pathways, and potential receptors. The outcome of Stage 1 is a definition of the objectives of the site investigation and an identification of data gaps. Stage 2 (Identify Data Uses/Needs) involves specifying the data necessary to meet the objectives set in Stage 1, selecting the sampling approaches and the analytical options for the site, and evaluating multiple-option approaches to allow more timely or cost-effective data collection and evaluation. In Stage 3 (Design Data Collection Program), the methods to be used to obtain data of acceptable quality are specified in such products as the SAP or the workplan.

Use of this guidance will help ensure that all environmental data collected in support of RI/FS activities are of known and documented quality.

4.1.5 OTHER DATA CONCERNS

The simple existence of a data collection plan does not guarantee usable data. The risk assessor should plan an active role in oversight of data collection to ensure that relevant data have been obtained. (See Section 4.9 for more information on the active role that the risk assessor must play.)

After data have been collected, they should be carefully reviewed to identify reliable, accurate, and verifiable numbers that can be used to quantify risks. All analytical data must be evaluated to identify the chemicals of potential concern (i.e., those to be carried through the risk assessment). Chapter 5 discusses the criteria to be considered in selecting the subset of chemical data appropriate for baseline risk assessment. Data that do not meet the criteria are not included in the quantitative risk assessment; they can be discussed qualitatively in the risk assessment report, however, or may be the basis for further investigation.

4.2 REVIEW OF AVAILABLE SITE INFORMATION

Available site information must be reviewed to (1) determine basic site characteristics, (2) initially identify potential exposure pathways and exposure points, and (3) help determine data needs (including modeling needs). All available site information (i.e., information existing at the start of the RI/FS) should be reviewed in accordance with Stage 1 of the DQO process. Sources of available site information include:

- RI/FS scoping information;
- PA/SI data and Hazard Ranking System (HRS) documentation;
- listing site inspection (LSI) data (formally referred to as expanded site inspection, or ESI);
- photographs (e.g., EPA's Environmental Photographic Interpretation Center [EPIC]);
- records on removal actions taken at the site; and
- information on amounts of hazardous substances disposed (e.g., from site records).

If available, LSI (or ESI) data are especially useful because they represent fairly extensive site studies.

Based on a review of the existing data, the risk assessor should formulate a conceptual model of the site that identifies all potential or suspected sources of contamination, types and concentrations of contaminants detected at the site, potentially contaminated media, and potential exposure pathways, including receptors (see Exhibit 4-1). As discussed previously, identification of potential exposure pathways, especially the exposure points, is a key element in the determination of data needs for the risk assessment. Details concerning development of a conceptual model for a site are provided in the DQO guidance (EPA 1987a,b) and the RI/FS guidance (EPA 1988a).

In most cases, site information available at the start of the RI/FS is insufficient to fully characterize the site and the potential exposure pathways. The conceptual model developed at this stage should be adequate to determine the remaining data needs. The remainder of this chapter addresses risk assessment data needs in detail.

4.3 ADDRESSING MODELING PARAMETER NEEDS

As discussed in detail in Chapter 6, contaminant release, transport, and fate models are often needed to supplement monitoring data when estimating exposure concentrations. Therefore, a preliminary site modeling strategy should be developed during RI/FS scoping to allow model input data requirements to be incorporated into the data collection requirements. This preliminary identification of models and other related data requirements will ensure that data for model calibration and validation are collected along with other physical and chemical data at the site. Exhibit 4-2 lists (by medium) several site-specific parameters often needed to incorporate fate and transport models in risk assessments.

Although default values for some modeling parameters are available, it is preferable to obtain site-specific values for as many input parameters as is feasible. If the model is not sensitive to a particular parameter for which a default value is available, then a default value may be used. Similarly, default values may be used if obtaining the site-specific model parameter would be too time consuming or expensive. For example, certain airborne dust emission models use a default value for the average wind speed at the site; this is done because representative measurements of wind speed at the site would involve significant amounts of time (i.e., samples would have to be collected over a large part of the year).

Some model parameters are needed only if the sampling conducted at a site is sufficient to support complex models. Such model parameters may not be necessary if only simple fate and transport models are used in the risk assessment.

4.4 DEFINING BACKGROUND SAMPLING NEEDS

Background sampling is conducted to distinguish site-related contamination from naturally occurring or other non-site-related levels of chemicals. The following subsections define the types of background contamination and provide guidance on the appropriate location and number of background samples.

4.4.1 TYPES OF BACKGROUND

There are two different types of background levels of chemicals:

(1) naturally occurring levels, which are ambient concentrations of chemicals present in the environment that have not been influenced by humans (e.g., aluminum, manganese); and

(2) anthropogenic levels, which are concentrations of chemicals that are present in the environment due to human-made, non-site sources (e.g., industry, automobiles).

Background can range from localized to ubiquitous. For example, pesticides -- most of which are not naturally occurring (anthropogenic) -- may be ubiquitous in certain areas (e.g.,

EXHIBIT 4-1

ELEMENTS OF A CONCEPTUAL EVALUATION MODEL

	VARIABLES	HYPOTHESES TO BE TESTED
SOURCES	• CONTAMINANTS • CONCENTRATIONS • TIME • LOCATIONS	• SOURCE EXISTS • SOURCE CAN BE CONTAINED • SOURCE CAN BE REMOVED AND DISPOSED • SOURCE CAN BE TREATED
PATHWAYS	• MEDIA • RATES OF MIGRATION • TIME • LOSS AND GAIN FUNCTIONS	• PATHWAY EXISTS • PATHWAY CAN BE INTERRUPTED • PATHWAY CAN BE ELIMINATED
RECEPTORS	• TYPES • SENSITIVITIES • TIME • CONCENTRATIONS • NUMBERS	• RECEPTOR IS NOT IMPACTED BY MIGRATION OF CONTAMINANTS • RECEPTOR CAN BE RELOCATED • INSTITUTIONAL CONTROLS CAN BE APPLIED • RECEPTOR CAN BE PROTECTED

SOURCE: EPA 1987a

EXHIBIT 4-2

EXAMPLES OF MODELING PARAMETERS FOR WHICH INFORMATION MAY NEED TO BE OBTAINED DURING A SITE SAMPLING INVESTIGATION

Type of Modeling	Modeling Parameters[a]
Source Characteristics	Geometry, physical/chemical conditions, emission rate, emission strength, geography
Soil	Particle size, dry weight, pH, redox potential, mineral class, organic carbon and clay content, bulk density, soil porosity
Ground-water	Head measurements, hydraulic conductivity (pump and slug test results), saturated thickness of aquifer, hydraulic gradient, pH, redox potential, soil-water partitioning
Air	Prevailing wind direction, wind speeds, stability class, topography, depth of waste, contaminant concentration in soil and soil gas, fraction organic content of soils, silt content of soils, percent vegetation, bulk density of soil, soil porosity
Surface Water	Hardness, pH, redox potential, dissolved oxygen, salinity, temperature, conductivity, total suspended solids, flow rates and depths for rivers/streams, estuary and embayment parameters such as tidal cycle, saltwater incursion extent, depth and area, lake parameters such as area, volume, depth, depth to thermocline
Sediment	Particle size distribution, organic content, pH, benthic oxygen conditions, water content
Biota	Dry weight, whole body, specific organ, and/or edible portion chemical concentrations, percent moisture, lipid content, size/age, life history stage

[a] These parameters are not necessarily limited to the type of modeling with which they are associated in this exhibit. For example, many of the parameters listed for surface water are also appropriate for sediments.

agricultural areas); salt runoff from roads during periods of snow may contribute high ubiquitous levels of sodium. Polycyclic aromatic hydrocarbons (PAHs) and lead are other examples of anthropogenic, ubiquitous chemicals, although these chemicals also may be present at naturally occurring levels in the environment due to natural sources (e.g., forest fires may be a source of PAHs, and lead is a natural component of soils in some areas).

4.4.2 BACKGROUND SAMPLING LOCATIONS

Background samples are collected at or near the hazardous waste site in areas not influenced by site contamination. They are collected from each medium of concern in these offsite areas. That is, the locations of background samples must be areas that could not have received contamination from the site, but that do have the same basic characteristics as the medium of concern at the site.

Identifying background location requires knowing which direction is upgradient/upwind/upstream. In general, the direction of water flow tends to be relatively constant, whereas the direction of air flow is constantly changing. Therefore, the determination of background locations for air monitoring requires constant and concurrent monitoring of factors such as wind direction.

4.4.3 BACKGROUND SAMPLE SIZE

In appropriate circumstances, statistics may be used to evaluate background sample data. Because the number of background samples collected is important for statistical hypothesis testing, at some sites a statistician should be consulted when determining background sample size. At all sites, the RPM should decide the level of statistical analysis applicable to a particular situation.

Often, rigorous statistical analyses are unnecessary because site- and non-site-related contamination clearly differ. For most sites, the issue will not be whether a difference in chemical concentrations can be demonstrated between contaminated and background areas, but rather that of establishing a reliable representation of the extent (in three dimensions) of a contaminated area. However, statistical analyses are required at some sites, making a basic understanding of statistics necessary. The following discussion outlines some basic statistical concepts in the context of background data evaluation for risk assessment. (A general statistics textbook should be reviewed for additional detail. Also, the box below lists EPA guidance that might be useful.)

STATISTICAL METHODS GUIDANCE

Statistical Methods for Evaluating Ground-water Monitoring Data from Hazardous Waste Facilities (EPA 1988b)

Surface Impoundment Clean Closure Guidance Manual (EPA 1988c)

Love Canal Emergency Declaration Area Habitability Study (EPA 1988d)

Soils Sampling Quality Assurance Guide (EPA 1989b)

A statistical test of a hypothesis is a rule used for deciding whether or not a statement (i.e., the null hypothesis) should be rejected in favor of a specified alternative statement (i.e., the alternative hypothesis). In the context of background contamination at hazardous waste sites, the null hypothesis can be expressed as "there is no difference between contaminant concentrations in background areas and onsite," and the alternative hypothesis can be expressed as "concentrations are higher onsite." This expression of the alternative hypothesis implies a one-tailed test of significance.

The number of background samples collected at a site should be sufficient to accept or reject the null hypothesis with a specified likelihood of error. In statistical hypothesis testing there are two types of error. The null hypothesis may be rejected when it is true (i.e., a Type I error), or not rejected when it is false (i.e., a Type II error). An example of a Type I error at a hazardous waste site would be to conclude that contaminant concentrations in onsite soil are higher than background soil concentrations when in fact they

Guidance documents on background.

are not. The corresponding Type II error would be to conclude that onsite contaminant concentrations are not higher than background concentrations when in fact they are. A Type I error could result in unnecessary remediation, while a Type II error could result in a failure to clean up a site when such an action is necessary.

In customary notations, α (alpha) denotes the probability that a Type I error will occur, and β (beta) denotes the probability that a Type II error will occur. Most statistical comparisons refer to α, also known as the level of significance of the test. If $\alpha = 0.05$, there is a 5 percent (i.e., 1 in 20) chance that we will conclude that concentrations of contaminants are higher than background when they actually are not.

Equally critical considerations in determining the number of background samples are β and a concept called "power." The power of a statistical test has the value $1 - \beta$ and is defined as the likelihood that the test procedure detects a false null hypothesis. Power functions for commonly used statistical tests can be found in most general statistical textbooks. Power curves are a function of α (which normally is fixed at 0.05), sample size (i.e., the number of background and/or onsite samples), and the amount of variability in the data. Thus, if a 15 percent likelihood of failing to detect a false null hypothesis is desired (i.e., $\beta = 0.15$), enough background samples must be collected to ensure that the power of the test is at least 0.85.

A small number of background samples increases the likelihood of a Type II error. If an insufficient number of background samples is collected, fairly large differences between site and background concentrations may not be statistically significant, even though concentrations in the many site samples are higher than the few background samples. To guard against this situation, the statistical power associated with the comparison of background samples with site samples should be evaluated.

In general, when trying to detect small differences as statistically significant, the number of background samples should be similar to the number of onsite samples that will be used for the comparison(s) (e.g., the number of samples taken from one well). (Note that this does not mean that the background sample size must equal the total number of onsite samples.) Due to the inherent variability of air concentrations (see Section 4.6), background sample size for air needs to be relatively large.

4.4.4 COMPARING BACKGROUND SAMPLES TO SITE-RELATED CONTAMINATION

The medium sampled influences the kind of statistical comparisons that can be made with background data. For example, air monitoring stations and ground-water wells are normally positioned based on onsite factors and gradient considerations. Because of this purposive placement (see Section 4.6.1), several wells or monitors cannot be assumed to be a random sample from a single population and hence cannot be evaluated collectively (i.e., the sampling results cannot be combined). Therefore, the information from each well or air monitor should be compared individually with background.

Because there typically are many site-related, media-specific sampling location data to compare with background, there usually is a "multiple comparison problem" that must be addressed. In general, the probability of experiencing a Type I error in the entire set of statistical tests increases with the number of comparisons being made. If $\alpha = 0.05$, there is a 1 in 20 chance of a Type I error in any single test. If 20 comparisons are being made, it therefore is likely that at least one Type I error will occur among all 20 tests. *Statistical Analysis of Ground-water Monitoring Data at RCRA Facilities* (EPA 1989c) is useful for designing sampling plans for comparing information from many fixed locations with background.

It may be useful at times to look at comparisons other than onsite versus background. For example, upgradient wells can be compared with downgradient wells. Also, there may be several areas within the site that should be compared for differences in site-related contaminant concentration. These areas of concern should be established before sampling takes place. If a more complicated comparison scheme is planned, a statistician should be consulted frequently to help distribute the sampling effort and design the analysis.

A statistically significant difference between background samples and site-related contamination should not, by itself, trigger a cleanup action. The remainder of this manual still must be applied so that the toxicological -- rather than simply the statistical -- significance of the contamination can be ascertained.

4.5 PRELIMINARY IDENTIFICATION OF POTENTIAL HUMAN EXPOSURE

A preliminary identification of potential human exposure provides much needed information for the SAP. This activity involves the identification of (1) media of concern, (2) areas of concern (i.e., general locations of the media to be sampled),[3] (3) types of chemicals expected at the site, and (4) potential routes of contaminant transport through the environment (e.g., inter-media transfer, food chain). This section provides general information on the preliminary identification of potential human exposure pathways, as well as specific information on the various media. (Also, see Chapter 6 for a detailed discussion of exposure assessment.)

4.5.1 GENERAL INFORMATION

Prior to discussing various specific exposure media, general information on the following is provided: media, types of chemicals, areas of concern, and routes of contaminant transport is addressed.

Media of concern (including biota). For risk assessment purposes, media of concern at a site are:

- any currently contaminated media to which individuals may be exposed or through which chemicals may be transported to potential receptors; and
- any currently uncontaminated media that may become contaminated in the future due to contaminant transport.

Several medium-specific factors in sampling may influence the risk assessment. For example, limitations in sampling the medium may limit the detailed evaluation of exposure pathways described in Chapter 6. To illustrate this, if soil samples are not collected at the surface of a site, then it may not be possible to accurately evaluate potential exposures involving direct contact with soils or exposures involving the release of contaminants from soils via wind erosion (with subsequent inhalation of airborne contaminants by exposed individuals). Therefore, based on the conceptual model of the site discussed previously, the risk assessor should make sure that appropriate samples are collected from each medium of concern.

Areas of concern. Areas of concern refer to the general sampling locations at or near the site. For large sites, areas of concern may be treated in the RI/FS as "operable units," and may include several media. Areas of concern also can be thought of as the locations of potentially exposed populations (e.g., nearest residents) or biota (e.g., wildlife feeding areas).

Areas of concern should be identified based on site-specific characteristics. These areas are chosen purposively by the investigators during the initial scoping meeting. Areas of concern should include areas of the site that:

(1) have different chemical types;

(2) have different anticipated concentrations or hot spots;

(3) are a release source of concern;

(4) differ from each other in terms of the anticipated spatial or temporal variability of contamination;

(5) must be sampled using different equipment; and/or

(6) are more or less costly to sample.

In some instances, the risk assessor may want to estimate concentrations that are representative of the site as a whole, in addition to each area of concern. In these cases, two conditions generally should be met in defining areas of concern: (1) the boundaries of the areas of concern should not overlap and (2) all of the areas of concern

together should account for the entire area of the site.

Depending on the exposure pathways that are being evaluated in the risk assessment, it may not be necessary to determine site-wide representative values. In this case, areas of concern do not have to account for the entire area of the site.

Types of chemicals. The types of chemicals expected at a hazardous waste site may dictate the site areas and media sampled. For example, certain chemicals (e.g., dioxins) that bioconcentrate in aquatic life also are likely to be present in the sediments. If such chemicals are expected at a particular site and humans are expected to ingest aquatic life, sampling of sediments and aquatic life for the chemicals may be particularly important.

Due to differences in the relative toxicities of different species of the same chemical (e.g., Cr^{+3} versus Cr^{+6}), the species should be noted when possible.

Routes of contaminant transport. In addition to medium-specific concerns, there may be several potential current and future routes of contaminant transport within a medium and between media at a site. For instance, discharge of ground water or surface runoff to surface water could occur. Therefore, when possible, samples should be collected based on routes of potential transport. For cases in which contamination has not yet reached points of human exposure but may be transported to those areas in the future, sampling between the contaminant source and the exposure locations should be conducted to help evaluate potential future concentrations to which individuals may be exposed (e.g., through modeling). (See Chapter 6 for additional discussion on contaminant transport.)

4.5.2 SOIL

Soil represents a medium of direct contact exposure and often is the main source of contaminants released into other media. As such, the number, location, and type of samples collected from soils will have a significant effect on the risk assessment. See the box on this page for guidance that provides additional detailed information concerning soil sampling, including information on sampling locations, general soil and vegetation conditions, and sampling equipment, strategies, and techniques. In addition to the general sampling considerations discussed previously, the following specific issues related to soil sampling are discussed below: the heterogeneous nature of soils, designation of hot spots, depth of samples, and fate and transport properties.

SOIL SAMPLING GUIDANCE

Test Methods for Evaluating Solid Waste (SW-846): Physical/Chemical Methods (EPA 1986a)

Field Manual for Grid Sampling of PCB Spill Sites to Verify Cleanups (EPA 1986b)

A Compendium of Superfund Field Operations Methods (EPA 1987c)

Soil Sampling Quality Assurance Guide (EPA Review Draft 1989b)

Heterogeneous nature of soils. One of the largest problems in sampling soil (or other solid materials) is that its generally heterogeneous nature makes collection of representative samples difficult (and compositing of samples virtually impossible -- see Section 4.6.3). Therefore, a large number of soil samples may be required to obtain sufficient data to calculate an exposure concentration. Composite samples sometimes are collected to obtain a more homogeneous sample of a particular area; however, as discussed in a later section, compositing samples also serves to mask contaminant hot spots (as well as areas of low contaminant concentration).

Designation of hot spots. Hot spots (i.e., areas of very high contaminant concentrations) may have a significant impact on direct contact exposures. The sampling plan should consider characterization of hot spots through extensive sampling, field screening, visual observations, or a combination of the above.

Element Concentrations in Soils and Other Surficial Materials of the Conterminous United States

By HANSFORD T. SHACKLETTE *and* JOSEPHINE G. BOERNGEN

U.S. GEOLOGICAL SURVEY PROFESSIONAL PAPER 1270

An account of the concentrations of 50 chemical elements in samples of soils and other regoliths

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ELEMENT CONCENTRATIONS IN SOILS AND OTHER SURFICIAL MATERIALS OF THE CONTERMINOUS UNITED STATES

By HANSFORD T. SHACKLETTE and JOSEPHINE G. BOERNGEN

ABSTRACT

Samples of soils or other regoliths, taken at a depth of approximately 20 cm from locations about 80 km apart throughout the conterminous United States, were analyzed for their content of elements. In this manner, 1,318 sampling sites were chosen, and the results of the sample analyses for 50 elements were plotted on maps. The arithmetic and geometric mean, the geometric deviation, and a histogram showing frequencies of analytical values are given for 47 elements.

The lower concentrations of some elements (notably, aluminum, barium, calcium, magnesium, potassium, sodium, and strontium) in most samples of surficial materials from the Eastern United States, and the greater abundance of heavy metals in the same materials of the Western United States, indicates a regional geochemical pattern of the largest scale. The low concentrations of many elements in soils characterize the Atlantic Coastal Plain. Soils of the Pacific Northwest generally have high concentrations of aluminum, cobalt, iron, scandium, and vanadium, but are low in boron. Soils of the Rocky Mountain region tend to have high concentrations of copper, lead, and zinc. High mercury concentrations in surficial materials are characteristic of Gulf Coast sampling sites and the Atlantic coast sites of Connecticut, Massachuetts, and Maine. At the State level, Florida has the most striking geochemical pattern by having soils that are low in the concentrations of most elements considered in this study. Some smaller patterns of element abundance can be noted, but the degree of confidence in the validity of these patterns decreases as the patterns become less extensive.

INTRODUCTION

The abundance of certain elements in soils and other surficial materials is determined not only by the element content of the bedrock or other deposits from which the materials originated, but also by the effects of climatic and biological factors as well as by influences of agricultural and industrial operations that have acted on the materials for various periods of time. The diversity of these factors in a large area is expected to result in a corresponding diversity in the element contents of the surficial materials.

At the beginning of this study (1961), few data were available on the abundance of elements in surficial materials of the United States as a whole. Most of the early reports discussed only the elements that were of economic importance to mining or agriculture in a metallogenic area or State; and the data, for the most part, cannot be evaluated with reference to average, or normal, amounts in undisturbed materials because they were based on samples of deposits expected to have anomalous amounts of certain elements, or were based only on samples from cultivated fields.

We began a sampling program in 1961 that was designed to give estimates of the range of element abundance in surficial materials that were unaltered or very little altered from their natural condition, and in plants that grew on these deposits, throughout the conterminous United States. We believed that analyses of the surficial materials would provide a measure of the total concentrations of the elements that were present at the sampling sites, and that analysis of the plants would give an estimate of the relative concentrations among sites of the elements that existed in a chemical form that was available to plants. Because of the great amount of travel necessary to complete this sampling, we asked geologists and others of the U.S. Geological Survey to assist by collecting samples when traveling to and from their project areas and to contribute appropriate data they may have collected for other purposes. The reponse to this request, together with the samples and data that we had collected, resulted in our btaining samples of surficial materials and plants from 863 sites. The analyses of surficial materials sampled in this phase of the study were published for 35 elements by plotting element concentrations, in two to five frequency classes, on maps (Shacklette, Hamilton, and others, 1971).

Soon after the publication of the results of this study, interest in environmental matters, particularly in the effects of contamination and industrial pollution, increased greatly. At the same time, technological advances in analytical methods and data processing facilitated measurements of geochemical and other parameters of the environment. In response to the need for background data for concentrations of certain elements of particular environmental concern, the samples of surficial materials that were collected for the first study (Shacklette, Hamilton, and others, 1971) (with some ad-

ditional samples) were analyzed for other elements, and the results were published in U.S. Geological Survey Circulars: for mercury, Shacklette, Boerngen, and Turner (1971); for lithium and cadmium, by Shacklette, and others (1973); and for selenium, fluorine, and arsenic, Shacklette and others (1974).

The collection of samples for this study continued, as opportunities arose, until autumn 1975, resulting in the sampling of an additional 355 sites that were selected to give a more uniform geographical coverage of the conterminous United States. This sampling continuation is referred to as phase two. These samples were analyzed, and the data were merged with those of the original samples to produce the results given in the present report. In addition, the availability of analytical methods for elements not included in the earlier reports permitted data to be given on these elements in the more recently collected samples.

The collection localities and dates, sample descriptions, and analytical values for each sample in the present report were published by Boerngen and Shacklette (1981). The elemental compositions of only the surficial materials are given in this report; the data on analyses of the plant samples are held in files of the U.S. Geological Survey.

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REVIEW OF LITERATURE

The literature on the chemical analysis of soils and other surficial materials in the United States is extensive and deals largely with specific agricultural problems of regional interest. Many of the papers were written by soil scientists and chemists associated with State agricultural experiment stations and colleges of agriculture, and most reports considered only elements that were known to be nutritive or toxic to plants or animals.

Chemists with the U.S. Department of Agriculture prepared most early reports of element abundance in soils for large areas of the United States. (See Robinson, 1914; Robinson and others, 1917). The 1938 yearbook of agriculture was devoted to reports on soils of the United States; in this book, McMurtrey and Robinson (1938) discussed the importance and abundance of trace elements in soils. Amounts of the major elements in soil samples from a few soil profiles distributed throughout the United States were compiled by the soil scientist C. F. Marbut (1935) to illustrate characteristics of soil units.

The use of soil analysis in geochemical prospecting began in this country in the 1940's, and many reports were published on the element amounts in soils from areas where mineral deposits were known or suspected to occur. Most of these reports included only a few elements in soils from small areas. This early geochemical work was discussed by Webb (1953) and by Hawkes (1957). In succeeding years, as soil analyses became an accepted method of prospecting and as analytical

methods were improved, many elements in soils were analyzed; still, the areas studied were commonly small.

An estimate of the amounts of elements in average, or normal, soils is useful in appraising the amounts of elements in a soil sample as related to agricultural, mineral prospecting, environmental quality, and health and disease investigations. Swaine (1955) gave an extensive bibliography of trace-element reports on soils of the world, and he also summarized reports of the average amounts of elements as given by several investigators. The most comprehensive list of average amounts of rare and dispersed elements in soils is that of Vinogradov (1959), who reported the analytical results of extensive studies of soils in the Union of Soviet Socialist Republics, as well as analyses of soils from other countries. He did not state the basis upon which he established the average values; however, these values are presumably the arithmetic means of element amounts in samples from throughout the world. In their discussions of the principles of geochemistry, Goldschmidt (1954) and Rankama and Sahama (1955) reported the amounts of various elements present in soils and in other surficial materials, Hawks and Webb (1962) and, more recently, Brooks (1972), Siegal (1974), Levinson (1974), and Rose and others (1979) gave average amounts of certain elements in soils as useful guides in mineral exploration.

A report on the chemical characteristics of soils was edited by Bear (1964). In this book, the chapter on chemical composition of soils by Jackson (1964) and the chapter on trace elements in soils by Mitchell (1964) gave the ranges in values or the average amounts of some soil elements.

Regional geochemical studies conducted by scientists of the U.S. Geological Survey within the past two decades have been largely directed to the establishment of baseline abundances of elements in surficial materials, including soils. Most of the earlier work investigated these materials that occurred in their natural condition, having little or no alterations that related to human activities, with the objective of establishing normal element concentrations in the materials by which anomalous concentrations, both natural or man induced, could be judged. Some of these studies were conducted in cooperation with medical investigators who were searching for possible relationships of epidemiological patterns to characteristics of the environment. In one study, the geochemical characteristics of both natural and cultivated soils were determined in two areas of Georgia that had contrasting rates of cardiovascular diseases (Shacklette and others, 1970). In an extensive geochemical study of Missouri, also conducted cooperatively with medical researchers, both cultivated and natural soils were sampled. The results were presented for the State as a whole, and for physiographic regions or other subdivisions and smaller areas, as follows: Erdman and others (1976a, 1976b); Tidball (1976, 1983a, 1983b); and Ebens and others (1973). The results of these studies, and of other regional geochemical investigations, were summarized and tabulated by Connor and Shacklette (1975).

Recent regional studies of soil geochemistry by the U.S. Geological Survey related to the development of energy resources in the western part of the United States, including North Dakota, South Dakota, Montana, Wyoming, Colorado, Utah, and New Mexico. These studies established regional geochemical baselines for soils, both in undisturbed areas and in areas that had been altered by mining and related activities. Some of these studies considered the elements in soils both as total concentrations and as concentrations that were available to plants of the region. The results of these studies were published in annual progress reports (U.S. Geological Survey, 1974, 1975, 1976, 1977, and 1978). The data on soils, as well as on other natural materials, in these reports were summarized and tabulated by Ebens and Shacklette (1981). In a study of the elements in fruits and vegetables from 11 areas of commercial production in the United States, and in the soils on which this produce grew, soils were analyzed for 39 elements, as reported by Boerngen and Shacklette (1980) and Shacklette (1980).

The average amounts of elements in soils and other surficial materials of the United States, as determined in the present study, are given in table 1, with the average values or ranges in values that were reported by Vinogradov (1959), Rose and others (1979), Jackson (1964), Mitchell (1964), and Brooks (1972). The averages from the present study given in table 1 are the arithmetic means. Although the averages were computed by the methods described by Miesch (1967), the values obtained are directly comparable with the arithmetic means derived by common computational procedures.

COLLECTION AND ANALYSIS OF GEOCHEMICAL DATA

SAMPLING PLAN

The sampling plan was designed with the emphasis on practicality, in keeping with the expenditures of time and funds available, and its variance from an ideal plan has been recognized from the beginning. Because the collection of most samples was, by necessity, incidental to other duties of the samplers, the instructions for sampling were simplified as much as possible, so that sampling methods would be consistent within the wide range of kinds of sites to be sampled. The samples were

TABLE 1.—*Average or median contents, and range in contents, reported for elements in soils and other surficial materials*

[Data are in parts per million; each average represents arithmetic mean; leaders (—) in figure columns indicate no data available. A, average; M, median. <, less than; >, greater than]

Element	This report		Rose, and others (1979) (elements useful in geochemical prospecting)	Vinogradov (1959) (presumably, averages from worldwide sampling)	Jackson (1964)	Mitchell (1964)	Brooks (1972)
	Average	Range			"Typical",[1] average, or range in values	Range in contents in Scottish surface soils	Average or range
Al	72,000	700 - <10,000	—	71,300	10,000 - 60,000	—	—
As	7.2	<0.1 - 97	7.5 (M)	5	—	—	5
B	33	<20 - 300	29 (M)	10	30	—	10
Ba	580	10 - 5,000	300 (M)	—	—	400 - 3,000	500
Be	.92	<1 - 15	0.5 - 4	6	—	<5 - 5	6
Br	.85	<0.5 - 11	—	5	—	—	—
C, total	25,000	600 - 370,000	—	20,000	—	—	—
Ca	24,000	100 - 320,000	—	13,700	7,000	—	—
Ce	75	<150 - 300	—	—	—	—	—
Co	9.1	<3 - 70	10 (M)	8	—	<2 - 80	10
Cr	54	1 - 2,000	6.3 (M)	200	—	5 - 3,000	200
Cu	25	<1 - 700	15 (M)	20	20	<10 - 100	20
F	430	<10 - 3,700	300 (M)	200	—	—	—
Fe	26,000	100 - >100,000	21,000 (M)	38,000	7,000 - 42,000		10,000 - 50,000
Ga	17	<5 - 70	—	30	—	15 - 70	20
Ge	1.2	<0.1 - 2.5	—	1	—	—	5
Hg	.09	<0.01 - 4.6	0.056 (M)	—	—	—	.01
I	1.2	<0.5 - 9.6	—	—	—	—	—
K	15,000	50 - 63,000	11,000 (M)	13,600	400 - 28,000	—	—
La	37	<30 - 200	—	—	—	<30 - 200	—
Li	24	<5 - 140	6.2 (M)	30	—	—	30
Mg	9,000	50 - >100,000	—	6,300	<6,000	—	—
Mn	550	<2 - 7,000	320 (M)	850	—	200 - 5,000	850
Mo	.97	<3 - 15	2.5 (A)	2	—	<1 - 5	2.5
Na	12,000	<500 - 100,000	—	6,300	—	—	—
Nb	11	<10 - 100	15 (A)	—	—	—	15
Nd	46	<70 - 300	—	—	—	—	—
Ni	19	<5 - 700	17 (M)	40	—	10 - 800	40
P	430	<20 - 6,800	300 (M)	800	500	—	—
Pb	19	<10 - 700	17 (M)	—	—	<20 - 80	10
Rb	67	<20 - 210	35 (M)	100	—	—	—
S, total	1,600	<800 - 48,000	100 - 2,000	850	—	—	—
Sb	.66	<1 - 8.8	2 (A)	—	—	—	.5
Sc	8.9	<5 - 50	—	7	—	<3 - 15	—
Se	.39	<0.1 - 4.3	0.31 (M)	.001	—	—	.5
Si	310,000	16,000 - 450,000	—	330,000	—	—	—
Sn	1.3	<0.1 - 10	10 (A)	—	—	—	10
Sr	240	<5 - 3,000	67 (M)	300	—	60 - 700	300
Ti	2,900	70 - 20,000	—	4,600	1,200 - 6,000	—	—
Th	9.4	2.2 - 31	—	—	—	—	13
U	2.7	0.29 - 11	1 (A)	—	—	—	1
V	80	<7 - 500	57 (M)	100	—	20 - 250	100
Y	25	<10 - 200	—	50	—	25 - 100	—
Yb	3.1	<1 - 50	—	—	—	—	—
Zn	60	<5 - 2,900	36 (M)	50	—	—	50
Zr	230	<20 - 2,000	270 (M)	300	—	200 - >1,000	—

[1]Author's usage; generally used to indicate the most commonly occurring value.

collected by U.S. Geological Survey personnel along their routes of travel to areas of other types of field studies or within their project areas.

The locations of the routes that were sampled depended on both the network of roads that existed and the destinations of the samplers. Sampling intensity was kept at a minimum by selecting only one sampling site every 80 km (about 50 miles; selected for convenience because vehicle od meters were calibrated in miles) along the routes. The specific sampling sites were selected, insofar as possible, that had surficial materials that were very little altered from their natural condition and that supported native plants suitable for sampling. In practice, this site selection necessitated sampling away from roadcuts and fills. In some areas, only cultivated fields and plants were available for sampling.

Contamination of the sampling sites by vehicular emissions was seemingly insignificant, even though many sites were within 100 m or less of the roads. Col-

lecting samples at about 20 cm depth, rather than at the upper soil horizons, may have avoided the effects of surface contamination on the samples. However, we had no adequate way of measuring any contamination that may have occurred. (See Cannon and Bowles, 1962.) Many of the sampled routes had only light vehicular traffic, and some were new interstate highways. Routes through congested areas generally were not sampled; therefore, no gross contamination of the samples was expected.

The study areas that were sampled follow: Wisconsin and parts of contiguous States, southeastern Missouri, Georgia, and Kentucky, sampled by Shacklette; Kentucky, sampled by J. J. Connor and R. R. Tidball; Nevada, New Mexico, and Maryland, sampled by H. L. Cannon; various locations in Arizona, Colorado, Montana, New Mexico, Utah, and Wyoming, sampled by F. A. Branson and R. F. Miller; Missouri, sampled by Shacklette, J. A. Erdman, J. R. Keith, and R. R. Tidball; and various locations in Colorado, Idaho, Montana, South Dakota, Utah, and Wyoming, sampled by A. T. Miesch and J. J. Connor. Sampling techniques used in these areas varied according to the primary objectives of the studies being conducted, but generally these techniques were closely similar to the methods used in sampling along the roads.

In general, the sampling within study areas was more intensive than that along the travel routes. To make the sampling intensity of the two sampling programs more nearly equal, only the samples from selected sites in the study areas were used for this report. The selected sites were approximately 80 km apart. Where two or more samples were collected from one site, they were assigned numbers, and one of these samples was randomly chosen for evaluation in this study.

SAMPLING MEDIA

The material sampled at most sites could be termed "soil" because it was a mixture of comminuted rock and organic matter, it supported ordinary land plants, and it doubtless contained a rich microbiota. Some of the sampled deposits, however, were not soils as defined above, but were other kinds of regoliths. The regoliths included desert sands, sand dunes, some loess deposits, and beach and alluvial deposits that contained little or no visible organic matter. In some places the distinctions between soils and other regoliths are vague because the materials of the deposits are transitional between the two. Samples were collected from a few deposits consisting mostly of organic materials that would ordinarily be classified as peat, rather than soil.

To unify sampling techniques, the samplers were asked to collect the samples at a depth of approximately 20 cm below the surface of the deposits. This depth was chosen as our estimate of a depth below the plow zone that would include parts of the zone of illuviation in most well-developed zonal soils, and as a convenient depth for sampling other surficial materials. Where the thickness of the material was less than 20 cm, as in shallow soils over bedrock or in lithosols over large rock fragments, samples were taken of the material that lay just above the rock deposits. About 0.25 liter of this material was collected, put in a kraft paper envelope, and shipped to the U.S. Geological Survey laboratories in Denver, Colo.

CHEMICAL-ANALYSIS PROCEDURES

The soil samples were oven dried in the laboratory and then sifted through a 2-mm sieve. If the soil material would not pass this sieve, the sample was pulverized in a ceramic mill before seiving. Finally, the sifted, minus 2-mm fraction of the sample was used for analysis.

The methods of analysis used for some elements were changed during the course of this study, as new techniques and instruments became available. For most elements, the results published in the first report (Shacklette, Hamilton, and others, 1971) were obtained by use of a semiquantitative six-step emission spectrographic method (Meyers and others, 1961). The methods used for other elements were: EDTA titration for calcium; colorimetric (Ward and others, 1963) for phosphorus and zinc; and flame photometry for potassium. Many of the elements analyzed in the 355 samples collected in phase two of the study were also analyzed by the emission spectrographic method (Neiman, 1976). Other methods were used for the following elements: flame atomic absorption (Huffman and Dinnin, 1976) for mercury, lithium, magnesium, sodium, rubidium, and zinc; flameless atomic absorption (Vaughn, 1967) for mercury; X-ray fluorescence spectrometry (Wahlberg, 1976) for calcium, germanium, iron, potassium, selenium, silver, sulfur, and titanium; combustion (Huffman and Dinnin, 1976) for total carbon; and neutron activation (Millard, 1975, 1976) for thorium and uranium.

DATA PRESENTATION

Summary data for 46 elements are reported in tables 1 and 2. In table 1, the element concentrations found in samples of soil and other surficial materials of this study are compared with those in soils reported in other studies. Arithmetic means are used for the data of this study to make them more readily compared with the data generally reported in the literature. These arithmetic means were derived from the estimated geometric means by using a technique described by Miesch (1967), which is based on methods devised by Cohen (1959) and Sichel (1952). The arithmetic means in table

1, unlike the geometric means shown in table 2, are estimates of geochemical abundance (Miesch, 1967). Arithmetic means are always larger than corresponding geometric means (Miesch, 1967, p. B1) and are estimates of the fractional part of a single specimen that consists of the element of concern rather than of the typical concentration of the element in a suite of samples.

Concentrations of 46 elements in samples of this study are presented in table 2, which gives the determination ratios, geometric-mean concentrations and deviations, and observed ranges in concentrations. The analytical data for most elements as received from the laboratories were transformed into logarithms because of the tendency for elements in natural materials, particularly the trace elements, to have positively skewed

TABLE 2.—*Mean concentrations, deviations, and ranges of elements in samples of soils and other surficial materials in the conterminous United States*

[Means and ranges are reported in parts per million (μg/g), and means and deviations are geometric except as indicated. Ratio, number of samples in which the element was found in measurable concentrations to number of samples analyzed. <, less than; >, greater than]

Element	Conterminous United States			Western United States (west of 96th meridian)					Eastern United States (east of 96th meridian)				
	Mean	Deviation	Estimated arithmetic mean	Ratio	Mean	Deviation	Observed range	Estimated arithmetic mean	Ratio	Mean	Deviation	Observed range	Estimated arithmetic mean
Al, percent	4.7	2.48	7.2	661:770	5.8	2.00	0.5 - >10	7.4	450:477	3.3	2.87	0.7 - >10	5.7
As	5.2	2.23	7.2	728:730	5.5	1.98	<0.10 - 97	7.0	521:527	4.8	2.56	<0.1 - 73	7.4
B	26	1.97	33	506:778	23	1.99	<20 - 300	29	425:541	31	1.88	<20 - 150	38
Ba	440	2.14	580	778:778	580	1.72	70 - 5,000	670	541:541	290	2.35	10 - 1,500	420
Be	.63	2.38	.92	310:778	.68	2.30	<1 - 15	.97	169:525	.55	2.53	<1 - 7	.85
Bi	.56	2.50	.85	113:220	.52	2.74	<0.5 - 11	.86	78:128	.62	2.18	<0.5 - 5.3	.85
C, percent	1.6	2.57	2.5	250:250	1.7	2.37	0.16 - 10	2.5	162:162	1.5	2.88	0.06 - 37	2.6
Ca, percent	.92	4.00	2.4	777:777	1.8	3.05	0.06 - 32	3.3	514:514	.34	3.08	0.01 - 28	.63
Ce	63	1.78	75	81:683	65	1.71	<150 - 300	75	70:489	63	1.85	<150 - 300	76
Co	6.7	2.19	9.1	698:778	7.1	1.97	<3 - 50	9.0	403:533	5.9	2.57	<0.3 - 70	9.2
Cr	37	2.37	54	778:778	41	2.19	3 - 2,000	56	541:541	33	2.60	1 - 1,000	52
Cu	17	2.44	25	778:778	21	2.07	2 - 300	27	523:533	13	2.80	<1 - 700	22
F	210	3.34	430	598:610	280	2.52	<10 - 1,900	440	390:435	130	4.19	<10 - 3,700	360
Fe, percent	1.8	2.38	2.6	776:777	2.1	1.95	0.1 - >10	2.6	539:540	1.4	2.87	0.01 - >10	2.5
Ga	13	2.03	17	767:776	16	1.68	<5 - 70	19	431:540	9.3	2.38	<5 - 70	14
Ge	1.2	1.37	1.2	224:224	1.2	1.32	0.58 - 2.5	1.2	130:131	1.1	1.45	<0.1 - 2.0	1.2
Hg	.058	2.52	.089	729:733	.046	2.33	<0.01 - 4.6	.065	534:534	.081	2.52	0.01 - 3.4	.12
I	.75	2.63	1.2	169:246	.79	2.55	<0.5 - 9.6	1.2	90:153	.68	2.81	<0.5 - 7.0	1.2
K, percent[1]	1.5	.79	None	777:777	1.8	.71	0.19 - 6.3	None	537:537	1.2	.75	0.005 - 3.7	--
La	30	1.92	37	462:777	30	1.89	<30 - 200	37	294:516	29	1.98	<30 - 200	37
Li	20	1.85	24	731:731	22	1.58	5 - 130	25	479:527	17	2.16	<5 - 140	22
Mg, percent	.44	3.28	.90	777:778	.74	2.21	0.03 - >10	1.0	528:528	.21	3.55	0.005 - 5	.46
Mn	330	2.77	550	777:777	380	1.98	30 - 5,000	480	537:540	260	3.82	<2 - 7,000	640
Mo	.59	2.72	.97	57:774	.85	2.17	<3 - 7	1.1	32:524	.32	3.93	<3 - 15	.79
Na, percent	.59	3.27	1.2	744:744	.97	1.95	0.05 - 10	1.2	363:449	.25	4.55	<0.05 - 5	.78
Nb	9.3	1.75	11	418:771	8.7	1.82	<10 - 100	10	322:498	10	1.65	<10 - 50	12
Nd	40	1.68	46	120:538	36	1.76	<70 - 300	43	109:332	46	1.58	<70 - 300	51
Ni	13	2.31	19	747:778	15	2.10	<5 - 700	19	443:540	11	2.64	<5 - 700	18
P	260	2.67	430	524:524	320	2.33	40 - 4,500	460	380:382	200	2.95	<20 - 6,800	360
Pb	16	1.86	19	712:778	17	1.80	<10 - 700	20	422:541	14	1.95	<10 - 300	17
Rb	58	1.72	67	221:224	69	1.50	<20 - 210	74	107:131	43	1.94	<20 - 160	53
S, percent	.12	2.04	.16	34:224	.13	2.37	<0.08 - 4.8	.19	20:131	.10	1.34	<0.08 - 0.31	.11
Sb	.48	2.27	.67	35:223	.47	2.15	<1 - 2.6	.62	31:131	.52	2.38	<1 - 8.8	.76
Sc	7.5	1.82	8.9	685:778	8.2	1.74	<5 - 50	9.6	389:526	6.5	1.90	<5 - 30	8.0
Se	.26	2.46	.39	590:733	.23	2.43	<0.1 - 4.3	.34	449:534	.30	2.44	<0.1 - 3.9	.45
Si, percent[1]	31	6.48	None	250:250	30	5.70	15 - 44	None	156:156	34	6.64	1.7 - 45	--
Sn	.89	2.36	1.3	218:224	.90	2.11	<0.1 - 7.4	1.2	123:131	.86	2.81	<0.1 - 10	1.5
Sr	120	3.30	240	778:778	200	2.16	10 - 3,000	270	501:540	53	3.61	<5 - 700	120
Ti, percent	.24	1.89	.29	777:777	.22	1.78	0.05 - 2.0	.26	540:540	.28	2.00	0.007 - 1.5	.35
Th	8.6	1.53	9.4	195:195	9.1	1.49	2.4 - 31	9.8	102:102	7.7	1.58	2.2 - 23	8.6
U	2.3	1.73	2.7	224:224	2.5	1.45	0.68 - 7.9	2.7	130:130	2.1	2.12	0.29 - 11	2.7
V	58	2.25	80	778:778	70	1.95	7 - 500	88	516:541	43	2.51	<7 - 300	66
Y	21	1.78	25	759:778	22	1.66	<10 - 150	25	477:541	20	1.97	<10 - 200	25
Yb	2.6	1.79	3.1	754:764	2.6	1.63	<1 - 20	3.0	452:486	2.6	2.06	<1 - 50	3.3
Zn	48	1.95	60	766:766	55	1.79	10 - 2,100	65	473:482	40	2.11	<5 - 2,900	52
Zr	180	1.91	230	777:778	160	1.77	<20 - 1,500	190	539:541	220	2.01	<20 - 2,000	290

[1]Means are arithmetic, deviations are standard.

frequency distributions. For this reason, the geometric mean is the more proper measure of central tendency for these elements. The frequency distributions for potassium and silicon, on the other hand, are more nearly normal if the data are not transformed to logarithms and the mean is expressed as the arithmetic average.

In geochemical background studies, the magnitude of scatter to be expected around the mean is as important as the mean. In lognormal distributions, the geometric deviation measures this scatter, and this deviation may be used to estimate the range of variation expected for an element in the material being studied. About 68 percent of the samples in a randomly selected suite should fall within the limits M/D and $M \cdot D$, where M represents the geometric mean and D the geometric deviation. About 95 percent should fall between M/D^2 and $M \cdot D^2$, and about 99.7 percent between M/D^3 and $M \cdot D^3$.

The analytical data for some elements include values that are below, or above, the limits of numerical determination, and these values are expressed as less than (<) or greater than (>) a stated value. These data are said to be censored, and for these the mean was computed by using a technique described by Cohen (1959) and applied to geochemical studies by Miesch (1967). This technique requires an adjustment of the summary statistics computed for the noncensored part of the data. The censoring may be so severe in certain sets of data that a reliable adjustment cannot be made; with the data sets used in the present study, however, no such circumstances were encountered. The use of these procedures in censored data to quantify the central tendency may result in estimates of the mean that are lower than the limit of determination. For example, in table 2 the geometric-mean molybdenum concentration in soils from the Eastern United States is estimated to be 0.32 ppm, although the lower limit of determination of the analytical method that was used is 3 ppm. Use of this procedure permits inclusion of the censored values in the calculation of expected mean concentrations.

The determination ratios in table 2—that is, the ratio of the number of samples in which the element was found in measurable concentrations to the total number of samples—permit the number of censored values, if any, to be found that were used in calculating the mean. This number is found by subtracting the left value in the ratio from the right.

The distribution of the sampling sites and the concentrations of elements determined for samples from the sites are presented on maps of the conterminous United States (figs. 1–47). Figure 1 shows the locations of sites where four elements, bismuth, cadmium, praseodymium, and silver, were found in the samples. These elements were determined too uncommonly for reliable mean concentrations to be calculated. Each of the remaining maps (figs. 2–47) gives the locations where an element was found in a sample from a site and the concentration of the element, shown by a symbol that represents a class of values. By examining the tables of frequency for concentration values of the elements, we were able to divide the ranges of reported values for many elements into five classes so that approximately 20 percent of the values fell into each class. The limited range in values for some elements, however, prohibited the use of more than two or three classes to represent the total distribution. Symbols representing the classes were drawn on the maps by an automatic plotter that was guided by computer classification of the data, including the latitude and longitude of the sampling sites. A histogram on each map gives the frequency distribution of the analytical values, and the assignment of analytical values to each class as represented by symbols.

We were able to obtain analyses of 11 more elements for the 355 samples of phase two of this study than for the 963 samples of phase one because of improved analytical methods and services. These elements are antimony, bromine, carbon, germanium, iodine, rubidium, silicon, sulfur, thorium, tin, and uranium. The constraints of resources and time prohibited analysis of the 963 samples of the first phase for these additional elements. Results of analysis of the plant samples that were collected at all soil-sampling sites are not presented in this report.

Some elements were looked for in all samples but were not found. These elements, analyzed by the semiquantitative spectrographic method, and their approximate lower detection limits, in parts per million, are as follows: gold, 20; hafnium, 100; indium, 10; platinum, 30; palladium, 1; rhenium, 30; tantalum, 200; tellurium, 2,000; and thallium, 50. If lanthanum or cerium were found in a sample, the following elements, with their stated lower detection limits, were looked for in the same sample but were not found: dysprosium, 50; erbium, 50; gadolinium, 50; holmium, 20; lutetium, 30; terbium, 300; and thulium, 20.

DISCUSSION OF RESULTS

The data presented in this report may reveal evidence of regional variations in abundances of elements in soils or other regoliths; single values or small clusters of values on the maps may have little significance if considered alone. Apparent differences in values shown between certain sampling routes, such as some of those across the Great Plains and the North Central States where high values for cerium, cobalt, gallium, and lead predominate, suggest the possibility of systematic er-

rors in sampling or in laboratory analysis. Some gross patterns and some of lesser scale, nevertheless, are evident in the compositional variation of regoliths, as shown in figures 2–47.

The lower abundances of some elements (notably aluminum, barium, calcium, magnesium, potassium, sodium, and strontium) in regoliths of the Eastern United States, and the greater abundances of the heavy metals in the same materials of the Western United States indicate a regional pattern of the largest scale. This visual observation of the maps can be substantiated by examining the mean concentrations for these two regions given in table 2. The abundances of these elements differ markedly on either side of a line extending from western Minnesota southward through east-central Texas. This line is generally from the 96th to 97th meridian, and corresponds to the boundary proposed by Marbut (1935, p. 14), which divides soils of the United States into two major groups—the pedalfers that lie to the east, and the pedocals to the west. Marbut (1928) attributed the major differences in chemical and physical qualities of these two major groups to the effects of climate on soils. A line approximating the 96th meridian also separates the Orders, Suborders, and Great Groups of moist-to-wet soils in the Eastern United States from the same categories of dry soils that lie to the west, as mapped by the [U.S.] Soil Conservation Service (1969). As shown in table 2, soils of the Western United States have the highest mean values for all elements considered in this report except for antimony, boron, bromine, mercury, neodymium, selenium, titanium, and zirconium. The differences, however, probably are not significant for these latter elements, except for zirconium.

Superimposed upon this large-scale compositional variation pattern are several features of intermediate scale. Perhaps the most notable of these are the low concentrations of many elements in soils of the Atlantic Coastal Plain. Soils of the Pacific Northwest are high in concentrations of aluminum, cobalt, iron, scandium, and vanadium, but low in boron, and soils of the Rocky Mountain region tend to be high in copper, lead, and zinc.

Several small-scale patterns of compositional variation can be noted, among them the high mercury concentrations in surficial materials from the Gulf Coast of eastern Texas, Louisiana, Mississippi, Alabama, and northwest Florida, and a similar pattern on the Atlantic Coast in Connecticut, Massachusetts, and Maine. High phosphorus values occur in soils along a line extending west across Utah and Nevada to the coast of California, then south-east in California and Arizona. At the State level, Florida shows the most striking pattern by having low soil concentrations of most of the elements considered in this study.

The concentrations of certain elements do not show well-defined patterns of distribution, and the regiona concentrations of some other elements cannot be evaluated because they were not present in detectable amounts in most of the samples, or because the sampling density was insufficient. The degree of confidence in regional patterns of element abundance is expectec to be in direct proportion to the number of samples analyzed from the region. As the observed patterns become smaller, the probability increases that the characteristics that form the patterns are the results o chance.

Some features of element-abundance patterns proba bly reflect geologic characteristics of the areas that the soils overlie. Samples from most of the regoliths overly ing basic volcanic rocks of Washington and Oregon con tained higher than average concentrations of iron anc other elements, as mentioned earlier. A few soil sam ples with high phosphorus content are associated witl phosphate deposits in Florida, and a single sample i Michigan with high copper content is known to be o soil that occurs over a copper deposit.

These data do not provide obvious evidences of north south trends in elemental compositions that might b expected to relate to differences in temperature re gimes under which the surficial materials developed There is, moreover, no consistent evidence of signifi cant differences in element abundances betwee glaciated and nonglaciated areas (the general area c continental glaciation includes the northern tier c States from Montana to Maine and south in places t about lat 40°N.; see fig. 1).

The world averages of abundance for some element in soils, as given by Vinogradov (1959) and by other (table 1), do not correspond to the averages of abun dance for these elements in the soils of the Unite States, according to the data presented in this report The world averages are too low for the concentration of boron, calcium, cerium, lead, magnesium, potassium and sodium in United States soils and other surficia materials, and too high for beryllium, chromium, galli um, manganese, nickel, phosphorus, titanium, vanadi um, and yttrium.

The stability of values for concentrations of most ele ments seems to be satisfactory because the addition c analytical values for 355 samples of phase two of th study to values for 963 samples of the first phase di not significantly change the geometric means and devia tions of element abundance that were reported earlie (Shacklette, Boerngen, and Turner, 1971; Shacklette Hamilton, and others, 1971; Shacklette and others

1974). Although additional sampling of the same t[illegible]as reported here might give a clearer picture of small-to-intermediate element-abundance patterns, mean values reported herein most likely would not change significantly.

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DETERMINATION OF BACKGROUND CONCENTRATIONS OF INORGANICS IN SOILS AND SEDIMENTS AT HAZARDOUS WASTE SITES

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INTRODUCTION

The National Engineering Forum is a group of U.S. Environmental Protection Agency (EPA) professionals representing EPA Regional Offices, committed to the identification and resolution of engineering issues affecting the remediation of Superfund sites. The forum has identified the need to provide remedial project managers (RPMs) and other state or private personnel working with hazardous waste sites a thought-provoking, technical-issue paper on how to determine background concentrations of inorganics in soils and sediments at hazardous waste sites. Mr. Frank Vavra and Mr. Bob Stamnes, Engineering Forum members, provided technical guidance and direction in the development of this Issue paper.

This paper was prepared by R. P. Breckenridge and A. B. Crockett. Support for this project was provided by the National Exposure Research Laboratory's Characterization Research Division with the assistance of the Superfund Technical Support Project's Technology Support Center for Monitoring and Site Characterization. For further information, contact Ken Brown, Technology Support Center Director, at (702) 798-2270, or R. P. Breckenridge at (208) 526-0757, U.S. Department of Energy, Idaho National Engineering Laboratory.

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PURPOSE AND SCOPE

The purpose of this paper is to provide RPMs and others investigating hazardous waste sites a summary of the technical issues that need to be considered when determining if a site (i.e., hazardous waste site/area of concern) has elevated levels of inorganics relative to the local background concentrations. This issue paper is narrowly focused and is for **educational use only** by project managers. It is not meant to be a formal guidance document or "cookbook" on determination of background concentrations of inorganics at hazardous waste sites. This issue paper provides the investigator with information needed to determine whether activities conducted at a site have resulted in elevated concentrations of inorganic contaminants in soils or sediments compared with naturally occurring and off-site anthropogenic concentrations of the same contaminant.

The first portion of this paper provides a definition for and discusses factors that influence background concentrations. The second portion is separated into Part A, "Comparing the Concentrations of Inorganics in Soils and Sediments at Hazardous Waste versus Background Sites," and Part B, "Guidance for Addressing High Background Concentrations of Inorganics at CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) Sites." Part A is a modification of the State of Michigan guidance on conducting soil surveys (Michigan 1991a, 1991b) and discusses issues that need to be considered by investigators attempting to establish background concentrations for hazardous waste sites. It can be used to provide potentially responsible parties a summary of issues they need to consider when determining whether a hazardous waste site has elevated concentrations of inorganics compared to a background site. Part B presents a summary of a draft issue paper titled, "Options for Addressing High Background Levels of Hazardous Substances at CERCLA Sites" (EPA 1992a) and includes updated information and approaches.

This paper addresses technical issues for scientists and engineers faced with how to determine background concentrations. It is **not** intended to address agency policy-related decisions on how to use background data to achieve cleanup levels or achieve applicable or relevant and appropriate requirements (ARARs). Technical issues discussed here include selection of background sampling locations, considerations in the selection of sampling procedures, and statistical analyses for determining whether contaminant levels are significantly different on a potential waste site and a background site. How to statistically define background for purposes of remediating a hazardous waste site to background levels is **not** addressed.

This paper focuses on **inorganics** and, in particular, metals. Radionuclides are not specifically addressed; however, metals with radioactive isotopes (e.g., cobalt-60) that may be encountered at hazardous waste sites are included. This paper does not specifically address background concentrations of organics at a site, but the approach would be very similar in many respects (except for partitioning), and some unique aspects regarding organics are noted.

Statistics play a major role in establishing background concentration levels, and methods vary widely in their degree of complexity. No specific recommendations regarding statistical techniques are provided because they could be misused or have policy implications. However, some general guidance is presented to acquaint the reader with issues that should be discussed with a statistician early in the design of a study. Statistics should be used throughout the development of a sampling plan in the same manner as quality assurance. Sampling objectives, design, data analysis, and reporting can all be influenced by statistical considerations.

To provide recommendations that can be used at a variety of sites, information was gleaned from several different approaches to the background issue. The approach employed by the State of Michigan (Michigan 1990, 1991b) provides one of the most straightforward and scientifically sound strategies that, in combination with EPA documents (EPA 1989a, 1989b) and scientific literature (Underwood 1970; Kabata-Pendias and Pendias 1984), form the basis for this issue paper. This paper discusses the generic issues from various strategies that should be

considered when addressing the background issue. However, information presented here may need to be modified to meet site-specific soil and sediment or data-quality objective concerns.

STATEMENT OF ISSUE

Hazardous waste sites may pose a threat to human health and the environment when toxic substances have been released. The hazardous substances at a site may originate from either "on-site" (i.e., resulting from releases attributable to site-specific activities) or "off-site" (i.e., resulting from sources not on-site). These "off-site" substances may result either from natural sources (e.g., erosion of naturally occurring mineral deposits) or anthropogenic sources (e.g., widespread lead contamination from automobile exhaust in urban areas) (EPA 1992a). To determine the appropriate action to take at a hazardous waste site, EPA must distinguish between substances directly attributable to the hazardous waste site (i.e., "site" contaminants) and those attributable to "natural background" concentrations.

Definitions

Soils and sediments for this issue paper are defined as all mineral and naturally occurring organic material located at a site and will mostly be related to the material <2 mm in size because it is usually the finer material that has a greater affinity for inorganic contaminants. The U.S. Department of Agriculture and the International Soil Science Society use the 2-mm breakpoint to differentiate between soils or sediment (consisting of sands, silts, and clays) and gravel (Breckenridge et al. 1991; Lewis et al. 1991). When establishing background concentration levels, it is usually more cost effective to focus on the finer materials; however, some bias is introduced. Large particles can be rinsed and the rinsate analyzed if necessary. Soils and sediments are heterogeneous and contain a wide range of sizes from fine clays to larger gravel and coarse fragments (Soil Science Society of America 1978).

In the soils literature, the term "background" usually refers to areas in which the concentrations of chemicals have not been elevated by site activities. In the sediment literature, terms such as "background sediment" (in the Code of Federal Regulations (CFR)—40 CFR 131.35-91) and "reference sediment" (ASTM 1990) are used in similar manners and are often interchangeable.

To minimize confusion, the term "background concentration" is defined in this document as the **concentration of inorganics found in soils or sediments surrounding a waste site, but which are not influenced by site activities or releases**. A "background site" should be a site that is geologically similar and has similar biological, physical, and chemical characteristics (e.g., particle size, percent organic carbon, pH) as the contaminated site (ASTM 1990) but also should be upstream, upgradient, or upwind of the site. Samples taken from a site to determine background concentrations will be referred to as background samples.

Almost anyone involved with hazardous waste site evaluations will at some time be involved in determining background concentrations of inorganics at a site. There are two issues to be considered when addressing background. The first is whether the site and local area have a high natural variability in concentrations of inorganics. The second is to differentiate between natural and anthropogenic sources at a site with high background concentrations (e.g., lead in soil due to automobile emissions). The broad range in concentrations of naturally occurring inorganics may lead to the erroneous conclusion that an area has been contaminated with inorganics. Establishment of background concentrations based on adequate site-specific sampling data and comparison to normal background ranges for a specific area and land use can help resolve the confusion.

EPA in its *Risk Assessment Guidance for Superfund: Volume 1, Human Health Evaluation Manual (Part A)* (often referred to as RAGS) (EPA 1989c) discusses two categories of background:

1. Naturally occurring--substances present in the environment in forms that have not been influenced by human activity.

2. Anthropogenic--natural and man-made substances present in the environment as a result of human activities not specifically related to the CERCLA site.

Figure 1 shows the relationship between the on-site-related and off-site-related "populations" of substances that contribute to concentrations at a site. In some locations, the background concentrations resulting from naturally occurring or anthropogenic sources may exceed contaminant-specific standards promulgated to protect human health (EPA 1992a). The background concentration defined in this document includes both the naturally occurring and local/regional anthropogenic contributions (see Figure 1).

Background concentrations are needed when deciding whether a site is contaminated. Knowledge of background concentrations helps address issues such as (a) the effects of past land use practices on levels of inorganics in soil and sediment, and (b) establishing lower limits when conducting risk assessments for soil and sediment contamination.

Figure 2 illustrates a process for determining whether contaminant concentrations in soil and sediments at a hazardous waste site are elevated relative to background concentrations.

Determining the effect of past land use practices on levels of inorganics in soils and sediments is an important initial step towards quantifying the potential threat to human health and the environment. Information obtained from this step can provide the first indication that background concentrations may be elevated. Preliminary site investigations should be carefully planned so that high-quality data can be gathered to gain an understanding of the nature and degree of threat posed by a site and to determine whether immediate response is required.

Usually, remedial action is taken only on sites that exceed a 10^{-4} incremental cancer risk or exceed a hazard index of 1.0 for systemic effects. Superfund cleanups are generally conducted to 10^{-6} incremental cancer risk or to a safe hazard index. However, many states have developed statutes (ARARs) that require more stringent cleanup levels than risk-based levels and sometimes require cleanup to natural background concentrations.

It is often best to compare mean concentrations between groups of similar samples from the hazardous waste and background sites. Mean values can be developed for a soil series or an operable unit. The operable unit is usually the smallest area that would be considered under a remediation plan (e.g., 10 m × 10 m if a bulldozer is used to remove the top 6 inches of soil). However, there may be cases when it is important to know if a single sample has a high probability of exceeding background. In this case, the single value can be compared to the background maximum limit (mean background concentration plus three standard deviations), which is discussed later.

Background Concentration

Numerous natural and anthropogenic sources influence background concentrations and need to be accounted for during an initial hazardous waste site investigation. Proper accounting of these sources is important when establishing cleanup standards and are critical if discussions about ARARs develop.

It is not feasible to establish a single universal background concentration for soils or sediments; it is more useful to discuss the **range** of background concentrations for a contaminant. Single values are hard to establish because concentrations vary depending on how physical, chemical, and biological processes, and anthropogenic contributions have affected parent geological material at a site. If a site has various soil or sediment textures (e.g., sands, loams), a range in inorganic concentrations should be developed for different soil series or textural groupings. Thus, physical and chemical parameters need to be identified when investigating a site to ensure that soils or sediments with similar parameters are compared. This is important because there are often different soil types at a site, and sediments differ depending on where (e.g., in a pool or main channel) and when samples are collected. The following parameters should be similar when

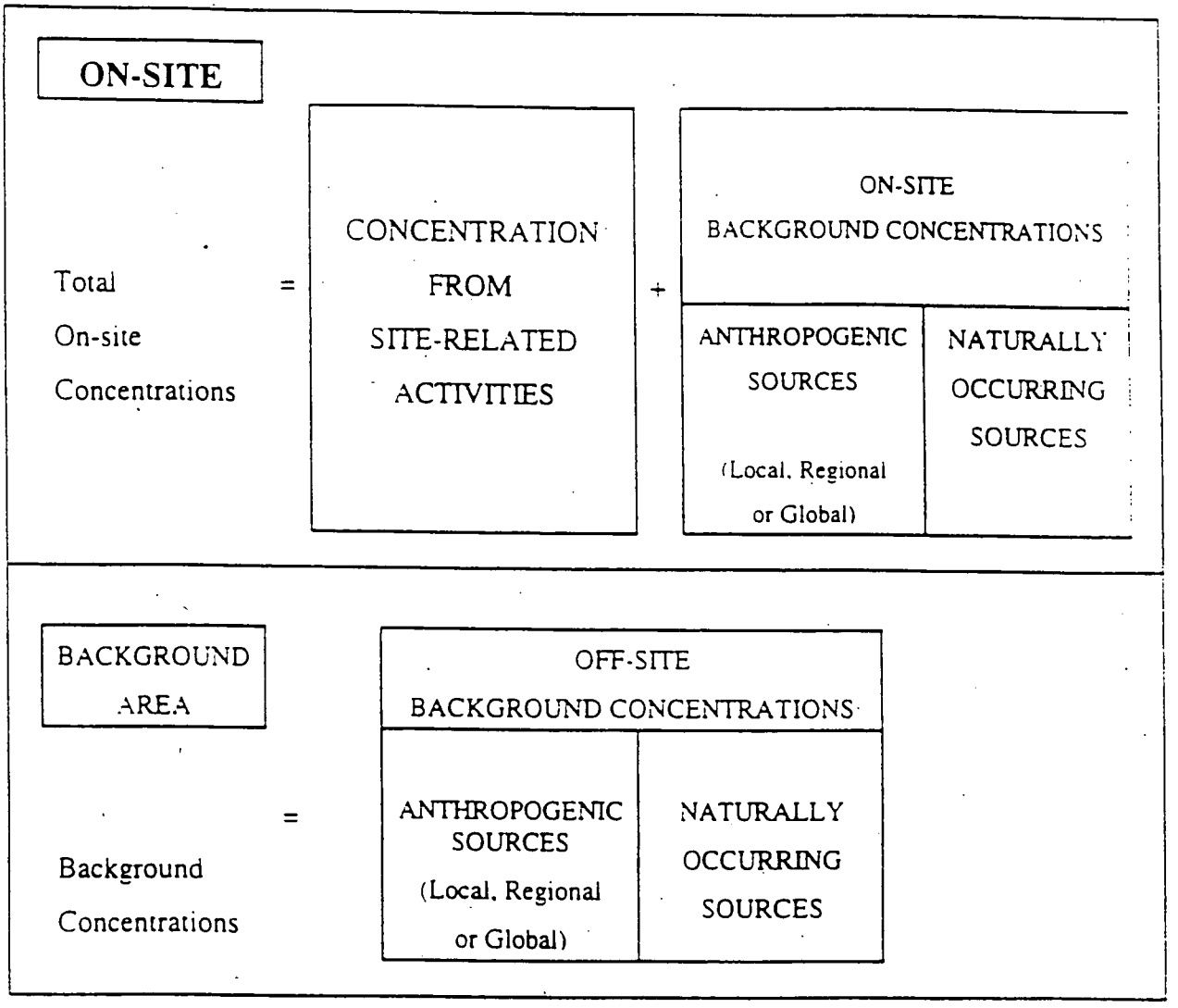


Figure 1. **Relationship between on- and off-site concentration groupings when defining background concentrations for hazardous waste sites.**

comparing paired hazardous waste site samples to background samples:

- pH/Eh
- salinity
- cation exchange capacity (CEC)
- percent organic carbon
- particle size and distribution
- thickness of horizon (soil)
- soil type, structure (soil)
- sample design
- depth of sampling
- sampling equipment and compositing regime (if applicable)
- number of samples
- digestion/analytical method
- acid volatile sulfide concentrations (sediment)
- simultaneously extracted metal concentrations (for determining sediment toxicity)

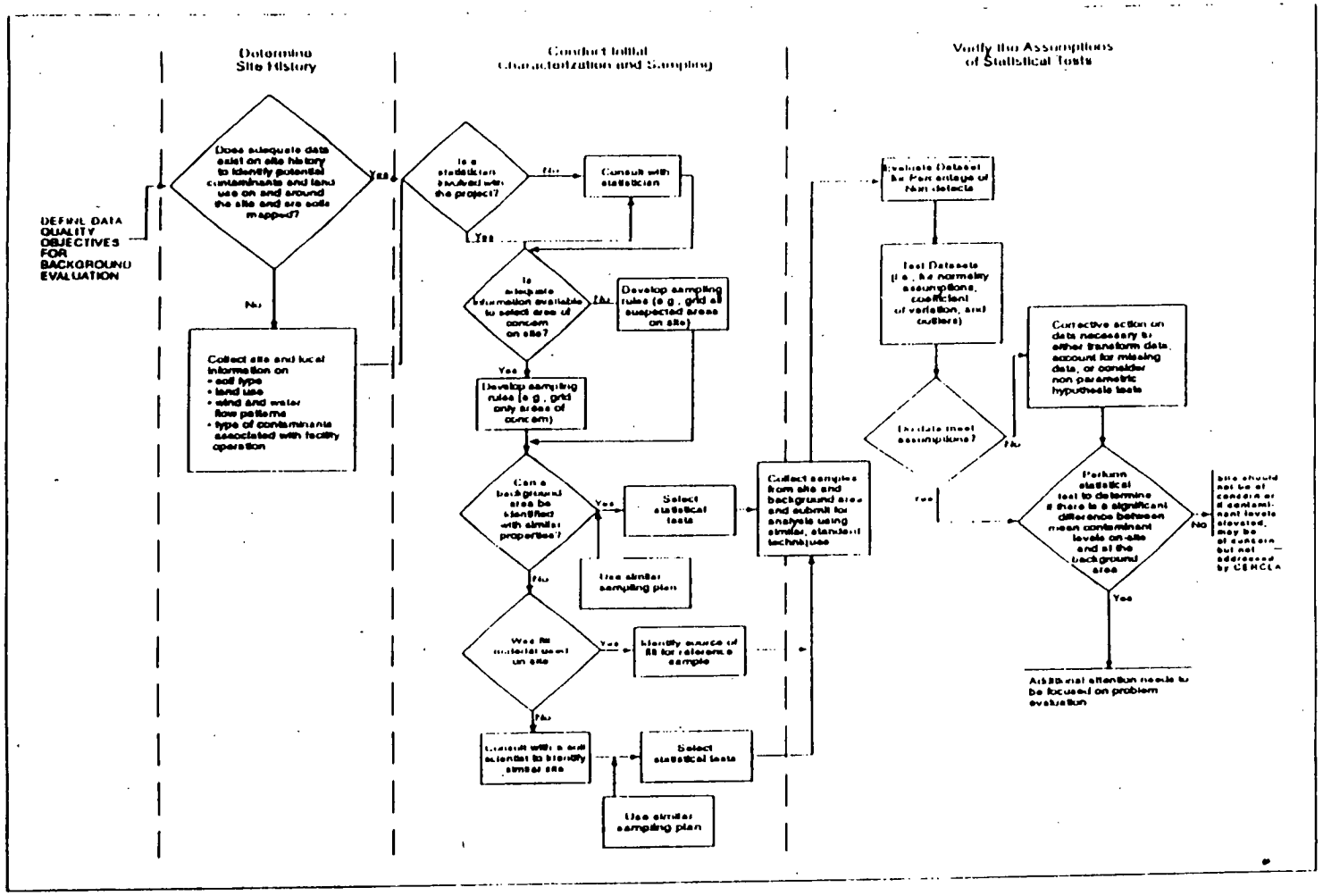


Figure 2. Process for determining if contaminant concentrations at a hazardous waste site are above background concentrations in soil and sediments.

At times some of these soil parameters such as percent organic carbon, pH and salinity may be altered by hazardous waste site activities. These changes in soil chemistry could falsely imply that the hazardous waste site and background site soil/sediment matrices are totally very comparable. For example, if oil were released at a hazardous waste site where mercury is of a concern, the percent organic carbon values could be much higher than at the background site. This could lead to an incorrect conclusion that the sites are not similar for comparison of inorganic concentrations.

Many of these soil parameters can be obtained by contacting the local Natural Resources Conservation Service (NRCS) Office and requesting a soil survey report for the county (usually free of charge) where the site is located. Most soils on private lands in the U.S. have been mapped by the NRCS. By using a soil survey report, the field personnel can evaluate how the soils were originally classified and gain access to average values for the soil series located at the site. By consulting with a soil scientist and comparing current site soils to those previously mapped, an assessment can be made of the amount of change and disturbance that has occurred to the soil profile. Aerial photographs used to map soils are also helpful in evaluating past land use, locating stream channels, determining parent material for sediment loading, and determining site factors that affect movement of contaminants (e.g., low percolation rate). More detail on how and why to characterize soils at hazardous waste sites can be found in a companion issue paper (Breckenridge et al. 1991).

A special case occurs for hazardous waste sites that contain fill. "Fill areas" may be present around construction or disposal areas and should be suspected if the site is located in areas frequently inundated with water. Sites where dredge material (e.g., sediments from shipping areas) is suspected to have been used as fill should be given additional attention because the dredge material may have elevated levels of contaminants. A soil scientist can usually identify fill locations and areas disturbed by construction because of the disturbed nature of the soil profile.

Natural and Regional Anthropogenic Contributions to Background Concentrations

Table 1 presents concentration ranges and mean values of inorganics in selected surface soils of the United States. Most of this contribution is due to natural and regional/global anthropogenic sources. The soil types presented are general, but cover many of the major categories found in the United States. There is one omission from the table and that is for cadmium, since cadmium mobility is strongly dependent on soil pH and percent organic carbon. The mean global content of cadmium in soils is between 0.07 and 1.1 ppm (ppm-dry weight - mg/kg for SI units); for the United States, values range from 0.41 to 0.57 ppm, but values of up to 1.5 ppm have been documented in some forest soils (Kabata-Pendias and Pendias 1984). In all cases, the higher cadmium values reflect anthropogenic contributions (from local and regional sources) to topsoils.

Table 2 provides average, range, and no-effect levels for selected inorganics in sediment and soils that can be used to compare to background concentrations for a site. The no-effect levels are the metal concentrations in sediment that have a low probability of causing a measurable impact on benthic populations. The control values for soils and sediments approximate the average concentrations of metals contributed by natural and anthropogenic (local and global) values (Lee et al. 1989; EPA 1992b). These values should not be used as background concentrations but can be used to guide investigators in determining whether elevated levels of contaminants may be present at a hazardous waste site.

Local Anthropogenic Sources that Influence Background Concentrations

Note: Some of the activities discussed here may not be waste handling or disposal activities; however, they could qualify as releases under Superfund (e.g., mining activities may result in releases that can be addressed under Superfund).

Numerous local anthropogenic activities can contribute to the inorganic concentrations at a hazardous waste site yet are not directly related to site activities. Local soils and sediments may be contaminated by ore deposits or mining, by

TABLE 1. CONCENTRATION OF INORGANICS IN SURFACE SOILS OF THE U.S. [IN PPM-DRY WEIGHT, DW), EQUIVALENT TO mg/kg-dw] (SOURCE: KABATA-PENDIAS AND PENDIAS 1984).

	Elements											
	As		Ba		Co		Cr		Cu		Hg	
Soil	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Sandy soils and lithosols on sandstones	<0.1-30.0	5.1	20-1500	400	0.4-20	3.5	3-200	40	1-70	14	<0.01-0.54	0.08
Light loamy soils	0.4-31.0	7.1	70-1000	555	3-30	7.5	10-100	55	3-70	25	0.01-0.60	0.07
Loess and soils on silt deposits	1.9-16.0	6.6	200-1500	675	3-30	11.0	10-100	55	7-100	25	0.01-0.38	0.08
Clay and clay loamy soils	1.7-27.0	7.7	150-1500	535	3-30	8.0	20-100	55	7-70	29	0.01-0.90	0.13
Alluvial soils	2.1-22.0	8.2	200-1500	660	3-20	9.0	15-100	55	5-50	27	0.02-0.15	0.05
Soils over granites and gneisses	0.7-15.0	3.6	300-1500	785	3-15	6.0	10-100	45	7-70	24	0.01-0.14	0.06
Soils over volcanic rocks	2.1-11.0	5.9	500-1500	770	5-50	17.0	20-700	85	10-150	41	0.01-0.18	0.05
Soils over limestones and calcareous rocks	1.5-21.0	7.8	150-1500	520	3-20	9.5	5-150	50	7-70	21	0.01-0.50	0.08
Soils on glacial till and drift	2.1-12.0	6.7	300-1500	765	5-15	7.5	30-150	80	15-50	21(a)	0.02-0.36	0.07
Light desert soils	1.2-18.0	6.4	300-2000	835	3-20	10.0	10-200	60	5-100	24	0.02-0.32	0.06(a)
Silty prairie soils	2.0-12.0	5.6	200-1500	765	3-15	7.5	20-100	50	10-50	20(a)	0.02-0.06	0.04(a)
Chernozems and dark prairie soils	1.9-23.0	8.8	100-1000	595	3-15	7.5	15-150	55	10-70	27	0.02-0.53	0.10
Organic light soils	<0.1-48.0	5.0	10-700	265	3-10	6.0	1-100	20	1-100	15	0.01-4.60	0.28
Forest soils	1.5-16.0	6.5	150-2000	505	5-20	10.0	15-150	55	7-150	17(a)	0.02-0.14	0.06(a)
Various soils	<1.0-93.2	7.0	70-3000	560	3-50	10.5	7-1500	50	3-300	26	0.02-1.50	0.17

TABLE 1. (CONTINUED)

Soil	Elements											
	Mn		Ni		Pb		Se		Sr		Zn	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Sandy soils and lithosols on sandstones	7-2000	345	<5-70	13.0	<10-70	17	0.005-1.5	0.5(a)	5-1000	125	<5-164	40.0
Light loamy soils	50-1000	480	5-200	22.0	<10-50	20	0.02-1.2	0.33(a)	10-500	175	20-118	55.0
Loess and soils on silt deposits	50-1500	525	5-30	17.0	10-30	19	0.02-0.7	0.26(a)	20-1000	305	20-109	58.5
Clay and clay loamy soils	50-2000	580	5-50	20.5	10-70	22	<0.1-1.9	0.5	15-300	120	20-220	67.0
Alluvial soils	150-1500	405	7-50	19.0	10-30	18	<0.1-2.0	0.5	50-700	295	20-108	58.5
Soils over granites and gneisses	150-1000	540	<5-50	18.5	10-50	21	<0.1-1.2	0.4	50-1000	420	30-125	73.5
Soils over volcanic rocks	300-3000	840	7-150	30.0	10-70	20	0.1-0.5	0.2	50-1000	445	30-116	78.5
Soils over limestones and calcareous rocks	70-2000	470	<5-70	18.0	10-50	22	0.1-1.1	0.19(a)	15-1000	195	10-106	50.0
Soils on glacial till and drift	200-700	475	10-30	18.0	10-30	17(a)	0.2-0.8	0.4	100-300	190	47-131	64.0(a)
Light desert soils	150-1000	360	7-150	22.0	10-70	23	<0.1-1.1	0.5	70-2000	490	25-150	52.5
Silty prairie soils	200-1000	430	<5-50	16.0	10-30	21(a)	<0.1-1.0	0.3	70-500	215	30-88	54.3(a)
Chernozems and dark prairie soils	100-2000	600	7-70	19.5	10-70	19	<0.1-1.2	0.4	70-500	170	20-246	81.5
Organic light soils	7-1500	260	<5-50	12.0	10-50	24	<0.1-1.5	0.3	5-300	110	<5-108	41.0
Forest soils	150-1500	645	7-100	22.0	10-50	20(a)	<0.1-1.6	0.4	20-500	150	25-155	45.7(a)
Various soils	20-3000	490	<5-150	18.5	<10-70	26	<0.1-4.0	0.31	7-1000	200	13-300	73.5

a. Data for whole soil profile.

TABLE 2. AVERAGE RANGE AND LOW- TO NO-EFFECT LEVELS OF SELECTED INORGANICS IN SEDIMENTS AND SOILS (mg/kg UNLESS OTHERWISE NOTED).

Media and source	Ag	As	Ba	Cd	Cr	Cu	Fe%	Hg	Mn	Ni	Pb	Zn
SEDIMENTS[a,b]												
Non-polluted, Great Lakes (U.S. Army Corps of Engineers 1977)	---	<3	<20	---	<25	<25	<1.7	<1.0	<300	<20	<40	<90
No effect level (Persaud et al. 1989)[b]	—	4.0		0.6	22	15	2.0	0.1	400	15	23	65
	0.5	8	--	1.0	33	28	--	0.1	—	—	21	68
Effects range low, marine sediments (Long et al. 1995)[b]	1.0	8.2	---	1.2	81	34	---	0.15	--	20.9	46.7	150
No adverse biological effects, marine sediments (WDOE 1991)[b]	6.1	57		5.1	260	390		0.41		--	450	410
Control sediments, Southern California (Lee et al. 1989)[a]	0.06-2.0	3-15	---	0.001-2	6.5-40	2.8-30		<1.0		<20.0	<10.0	<70.0
Control sediments, Puget Sound (Lee et al. 1989)[a]	1.2	3-15		3.1-18.3	20.9	10-50		0.02-0.12		13.0	8	
Control sediments, Yaquina Bay (Lee et al. 1989)[a]	0.55			0.47	19.3	6.3				14.5	5.5	26.3
No effect threshold, freshwater sediments[b] (Environment Canada 1992)	—	3.0		0.2	55	28		0.05		35	23	100
Lowest effect level, freshwater sediments (Persaud et al. 1992)	0.5	6		0.6	26	16		0.2	460	16	31	120
Threshold effect levels for freshwater sediments (Environment Canada 1994)	—	5.9	---	0.596	37.3	35.7		0.174	--	18.0	35.0	123.1
Threshold effect levels for marine sediments (Environment Canada 1994)	0.73	7.24	—	0.676	52.3	18.7		0.13	--	15.9	30.2	124
Effects range low, freshwater (Ingersoll et al. 1995)	—	13	--	0.70	39	41	20	--	730	24	55	110
SOILS (control values)[a]												
Average and common range in natural soils (summarized in Shields 1988)	0.05 0.01-5	5 0.1-40	430 100-3500	0.06 0.01-7	100 5-3000	30 2-100		0.11 0.01-0.8	600 100-4000	40 5-1000	10 2-200	50 10-300
Average concentration in earth's crust (Merck 1989)	---	0.5	500	0.1-0.2	100-300	70	5	0.5	850	180	20	200
Average concentration in earth's crust (CRC 1992)	0.07	1.8	425	0.2	100	55	5.63	0.08	950	75	12.5	70
Relative abundance in soils (Martin and Whitfield 1983)	0.05	6.0		0.35	70	34	4.0		1000	50	35	90

a Control values approximate natural background

b No effect refers to no measurable impact to benthic organisms when exposed to sediments with stated levels of metal.

agricultural application of pesticides or sewage sludge, and by emissions from motor vehicles. In urban areas, sites may become contaminated by air emissions from home heating, automobiles, and industry. Table 3 provides ranges of contaminant levels in surface soils from some local anthropogenic sources of inorganics that could contribute to background concentrations at or near a hazardous waste site. Table 4 provides a review of some of the more common agricultural sources of inorganics associated with practices such as sludge, pesticides, and fertilizer applications.

These tables identify elements that could be associated with different land uses at or around a hazardous waste site. For example, if the site is located in an area with high agricultural chemical usage, elevated background concentrations of arsenic, bromine, lead, vanadium, and zinc could be expected. To determine what background concentrations might be without the agricultural contribution, the investigator needs to rely on some investigative skills. These skills are detailed in Part A of this document.

Accessing Data and Methods for Establishing Background Concentrations

The previous discussion presented information on ranges of background concentrations that could be expected for inorganics of greatest concern at hazardous waste sites. Additional information sources that should be consulted include soil scientists from the NRCS and county extension agents who may have conducted soil surveys that describe the natural soils' physical, chemical, and biological status. However, many of these surveys were conducted for purposes such as mineral development, farming, and soil conservation; the data focus on properties of soils. The NRCS maintains the SOILS-5 data base that provides attributes of soils (e.g., texture, pH, CEC, salinity, clay content) that can be accessed at the local NRCS Office or through the NRCS Office of Technology, Cartography and Geographic Information System Division at (202) 447-5421. Many data sets are available on World Wide Web (WWW). The U.S. Geological Survey (USGS) Global Land Information (GLI) system is another source for most land-based data and can be located on WWW at *http://edcwww.cr.usgs.gov/glis/glis.html*. The Agricultural Stabilization and Conservation Service can also be a good source of aerial photographs for hazardous waste site assessment. Information on soil surveys, aerial photographs, and other sources that may be useful for identifying soil types and land use in the United States is presented in Table 5.

Several large projects have been conducted to address the issue of characterizing background soil concentrations. For example, the Oak Ridge Reservation (a U.S. Department of Energy facility) conducted a background soil characterization project to establish a database, to recommend how to use the data for contaminated site assessments, and to provide estimates of the potential health and environmental risks associated with the background level concentrations of potentially hazardous constituents (see Table 5, ORNL 1993). This source provides a detailed approach for those faced with conducting a detailed background investigation.

Approach for Establishment of Background Reference Values

The approaches described in this document, for the most part, combine discussion of issues generic to soils and sediments. However, when warranted, attributes unique to the two different media are discussed in separate sections. One such section discusses sediments that require sampling through overlying water.

PART A

COMPARING THE CONCENTRATIONS OF INORGANICS IN SOILS AND SEDIMENTS AT HAZARDOUS WASTE VERSUS BACKGROUND SITES

The objective of Part A is to determine whether hazardous waste site-related activities have caused an increase in the levels of inorganic contaminants in soils and sediments compared to background concentrations.

SOILS

Step 1—Evaluation of Land Use History and Existing Data

Purpose: This effort is designed to identify land use history both on and near the hazardous waste site (i.e., within the air and watershed connected to

TABLE 3. INORGANIC CONTAMINATION OF SURFACE SOILS, AVERAGE VALUES FROM VARIOUS ANTHROPOGENIC SOURCES IN THE UNITED STATES (PPM-DW)[a] (SOURCE: KABATA-PENDIAS AND PENDIAS 1984).

Element	Site and pollution source	Mean or range of content
Arsenic (As)	Metal-processing industry	10-380
	Application of arsenal pesticides	31-625
Cadmium (Cd)	Metal-processing industry	26–160
	Urban garden	0.02–13.6
	Vicinity of highways	1–10
Cobalt (Co)	Mining or ore deposit	13–85
	Metal-processing industry	42–154
	Roadside or airport area	7.9
Copper (Cu)	Urban gardens, orchards, and parks	3-140
	Sludged farmland	90
Lead (Pb)	Metal processing industry	500–6,500
	Urban garden and urban vicinity	218–10,900
	Roadside soil	960–7,000
	Non-ferric metal mining	15–13,000
Mercury (Hg)	Hg mining or ore deposit	0.1–40
	Urban garden, orchard, and parks	0.6
Zinc (Zn)	Non-ferric metal mining	500-53,000
	Metal processing industry	155-12,400
	Urban gardens and orchards	20-1,200

a. Equivalent to mg/kg-DW.

or in proximity to the site) to determine what contribution the anthropogenic activities from previous land use at or near the hazardous waste site have had on background concentrations.

Approach: Early in a hazardous waste site investigation, site history should be determined by examining available records and by interviewing personnel familiar with the site. This information can be used to assess the types of contaminants associated with past operations that may be of concern and may be compared to Appendix IX, Superfund and Priority Pollutant Compounds, lists which identify the inorganic contaminants of concern. Evaluation of site history can provide important data when determining those compounds for which background concentrations need to be established. For example, if releases of cadmium and lead are suspected at a hazardous waste site and the site is located in a heavily industrialized area, there is high potential that metals like mercury, lead, and cadmium may be present and elevated in soils and sediment from off-site contributions. An initial evaluation of on-site data should be sensitive to the issue of elevated background so that off-site contributions can be properly accounted for.

Another advantage of evaluating existing hazardous waste site data is to determine if pre-site operation values are available for inorganics in sediments or soil. These data can be obtained from site records or other existing sources discussed later in this paper. NRCS soil surveys should be checked both for aerial photographs that sh w previous land use on or near the site and for average physical and chemical properties for soils at and around the hazardous waste site. Local county agricultural

TABLE 4. AGRICULTURAL SOURCES OF INORGANIC CONTAMINATION IN SOILS (PPM DW)[a] (KABATA-PENDIAS AND PENDIAS 1984).

Element	Sewage sludges	Phosphate fertilizers	Limestones	Nitrogen fertilizers	Manure	Pesticides (%)
As	2–26	2–1,200	0.1–24.0	2.2–120	3–25	22–60
B	15–1,000	5–115	10		0.3–0.6	
Ba	150–4,000	200	120–250		270	
Be	4–13	–	1		–	
Br	20–165	3–5		185–716	16–41	20–85
Cd	2–1,500	0.1–170	0.04–0.1	0.05–8.5	0.3–0.8	
Ce	20	20	12		–	
Co	2–260	1–12	0.4–3.0	5.4–12	0.3–24	–
Cr	20–40,600	66–245	10–15	3.2–19	5.2–55	–
Cu	50–3,300	1–300	2–125	<1–15	2–60	12–50
F	2–740	8,500–38,000	300	–	7	18–45
Ge	1–10	–	0.2		19	–
Hg	0.1–55	0.01–1.2	0.05	0.3–2.9	0.09–0.2	0.8–42
In	–	–	–		1.4	–
Mn	60–3,900	40–2,000	40–1,200	–	30–550	–
Mo	1–40	0.1–60	0.1–15	1–7	0.05–3	–
Ni	16–5,300	7–38	10–20	7–34	7.8–30	–
Pb	50–3,000	7–225	20–1,250	2–27	6.6–15	60
Rb	4–95	5	3	–	0.06	–
Sc	0.5–7	7–36	1	–	5	–
Se	2–9	0.5–25	0.08–0.1	–	2.4	–
Sn	40–700	3–19	0.5–4.0	1.4–16.0	3.8	–
Sr	40–360	25–500	610	–	80	–
Te	–	20–23	–		0.2	–
U	–	30–300	–		–	–
V	20–400	2–1,600	20		–	45
Zn	700–49,000	50–1,450	10–450	1–42	15–250	1.3–25
Zr	5–90	50	20		5.5	–

a. Equivalent to mg/kg-DW.

TABLE 5. SOURCES OF INFORMATION FOR IDENTIFYING SOIL TYPES, LAND USE, AND DETERMINING BACKGROUND LEVELS OF INORGANICS IN SOILS AND SOME SEDIMENTS IN THE U.S.

Source	Supporting background information	Locations	Contact point
Bureau of Land Management—BLM	Provides data on areas in the country that have naturally occurring substances that pose a hazard to humans or the environment.	Mostly western U.S.	BLM Service Center Denver Federal Center Lakewood, CO 80225 (303) 236-0142
National Park Service (NPS)	Inventory and monitoring of trace levels of inorganics in soils in natural areas.	Nationwide	Local NPS Headquarters
U.S. Geological Survey	Several reports on the concentration of inorganics in the environment:	Nationwide	Water Resources Information Center: (703) 648-6818
	Background geochemistry of some rocks, soils, plant, and vegetables in the conterminous U.S. "Geological Survey," professional paper 574-F. 1975—Summary of determination between natural and anthropogenic contributions—shows natural values vary widely and are highly site specific and regionally dependant.	Nationwide	National Technical Information Service (NTIS) U.S. Department of Communication (703) 487-4650
	An accounting of pesticides in soils and ground water in the Iowa River Basin, 1985-88 (IA 86-055).	Midwest	NTIS
U.S. Geological Survey	Aerial photographs of sites.	Nationwide	USGS, Salt Lake City ESIC 8105 Federal Bldg. 125 South State St. Salt Lake City, UT 84138-1177 (801) 524-5652/Fax: (801) 524-65[illegible]
USDA-Agricultural Stabilization and Conservation Service (ASCS/SCS)	Aerial photographs of current and previous land use and soils types including erosion potential.	Nationwide	ASCS/SCS Aerial Photography Field Office. P.O. Box 30010 Salt Lake City, UT 84130-0010 (801) 975-3503/Fax: (801) 975-35[illegible]
National Ocean Service (NOS)	Coastal and Geodetic Surveys including aerial photographs.	Coastal areas	National Ocean Service Coast and Geodetic Survey Support Sec. N/CG236 SSMC#3, Rm. 5212 1315 East-West Highway Silver Spring, MD 20910 (301) 713-2692/Fax: (301) 713-04[illegible]

TABLE 5. (CONTINUED)

Source	Supporting background information	Locations	Contact point
National Archives Research Administration/National Air Survey (NARA/NASC)	Series of infrared Landsat photographs for mid-1970s by state.	Nationwide	NARA/NASC National Air Survey 4321 Baltimore Ave. Bladensburg, MD 20710 (301) 927-7180/Fax: (301) 927-5013
* U.S. Forest Service (FS)	Often have data on trace elements as part of soils inventory and monitoring program.	Nationwide	Nearest FS experiment station
U.S. Department of Energy (DOE)	Collects and publishes data on trace metals and radionuclide concentrations around DOE facilities and for reference sites.	Nationwide	Nearest DOE office, Environmental Monitoring Division
* Oak Ridge National Laboratory	The background soil characterization project provides background levels of selected metals, organic compounds, and radionuclides in soils from uncontaminated sites at the Oak Ridge Reservation. Also a good approach for evaluating background for use in baseline risk assessments	Local - Roane County, TN Approach useful nationwide	D.R. Watkins Oak Ridge Reservation Environmental Restoration Div. P.O. Box 2003 Oak Ridge, TN 37831-7298 (615) 576-9931 See ref. ORNL 1993.
National Climatic Data Center	Provide data on wind roses and climate parameters for most areas of the country.	Nationwide	User Service Branch Asheville, NC (704) 259-0682
EPA	Most complete source of data that includes EPA and other Agency information on Hazard ID, Dose-Response, and Risk Characterization.	Nationwide	EPA/540/1-86/061 (EPA 1986)
	STORET (physical and chemical parameters in soils and sediments).		EPA Office of Water and Hazardous Material (202) 382-7220 Commercial product—more user friendly, EarthInfo: (303) 938-1788
Journal Articles	Can provide local, regional, or national background concentration values. Can be accessed via literature searches, but usually need to be searched by element or media.	Local to National	Selected references: (1) Metals in Determining Natural Background Concentrations in Mineralized Areas, 1992 (Runnells et al. 1992), and (2) Sediment Quality and Aquatic Life Assessment (Adams et al 1992).

agents and state, county, and federal environmental quality officials are also sources of information on local emissions or previous sampling data that may be used to establish background concentrations. EPA or state regulators of chemical storage, use, and emission data bases of local industries may be a good source of chemicals used or stored in the local area. EPA's STORET data base should be checked

Step 2—Establishment of Data Quality Objectives

Purpose: The purpose of Step 2 is to establish data quality objectives (DQOs) (EPA 1993) for the decision-making process.

Approach: The DQO process is described in "Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives" (ASTM 1995) and is summarized in a companion issue paper titled, "Characterizing Soils for Hazardous Waste Site Assessments" (Breckenridge et al. 1991). The companion issue paper explains how to classify soils when faced with different classification systems and what soils data need to be considered when establishing DQOs. EPA's external working draft, "Guidance for Data Quality Assessment" (EPA 1995), is helpful in discussing the role of statistics in the DQO process. This document has a companion PC-based software program to help support the document. Since this is designed as a "living document," contact the Quality Assurance Division (Fax number (202) 260-4346) in the Office of Research and Development (401 M Street, S.W., Washington, D.C. 20460) to obtain the latest version.

Step 3—Determining Sample Location and Numbers to Collect

Purpose: The purpose is to design a statistically valid approach that yields representative samples from areas of concern and from background areas and to factor judgement (bias sampling) into selecting sampling locations to maximize the possibility of detecting elevated levels of contaminants on-site.

Approach: There are a number of options in sampling design that determine where to collect samples from a hazardous waste site to compare against a background site. The investigator needs to discuss the DQOs with a statistician to select the appropriate design. Numerous design options are available. One option is for those areas where the sites' soil and sediment matrix and distribution of suspected contaminants appear to be homo-geneous. Establishing a consistent grid (i.e., systematic sampling grid) across the entire site and sampling at set locations should provide a reasonable characterization of the contamination values across the site. A second option may apply if certain parts of a site are suspected of being contaminated due to historical use. In this case, bias sampling or intensifying the grid in highly suspected areas could be considered. This approach maximizes the possibility of determining whether contaminant concentrations at a site are above background and minimizes the risk of not taking action at a hazardous waste site.

There is a wealth of guidance on soil sampling. One document that is useful because of its coverage of soil sampling methods and design for reducing various sources of sampling error is titled, "Preparation of Soil Sampling Protocols: Sampling Techniques and Strategies" (EPA 1992c). This document also provides information for those uncertain about sampling design options and composite collection techniques.

The following discussion points should be considered when selecting and designing the sampling plan.

Point A—For a given site, there may be several areas of concern based on known or suspected past site activities. Once these areas are identified, a sampling plan can be developed. Historical data should be identified and evaluated early in the process to determine their use in identifying areas of concern or if the entire site needs to be sampled. Historical and land use information identified from Step 1 plays a key role in determining the degree of bias in the sampling plan. Factors such as location of tanks, piping, staging areas, disposal ponds, and drainage areas (e.g., sumps) should be considered when designing a sampling plan. Several soil properties or processes that govern the mobility of contaminants can also bias sample location:

Soil pH: A quick check using a field test kit can identify if the pH of the soil is in a range to mobilize contaminants. In acid soils (pH <6.5), inorganics

such as zinc, manganese, copper, iron, cobalt, and boron are easily leached. However, if soil pH is above 7.0, these inorganics form stable compounds. Other inorganics, such as molybdenum and selenium, are mobilized in alkaline soils, whereas in acid soils they become almost insoluble. Thus, pH and contaminants of concern need to be factored into the selection of sampling depth in soils.

Soil Texture: Most soils are a combination of the following grain sizes:

Medium to large grain size material has moderate to high porosity (15 to 40 percent) and low capacity for adsorbing inorganics. These soils have low capacity to hold contaminants in the grain interstices due to low cation exchange capacity and low capillary action. Investigators should look for surface staining and consider sampling at deeper depths.

Fine sands to silt materials have a stronger capillary action, and silts are capable of sorbing inorganics. Special attention should be given to sampling at the interface between fine material layers and larger grains, or where fine sand lenses are mixed in clay soils (these often form conduits for contaminant movement).

Clays are fine particles and possess a net negative charge, and most have high cation exchange capacities. This may cause heavy metal cations (e.g., Cr^{+6}, Cd^{+2}, Pb^{+2}) to adsorb to the clay surface. Clays also form large cracks and fractures due to shrink/swell and freeze/thaw effects. Investigators should look at the profile in clay soils to determine if inorganics (e.g., iron and manganese) have oxidized or been reduced in fractures causing a color change (e.g., under oxidation, iron changes to a red/yellow/brownish color compared to the natural blue/gray color). The sample design should consider these factors by collecting samples from fractures and especially from areas that show signs of oxidation.

Soil Organic Carbon Content: Organic carbon content plays a key role in the sorption of contaminants. Special attention should be given to sampling layers that have excessive organic carbon (e.g., darker soils, upper soil layers, peat).

Cation Exchange Capacity (CEC): The ability of the solid soil phase to exchange cations is one of the most important soil properties governing movement of inorganics in soils. In general, the CEC is related to the surface area of the soils and sediments (Kabata-Pendias and Pendias 1984). Soils and sediments that have larger surface areas (e.g., clays) have a greater CEC, while those with smaller surface areas (e.g., sands) have a lower CEC.

Transport: The transport of dissolved or colloidal inorganics takes place through the soil solution (diffusion) and with the moving soil solution (leaching) (Kabata-Pendias and Pendias 1984). Investigators should be aware that in cool, humid climates, inorganics generally leach downward through the profile; in warm, dry climates and hot, humid areas, the movement is often upward. However, specific soil properties, mainly the soil's CEC and moisture availability, control the rate of migration of inorganics in a soil profile.

Point B—A grid system can be used to establish the locations to be sampled. A grid will also help define the total population from which a subset may be selected using a statistical approach (e.g., systematic random, random, or stratified random) to identify the specific sample population. If the site has excavations or steep depressions, sample points along both sidewalls and the base of any excavations should be included in the grid. If samples are collected from excavations, similar soils (i.e., same depth, type, and horizon) should be sampled from the background site for evaluation. However, soils are heterogenous and spatial patterns do exist. Some soil types exhibit spatial correlations that should be considered by the project's statistician. The area represented by each grid point should be proportional to the size of the area for equal weighting and be equal to or greater than the operable unit (discussed earlier). One of the following equations may be used to determine grid intervals for three different size categories (Michigan 1991b):

$$\frac{\sqrt{A/\pi}}{2} = GI \qquad \text{Small site (0 to 0.25 acre)} \qquad (1)$$

$$\frac{\sqrt{A/\pi}}{4} = GI$$ Medium site (0.25 to 3 acre) (2)

$$\sqrt{\frac{A\pi}{GL}} = GI$$ Large site (>3.0 acre) (3)

where:

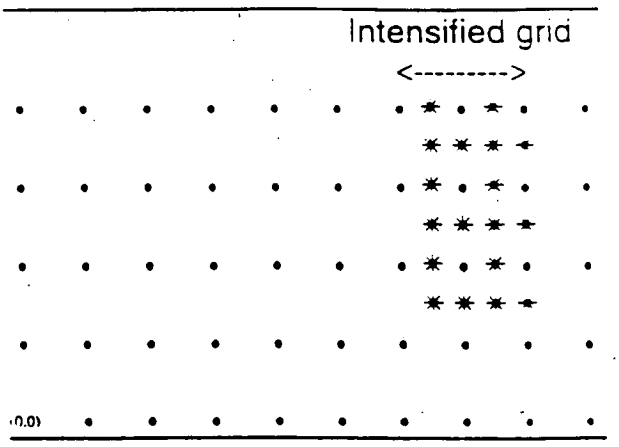
GI = grid interval
A = area to be gridded (in square feet)
GL = length (or longest side) of area to be gridded.

For example, for a 1.5-acre site (the longest side being 280 feet), and given that 1 acre = 43,560 square feet, substituting values in Equation (2) above, we have:

$$\frac{\sqrt{65{,}340/3.14}}{4} = 36 \text{ feet between grid points}$$

Grid systems are useful but have limitations. An option is to select a sampling area that is equal to an operable unit (i.e., the size of the smallest remedial action unit) and divide the site into equal units. Samples can then be collected, following a statistical design that represents the unit.

Point C—After the grid point interval is determined, a scaled grid overlay can be made and superimposed on a map of both the hazardous waste and background sites. Some specified point (e.g., the southwest corner) should be designated as the (0,0) coordinate. The grid can then be oriented to maximize sampling coverage. Some grid orientation may be necessary for unusually shaped areas. Also, the site can be subdivided with different calculated grid intervals so that proportional sampling can be intensified for suspect areas, such as sumps or sinks or low-lying drainage areas where contaminants have a higher probability of concentrating. The following is an example of a grid:



Point D—Several options exist for collecting samples: (a) collect a sample at all (or a minimum of four) grid points as discussed under Point B, (b) use the systematic random sampling approach referenced in SW-846, Third Edition, Section 9.1.1.3.3 or (c) use a stratified random design with an intensified grid for suspected problem areas. The selected number of sample locations are determined by sampling objectives, number of analytes to be evaluated per sample, the analytical techniques to be used, and budget constraints.

Point E—The determination of depth sampling increments are dependent on DQOs and the capacity of different soil layers to hold (sorb) metals. Recommended depth sampling increments are for the following: clay and organic soils on-site, 0.25 to 0.5 feet or by major horizon; silts and loams, 1.0 to 2.5-foot intervals or by master horizons; and sands, 1.0 to 5.0 feet. The selection of depth sampling increments also depends on the suspected amount of contamination released, mobility of contaminant, amount of water or liquid available for transport (e.g., ponding), and funding. Samples collected from specified depths can be either single or in multiple replicates, depending on the statistical method used for background data comparison (see Step 5). At locations where soil type is the same, compositing can be considered to save costs and more precisely estimate the mean value. However, compositing may be a concern if the data are used for future enforcement purposes.

Point F—For a background site, a minimum of four samples collected from the same soil type are needed to establish "background" concentration for a soil type (Michigan 1991a). These sample numbers will help account for natural constituent occurrences and inherent variability (i.e., range)

within each distinctive soil type. When determining if contaminants have moved into a profile (i.e., by depth), samples should be taken at comparable depths from similar soil types for both the background site and the hazardous waste site. If site environmental conditions have resulted in leaching of contaminants into the soil profile, the major soil horizons (i.e., O, A, and B) for a soil type may need to be sampled at both the contaminated and background site. If the site is sampled by major horizon, a minimum of four samples should be collected from each horizon) (see Figure 3). Sample size (e.g., weight) at all locations at the hazardous waste and background sites should be the same.

GROUND SURFACE	
1st major horizon—Brown medium-coarse SAND	4 samples
2nd major horizon—Lt. brown silty fine SAND	4 samples
3rd major horizon—Gray silty CLAY w/trace of fine-medium sand	4 samples

Figure 3. Approach for sampling sites where comparison is needed between major soil horizons or layers within a soil type.

Point G—Background samples should be taken from areas unaffected by site activities. If similar soils cannot be found in areas unaffected by site activities, possible locations for determining background are areas on-site, such as under stationary objects like storage sheds or porches, large flagstones, and old trees.

Point H—Wind rose data can be used to identify background sample locations in the predominant upwind direction from the hazardous waste site. Wind rose data usually provide monthly averages (based on hourly observations) on the percentage of time the wind blew from the 16 compass points or was calm. Wind rose data can be obtained for the area from the local weather station or the National Oceanic and Atmospheric Administration (NOAA).

Generally, if airborne deposition is the primary method of contaminant release from sites in arid environments, the investigator should focus on sampling the soils near the surface. However, consideration must be given to the mobility of the contaminant and texture of the soil.

Step 4—Sample Collection, Preservation, Handling, Analysis, and Data Reporting

Purpose: The purpose is to ensure that all samples are handled in a manner that protects their integrity and are analyzed using comparable, standard methods.

Approach: The following is the recommended approach:

1. All sample collection, preservation, preparation, handling, and analytical methods should follow standard methods [e.g., U.S. EPA SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" (EPA 1986)]. It is important that all samples are handled using comparable methods when preparing for and during analysis. For example, using different digestion methods can change results significantly.

2. For inorganics, it is recommended to use a total metals procedure with results reported in mg/kg (or percent for iron) on a dry weight basis. This minimizes additional sources of variation, since these constituents are often naturally occurring. To assess the bioavailability of metals in anoxic sediments, acid volatile sulfide and simultaneously extracted metals should be determined (Di Toro et al. 1990, 1992).

Step 5—Statistical Comparison of Hazardous Waste and Background Sites

Purpose: The objective is to determine if concentrations of inorganics from a hazardous waste site are elevated compared to those from a background site.

Approach: The following discussion outlines some basic statistical concepts in the context of background data evaluation. A general statistics textbook such as *Statistical Methods for Environmental Pollution Monitoring* (Gilbert 1987) should be consulted for additional detail. Also, the following list of published statistical guidance may be useful (Figure 4). There are numerous statistical approaches that are applicable when collecting, assessing, and analyzing background data. The approaches presented here have been adopted by the State of Michigan (Michigan 1990, 1991b) and modified based on the authors' experience. They are readily understandable and easy to use. However, it is recommended that investigators consult a

statistician to assist in the design or review of a sampling plan prior to collecting samples.

1. Careful consideration must be given to the selection of a statistical procedure based on site-specific factors. These include the size of the background data base and the number of samples available for comparison, variability of soil type, and coefficient of variation of data. The following are some statistical methods that can be used **if data from the site follow a normal distribution**. Some environmental sample sets are normally distributed. However, the majority of environmental contamination data sets are not normally distributed. Some of the more commonly used tests of normality are presented in Table 6. Tests should be conducted on all data to determine if the data meet the assumption of normality. If the data are not normally distributed, log or other types of transformations should be conducted to approximate normality prior to using the data sets in statistical comparisons, such as t-tests or analysis of variance procedures (ANOVA).

If the data **cannot be normalized**, additional attention needs to be given to selecting appropriate statistical tests, and the situation needs to be discussed with a statistician. Special statistical consideration may be warranted if samples are composited and the data are needed to support regulatory requirements discussed in Part B.

Statistical Methods Guidance[a]

Basic

Statistical Methods for Environmental Pollution Monitoring, Van Nostrand Reinhold Company (Gilbert 1987).

Guidance for Data Quality Assessment (EPA 1995).

Soils Sampling Quality Assurance Guide (EPA 1989d).

Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA (EPA 1988).

EPA's *Guidance Manual: Bedded Sediment Bioaccumulation Tests*, pp. 82-91 (Lee et al. 1989).

Statistical Guidance for Ecology Site Managers, Washington State Department of Ecology (WDOE 1992).

Risk Assessment Guidance for Superfund, Volume 1: Human Health Evaluation Manual (Part A), pp. 4-5 to 4-10 (EPA 1989c).

Advanced

Estimation of Background Levels of Contaminants (Singh and Singh 1993).

Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities (EPA 1992d).

Background and Cleanup Standards

Methods for Evaluating the Attainment of Cleanup Standards, Volume 1: Soils and Solid Media (EPA 1989b) (detailed statistical discussion).

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[a]If time and resources are limited, Gilbert (1987), Hardin and Gilbert (1993), and EPA (1995) provide some of the most relevant statistical information.

Figure 4. Statistical Methods Guidance.

TABLE 6. TESTS FOR EVALUATING NORMALITY OF DATA SETS. SOURCE: EPA (1995)

Test[1]	Sample Size (N)	Notes on Use	Reference
Shapiro Wilk W Test	≤ 50	Highly recommended	Gilbert (1987) EPA (1992c)
Filiben's Statistic	≤ 100	Highly recommended	EPA (1995)
Studentized Range Test	≤ 1000	Highly recommended	EPA (1995)
Lilliefors Kolmogorov-Smirnoff Test	> 50	Useful when tables for other tests are not available	Madansky (1988)
Coefficients of Skewness and Kurtosis Tests	> 50	Useful for large sample sizes	EPA (1995)
Geary's Tests	> 50	Useful when tables for other tests are not available.	EPA (1995)
Coefficient of Variation Test	≤ 50	Use only to discard assumption of normality quickly.	EPA (1995)
Chi-Square Test	Large[2]	Useful for group data and when the comparison distribution is known.	Introductory Statistics Books

[1]By order of Recommendation.
[2]The necessary sample size depends on the number of groups formed when implementing this test Each group should contain at least five observations.

When comparing a contaminated site with a background site, a null hypothesis should be developed. For example, a null hypothesis could be: *There is no difference between the mean contaminant concentration of the hazardous waste site and background site*. The alternate hypothesis would be: *The mean concentration for the contaminated site is different from that of the background site*. If parametric statistics are used for this assessment, such as a t-test or ANOVA, the data can be normalized to selected parameters (e.g., organic carbon, particle size). Many parametric and non-parametric statistical procedures exist to compare a background site with one or more hazardous waste sites. A variety of such procedures are reviewed in Lee et al. (1989), EPA's *Risk Assessment Guidance for Superfund, Volume I* (EPA 1989c), and EPA's Guidance for Data Quality Assessment (EPA 1995). The latter source provides examples and a discussion of most of the tests needed to conduct comparisons between data sets.

a. Empirical Rule. (Note: Many of the following calculations can be performed using calculators that are preprogrammed.) Use mean ($\bar{x}_b$) and variance (S_b^2) of background concentrations to establish an "upper limit" for delineating significant concentrations, such as:

1) Calculate the background mean ($\bar{x}_b$) by dividing the sum of the total background readings by the total number of background readings for each element of concern:

$$\bar{x}_b = \frac{x_1 + x_2 + \ldots x_n}{n}$$

2) Calculate the background variance (S_b^2) by taking the sum of the squares of the difference between each reading and the mean, and dividing by the degrees of freedom (the total number of background samples minus one):

$$S_b^2 = \frac{(x_1 - \bar{x}_b)^2 + (x_2 - \bar{x}_b)^2 + \ldots (x_n - \bar{x}_b)^2}{n-1}$$

3) Calculate the background standard deviation (S_b) by taking the square root of the variance:

$$S_b = \sqrt{S_b^2}$$

4) The Coefficient of Variation Test (CV) where $CV = s_b / \bar{x}_b$ is used to evaluate data distribution. The background data should have a CV of less than 0.5 for sandy soils, less than 0.75 for finer soils, or an explanation accounting for higher CV values. The maximum recommended CV is 1.00. If the data distribution exceeds a CV of 1.00, then a thorough evaluation should be made to account for this variability (e.g., laboratory QA/QC, soil classification, sample location, outlier classification, and sample location), and the outlier data addressed (see EPA 1989c). Additional samples may need to be analyzed to ensure that a sufficient data base population (n) is achieved.

There are several classical procedures (Gilbert 1987; EPA 1995) and robust outlier tests (Singh and Nocerino 1994) available in the statistical literature. Consult *Outliers in Statistical Data* by Barnett and Lewis (1994) for a full account of this issue. Outliers often distort statistical estimation, and resulting inferences and can lead to incorrect conclusions. The solution is to consult a statistician who understands outliers and knows how to use robust procedures to identify multiple outliers.

If an outlier is found, an option is to take a substitute sample, have it analyzed, and repeat the statistical process. (To avoid costly delays, it is recommended to collect extra samples for laboratory analysis.)

For example, four background samples are collected from a site for lead analysis. The lead values from the laboratory analysis were 56, 25, 18, and 35 mg/kg. The investigator wants to examine the data set to determine if the 56-mg/kg sample is an outlier. The summary statistics for these samples are:

$$\bar{x}_b \text{ (mean)} = \frac{56 + 25 + 18 + 35}{4} = 33.5$$

$$S_b^2 \text{ (variance)} = [(56 - 33.5)^2 + (25 - 33.5)^2 + (18 - 33.5)^2 + (35 - 33.5)^2] / 3 = \frac{821}{3} = 273.67$$

$$S_b \text{ (standard deviation)} = \sqrt{S_b^2} = \sqrt{273.67} = 16.5$$

$$CV \text{ (coefficient of variation)} = \frac{S_b}{\bar{x}} = \frac{16.5}{33.5} = 0.49$$

The test for a single outlier in a normal sample with the population mean and variance unknown (Barnett and Lewis 1994, p. 218-222) is appropriate for the above identified sample. The test statistic is:

$$\frac{X_{max} - \bar{x}}{s} = \frac{56 - 33.5}{16.5} = 1.36$$

The theoretical cut-off point (Barnett and Lewis (1994), Table XIII, p. 485) for $\alpha = 0.05$ is 1.46. Since the calculated value of the test statistic (1.36) is less than the theoretical cut-off point (1.46), the 56 mg/kg sample is not an outlier.

Background concentrations should be determined for major soil types at the hazardous waste site. If this is not feasible, then a mean background concentration should be determined on the soil type at the hazardous waste and background sites with the lower absorption capacity (usually the sandiest soil) and those with the higher absorption capacity (usually silts and clays). The finer-texture soils (silts and clays) will usually sorb the most contaminants and provide a good value for comparison. If the mean concentration from the fine textured soils from the hazardous waste site is above similar values for the background site, there is a high probability that the site is contaminated.

Once a mean background concentration is established, similar statistical tests should be conducted on the data from the hazardous waste site. After the data sets have met the assumptions for normality or have been corrected (see Figure 2), then statistical comparisons can be made between the site and background data sets.

b. t-Test. Any t-test should be discussed with a statistician prior to use since there are a number of variations and assumptions that can apply. The Gosset Student T-test has good application when comparing background sites to potentially contaminated sites (Michigan 1991a).

c. Cochran's Approximation to the Behrens-Fisher Student's t-test. This test is also available for evaluating background variance versus exceedances (i.e., contamination) as referenced in 40 CFR Part 264, Appendix IV. Note that this statistical comparison method does require that two or more discrete samples be taken at each sampling location.

d. In some cases, it may be of interest to establish an upper limit of background for the site. This would be useful if the investigator wanted to compare single values for a soil type from the hazardous waste site with the background population for a similar soil. The mean background concentration ($\bar{x}_b$) plus three standard deviations ($3S_b$) comprises a reasonable maximum allowable or upper limit.

2. **Procedures for non-detect values.** If more than 50 percent of the background analytical values are below the detection limit (DL), either of the

following procedures could be used with any of the preceding statistical methods:

a. For any <DL in a data set, alternate "0" and the detection limit (DL); this will result in a net value of half the detection limit, with a variance, or use b. For example:

Actual Value	Substitute Value
<DL	DL
<DL	0
<DL	DL
<DL	0

Note: This process assumes that values below the DL are normally distributed in a regulatory context; this may not be determined to be conservative enough. For regulatory cases, a more robust estimation of mean and variance with lowest DL values should be used. The restricted maximum likelihood (RMLD) method (Perrson and Rootzen 1977, Haas and Scheff 1990) is relatively simple and provides a good robust estimate.

If data are not normally distributed, which is often the case for environmental data [see Ott (1990) and McBean and Rovers (1992) for discussions of why environmental measurements follow a lognormal pattern], an alternative approach like the one discussed in EPA (1989e) or EPA (1995) could be used if data are lognormally distributed.

b. The Continuity Correction procedure with the t-test (EPA 1983). If the background data are non-detect (<DL), then the value can be determined to be $0.25 \times DL$ (consultation with a statistician is recommended to explain and perform the t-test with Continuity Correction). Other tests such as the Wilcoxon rank sum test [see Gilbert (1987), pp. 247-249] can be used to test for a shift in location between two independent populations even with non-detect values. There are also numerous other approaches/methods for handling non-detection limits that could be considered but need to be discussed with a statistician.

SEDIMENT

Step 1—Collection of Available Data for Use as Background Reference Sediment

Prior to implementing a sampling and analysis project, an effort should be made to determine whether useful background sediment concentration data are available. Samples may have been collected at the same site prior to the contaminated source, or data may have been collected at sites upstream by the state, EPA, USGS, or permittees and may be documented in STORET (Bolton et al. 1985) (also see Table 5) or the developing National Sediment Inventory (EPA 1994a).

The use of existing background site data for comparison with on-site data is valuable. However, it is critical to determine whether both sets of data are comparable. Questions that need to be addressed are:

1. Were comparable analytical methods used for both on-site and background site samples (e.g., acid-extractable metals or total digestion methods)?

2. Are the total organic carbon (for organic contaminants) and particle size (for metals and inorganics) data for both sites available and similar?

3. Is the background site acceptably representative of the chemical contamination levels immediately upcurrent of the hazardous waste site?

4. Were similar sample collection methods used [different sampling devices can produce greatly different results (Baudo 1990)]?

5. Were the depths of sampling similar (e.g., top 10 cm of sediment)?

6. How long ago were the background sediments collected compared to the contaminated site sediments?

7. Are contaminant levels expressed on the same basis (wet or dry weight)?

8. If data on acid volatile sulfides (AVS) and simultaneous extracted metals were collected, were both data sets collected during the same season of the year (AVS affects the biological availability of some metals in anoxic sediments)?

9. Is the quality of the data acceptable?

The levels of metals in sediments are strongly related to total organic carbon and sediment particle size, while organic contaminants in sediments are related primarily to total organic carbon. The higher the level of organic carbon in a sediment, the greater the potential concentration of non-ionic organic contaminants. For metals, the finer the particle size and the higher the organic carbon, the greater the potential for accumulating metals. Toxic effects are less likely as the organic carbon content increases for a given non-ionic organic contaminant level. For

metals, toxic potential is reduced as particle size decreases or organic carbon increases. If the particle size or organic carbon content of the background and contaminated site sediments differ significantly, it is not appropriate to directly compare contaminant residue levels without normalizing the data. Some organic contaminants can be normalized to organic carbon by dividing by the fraction of organic carbon (Adams et al. 1992); the same approach has been used for divalent cationic metals—lead, nickel, copper, cadmium, and zinc. Metals data can be normalized to acid volatile sulfide levels (Di Toro et al. 1990, 1992), a key element such as aluminum (Schropp and Windom 1988; Daskalakis and O'Conner 1995), or particle size (NOAA 1988). EPA is also refining its equilibrium partitioning approach, which could be used to normalize contaminant levels among different sediments (Adams et al. 1992; EPA 1992b). Further discussion of these procedures is beyond the scope of this paper, and expert assistance should be obtained.

Step 2—Comparison of On-site Data to Sediment Quality Criteria

Simply comparing the level of metals in bulk sediments, deposited under similar conditions, upstream and downstream from a suspected facility can provide an indication that a facility may have contaminated the downstream site. These data, however, provide no indication of bioavailability that may justify remediation. Indeed, bulk sediment contamination is only poorly correlated with adverse impacts. For metals, the key parameter in determining toxicity is the pore water concentration of a metal. In situations where no background site data exist, yet contaminated site data do, it may be useful to compare sediment contamination levels to various sediment quality criteria.

EPA is developing sediment quality criteria for metals, but the factors determining bioavailability are complex, and an approach has yet to be selected (Ankley et al. 1994). Research has shown that in anaerobic sediments, toxic impacts due to cadmium, copper, lead, nickel, and zinc are not present when the sum of the molar concentrations of these metals divided by the AVS concentration is less than one (Di Toro et al. 1990, 1992). Essentially, when excess sulfide is present, the metals are complexed and metal concentrations in pore water are low.

While bulk sediment contamination levels do not correlate well with toxic effects, a number of statistically based, sediment-quality indices have been developed. If resources are limited, and useful background site data do not exist, concentrations at the contaminated site can be compared with metal concentrations in bulk sediment known to have a low probability of causing adverse impacts on benthic organisms. Several "no-effect" levels are presented in Table 2. NOAA developed effects-based guidelines including no-effects, possible effects, and probable-effects levels (Long and Morgan 1990) based on National Status and Trends Program data, and MacDonald (1992) used the same approach with additional data to develop similar marine guidelines. The guidance for marine sediments was further updated by Long et al. (1995). The most recent guidance on metals is presented in Interim Sediment Quality Assessment Values (Environment Canada 1994), in which NOAA National Status and Trends Program data and spiked-sediment toxicity tests were used to develop threshold effects values for fresh and marine waters, presented in Table 2. If the contaminated site levels are below the no-effects levels, further investigation may not be required even if the site has been contaminated. If the no-observed-effects levels are exceeded, further investigation may be justified. Bulk sediment guidelines have also been developed by EPA Region V (U.S. Army Corps of Engineers 1977) for classifying sediments of Great Lakes harbors. The Ontario Ministry of Environment (Persaud et al. 1989) and other guidelines are summarized in EPA's *Guidance Manual: Bedded Sediment Bioaccumulation Tests* (Lee et al. 1989). In addition, these and other guidelines have been reviewed and summarized by Giesy and Hoke (1990).

In areas where an entire watershed has been impacted, such as from mining activities, it may not be possible to select a suitable background site. In such situations, historical data (Runnells et al. 1992) or archived samples may be the best source of data. Another approach would be to sample surficial sediments and compare them to deeper uncontaminated sediments (those laid down prior to the watershed being impacted).

No specific rules can be provided regarding the use of existing background reference data for sediments or soils. Judgement should be made with full knowledge of the specific objectives of the investigation, data limitations, and qualifications and with the help of appropriate experts (e.g., chemists,

hydrologists, statisticians, benthic ecologists, and sampling experts).

Step 3—Selection of Sites for Collection of Background Sediment

The ideal background site data for comparison with contaminated site data are obtained from samples:

1. Collected immediately upcurrent of the contaminated site in an area not impacted by the suspected contaminant source.

2. Collected at the same time the contaminated sediment is sampled.

3. Having very similar particle size and organic carbon content.

4. Collected using identical sampling equipment.

5. Collected using the same statistically based sampling design (i.e., numbers and configuration) and compositing handling procedures (if any).

6. Analyzed using identical analytical methods.

When comparing data sets, it is important that everything about the sampling and analytical procedures for the background and contaminated site sediments be as similar as practical. If both fine and coarse sediments are available for sampling at the contaminated site and the background site, the finer sediments are preferred because they have a greater affinity for metals.

The ideal situation is seldom achieved, and compromises may have to be made. For streams, it may be practical to sample directly opposite from the contaminant or contaminant source or even downstream as long as the background site is not impacted by the plume of concern. Contaminated and background site sediment characteristics will be most alike where the currents are similar, with fines being deposited in areas of low currents and coarser material being associated with faster currents. A significant complication of sampling streams is the potential for severe erosion, which may remove massive amounts of sediments during flood conditions. Thus, even the contamination observed in the sediments directly downstream of a point source may not be attributable to the existing source. The surface sediments after a flood may represent contamination deposited from upstream sources or historical contamination from another facility previously operating at the hazardous waste site. Knowledge of a suspected contaminated source's effluent, the processes generating the effluent, and historical stream flow information can be helpful to link the suspected source and the contaminated site's metal concentration. Since it is difficult to establish a background reference site after a major flood event has occurred, previous data or deep sediments may be the best source for background reference data.

For estuarine and marine sites, selection of a similar but unimpacted background site also can be difficult. The process may involve the use of hydrologic models to simulate tides and currents to avoid areas impacted by the contaminated plume. It may be necessary to select distant background sites when currents are highly variable. The same considerations need to be addressed in lakes with wind-driven currents. When questions arise about site selection, it is best to consult with an expert who is familiar with the hydrology of the area.

When it is not possible to obtain background sediment with the same particle size and organic carbon content, normalization procedures, discussed previously, should be considered. While it is beyond the scope of this document to recommend specific sampling and assessment methods, excellent comprehensive references for such information are *Procedures for the Assessment of Contaminated Sediment Problems in the Great Lakes* (IJC 1988), *Assessment and Remediation of Contaminated Sediments (ARCS) Program, Assessment Guidance Document* (EPA 1994b), and *Manual of Aquatic Sediment Sampling* (Mudroch and Azcue 1995). Additionally, EPA's Office of Science and Technology within the Office of Water is developing a methods manual that will cover all aspects of sediment monitoring, from sample collection to analytical methods to assessment techniques (EPA 1994c).

PART B

APPROACHES FOR DETERMINING BACKGROUND LEVELS OF INORGANICS THAT CAN BE COMPARED WITH CONCENTRATIONS OF INORGANICS AT CERCLA SITES

Part B was developed to address issues that need to be considered when the establishment of background under CERCLA is required. Part B also provides a summary of technical issues rather than an in-depth statistical evaluation of the topic. Those needing an in-depth level of statistical evaluation

should seek the expertise of a statistician and may benefit from a paper that addresses estimation of background concentrations of contaminants, for example Singh and Singh (1993) or Hardin and Gilbert (1993).

Step 1—Conduct On- and Off-site Reconnaissance as Preliminary Assessment Phase of CERCLA

Purpose: The initial reconnaissance is performed to identify concerns associated with on-site or off-site activities that may have resulted in contributing to enhanced inorganic background concentrations.

Approach: See Step 1 under Part A (a similar approach should be considered).

Step 2—Collect Preliminary Information and Samples About Background Levels of Concern

Purpose: During the preliminary assessment/site investigation (PA/SI) stage, existing soil and sediment analytical data for contaminated sites and background sites can provide initial information to identify problems that might be encountered with establishing background values.

Approach: The PA/SI stage is not designed to evaluate all concerns at the site. However, an initial site visit can be advantageous to evaluate site condition, assess analytical data, or collect samples of equal number (i.e., number from contaminated site = number from background site) from media that have similar physical (e.g., texture) and chemical (e.g., pH, percent organic carbon, CEC) properties. During the SI phase, sufficient information is needed to support the hazard ranking score (HRS) to identify if a contaminated site should be nominated for inclusion to the National Priority List (NPL) due to high threat to humans or the environment (HRS scores ≥28.5 are usually nominated for inclusion to the NPL). The SI stage may present the first opportunity to actually measure background concentrations for assessing if observed releases have occurred. Section G of the preamble to the HRS final rule (55 FR 51546) on "Observed Releases" states that an observed release is established when a sample measurement that equals or exceeds the sample quantitation limit is at least three times the background level (EPA 1992a, p. 2-3).

Step 3—Determine Potential Magnitude of a Problem by Combining Information from Steps 1 and 2

Purpose: Combining information on past land use and site operations with data from local, regional, and global contributions can help alert investigators that the issue of background concentration might require more attention when developing a sampling and analysis plan during the remedial investigation (RI) process.

Approach: Information sources other than chemical analysis (e.g., information or data obtained from other sources or Steps 1 and 2) may be used for characterizing the background concentrations for a site. A multi-tiered approach is often helpful to lump background concentrations, such as:

1. Global contributions—mostly atmospheric contributions from wet and dry deposition.

2. Regional contributions—influence of geological formations (e.g., increased selenium in western regions).

3. Local contributions—contributions due to land use (e.g., high arsenic, lead, and mercury values due to pesticide use in fruit production), local air emission sources, and nearly all industrial activities.

Step 4—Establish a Clear Statement of the Problems at the Site and Develop RI Sampling Strategy

Purpose: The RI process is the time to conduct detailed measurements of background concentrations at CERCLA sites. Section 300.430(b)(8) of the National Contingency Plan requires that a sampling and analysis plan (SAP) be developed during the scoping phase of the RI process.

Approach: A number of EPA guidance documents discuss the need to characterize background concentrations as part of the SAP formulation step. For example, according to the *Guidance for Data Useability in Risk Assessment* (Data Useability Guidance) (EPA 1989a), the SAP should be developed to resolve four fundamental risk assessment decisions, one of which is to determine "whether site concentrations are sufficiently different from background." Similarly, the *Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA* (RI/FS Guidance) (EPA 1988) states that when determining the nature and extent of contamination at a site, background sampling should be conducted to help identify the

respective areas of both site-related contamination and the background concentrations.

Step 4a—Confidence Interval Determination

Purpose: The purpose is to develop confidence intervals for determining mean metals values and problem statements for a contaminated site.

Approach: Literature sources such as those presented in Table 5 can be useful to determine if a site has a potential contamination problem. However, literature values should be used only to support or help evaluate data from contaminated and background site samples. Site variability must be accounted for when conducting a characterization. Some sites have fairly homogenous soils, sediments, and areas impacted by emissions. More often, a site has a high degree of variability, and the problem statement and SAP need to reflect this. For many sites, a 95 percent confidence interval of the mean metals concentrations would be reasonable (i.e., if the mean for lead is 20 ppm-dry weight ±4, the 95 percent confident background value would be between 16 and 24 ppm-dry weight). However, if the site is complex due to different soils/sediments and areas of concern, a 90 percent confidence interval may be more acceptable due to an increased number of samples and cost. Once a confidence interval is developed, a problem statement for the site can be formulated to guide further effort. An example of a problem statement could be: "Are on-site concentrations of mercury, lead, arsenic, and zinc statistically different from off-site background concentrations?"

Step 4b—Develop Hypotheses for Testing

Purpose: EPA's RAGS "provides guidance on developing hypotheses to frame a problem in a manner that can be tested."

Approach: There are two types of hypothesis most often used: null hypothesis (a) — the site-related concentration is less than or equal to the background concentration, and null hypothesis (b) — the site-related contaminant concentration is greater than or equal to the background concentration. Additional guidance on selecting hypotheses is presented in the *Risk Assessment Guidance for Superfund, Volume I* (EPA 1989c).

Step 4c—Determine Level of Precision

Purpose: RI/FS guidance is that the level of precision be determined before sampling and analysis strategies are developed. This will guide the number and location of samples.

Approach: Determining the level of precision early in the development of a SAP will minimize many future problems. Two types of statistical errors are encountered when testing hypotheses about differences between on-site and off-site concentrations. The following definitions are true only if the null hypothesis (a) is used, but not with (b).

1. Type I error (α) (false positive): "Rejecting the null hypothesis when it is true." Because of the uncertainty related to sampling variability, an individual could falsely conclude that the site-related contaminant concentration is greater than background concentration when it actually is not. In this case, the null hypothesis is rejected, and the site-related concentration is considered to be statistically different from the background concentration.

2. Type II error (β) (false negative): "Accepting the null hypothesis when it is false." Alternatively, an individual might accept the null hypothesis that the contaminated site-related concentration is less than or equal to background concentration when it actually is not. In this case, the null hypothesis is accepted and the site-related concentration is considered to be no different from the background concentration.

A decision based on a Type I error could result in unnecessary remediation, while a Type II error could result in the failure to clean up the contaminated site when remediation is necessary. The Greek letter alpha (α) is used to represent the probability of a false positive, and beta (β) is used to represent the probability of a false negative decision.

Precision associated with hypothesis testing is defined by the parameters of confidence level and power. These are defined in EPA (1992a) and EPA (1989a) as:

1. Confidence level (100 percent - α)—One hundred percent minus the confidence level is the percent probability of concluding that the contaminated site-related concentration is greater than background when it is not (Type I error or "false positive"). As the confidence level is lowered (or alternatively, as α is increased), the likelihood of committing a Type I error increases.

2. Power (100 percent - β)—One hundred percent minus the power is the percent probability of concluding that the site-related concentration is less than or equal to background when it is not (Type II error or "false negative"). As the power is lowered (or alternatively, as β is increased), the likelihood of committing a Type II error increases.

Although a range of values can be selected for these two parameters, as the demand for precision increases, the number of samples and cost will generally also increase. The Data Useability Guidance states that for risk assessment purposes, the minimum recommended performance measures are: Confidence, 80 percent (α = 20 percent) and Power, 90 percent (β = 10 percent). These values can be interpreted to mean the following:

1. Confidence level = 80 percent—In 80 out of 100 cases, contaminated site-related concentrations would be correctly identified as being no different (statistically) from background concentrations, while in 20 out of 100 cases, site-related concentrations could be incorrectly identified as being greater than background concentrations.

2. Power = 90 percent—In 90 out of 100 cases, site-related contaminants would be correctly identified as being greater than background concentrations, while in 10 out of 100 cases, site-related concentrations would be incorrectly identified as being less than or equal to background concentrations.

If the site situation requires a higher level of precision to reduce the probability of committing a Type I or II error, it can only be accomplished by increasing the number of samples and overall cost [see guidance in EPA (1995)]. These decisions need to be made on a site-specific basis and are primarily related to remediation and risk reduction goals.

Step 5—Develop a Sampling Approach That Will Answer the Problem Statement and Meet the Established Level of Precision

Purpose: The environmental scientist can develop a range of costs and options for different ranges of probability values of committing either a Type I or II error. The guidance developed in Step 1 of conducting a preliminary background evaluation can be expanded, with the assistance of a statistician, to determine the number of samples, location of samples, and statistical test to employ.

Approach: Developing a full-scale SAP directed at determining if there is a difference between contaminated site and background values requires knowledge about how the inorganics of concern move in the environment, site variability, and level of precision. The environmental scientist should initially seek the support and guidance of scientists and a statistician familiar with the issues. A SAP can then be devised to evaluate questions about background where off-site concentrations are elevated due to off-site anthropogenic contributions. Guidance for reaching decisions in these cases can be obtained from the Draft Issue Paper (EPA 1992a).

CONCLUSIONS AND RECOMMENDATIONS

The issue of establishing background concentrations for inorganic metals for comparison to levels at a potentially contaminated site can be complicated by natural and anthropogenic contributions to total background concentrations. The issues presented in this paper are designed to provide investigators with sufficient knowledge to assess whether concentrations of inorganics at a hazardous waste site are statistically above background concentrations. There are also discussions on how to approach background determinations at a hazardous waste site if there is a high potential for regulatory enforcement action.

There are a wide variety of methods that are available in the literature and in various EPA documents for evaluating background. Each method is slightly different, but there are a number of common issues that are presented in this paper. The most important factor to consider when determining background concentrations is to ensure that the physical, chemical, and biological aspects of the media to be sampled at both the contaminated site and the background site are as similar as possible. There are references and data included in this paper that provide average concentrations and reference values for selected soils and sediments in the United States. Most of the values in the literature are for concentrations that include natural and global anthropogenic contributions. These should be considered but should not take the place of conducting a thorough site-specific investigation to determine the previous land use both on and in the vicinity of the hazardous waste site to determine local anthropogenic contributions. The time spent using well-documented investigative skills to identify unaffected background sites that are similar geologically to the contaminated site will be of great value when establishing background concentrations.

This paper presents the issues that are important to consider when comparing if inorganics at a hazardous waste site are statistically different from those found at a background site areas.

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Chapter 4.

THE SOIL CHEMISTRY OF HAZARDOUS MATERIALS

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natural environmental conditions.

Relatively little is known about the first two types of soil mineral fixation reactions discussed above. However, these are not considered to be extensively occurring reactions. On the other hand, the fixation of elements via incorporation into the structure of soil minerals during mineral precipitation is an extremely important reaction. This chapter will focus on the types and amounts of elements found in soil, how these elements are fixed into mineral structures, and how some remedial actions have utilized element fixation.

ELEMENT CONCENTRATIONS IN SOIL

Eleven of the elements listed in Table 3.1, along with carbon, hydrogen, and oxygen, constitute over 99 percent of the total elemental content of soil: Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si, and Ti. The remaining one percent is comprised of elements known commonly as the "trace elements." The word "trace" identifies the fact that they occur in soil in minute amounts; it has no bearing or relationship to any concentration limit protecting human health or biota.

Table 3.1 lists the mean concentrations, typical ranges, and observed limits of several elements in natural soil (i.e. background concentrations). The total concentration of any element, C_{Total}, in a soil is equal to:

$$C_{Total} = C_{Fixed} + C_{Adsorbed} + C_{Water} \quad (3.1)$$

where:

C_{Fixed} = concentration of fixed element comprising part of the structure of clay and soil minerals, in mg element/kg soil.

$C_{Adsorbed}$ = concentration of element adsorbed onto the surface of soil minerals and onto organic matter exchange sites, in mg element/kg soil.

C_{Water} = concentration of element in soil water or groundwater in equilibrium with $C_{Adsorbed}$, in mg soluble element/kg soil. (See Table 3.2 for natural background levels found in groundwater).

C_{Fixed} represents the "immobile" fraction of C_{Total}. The sum of $C_{Adsorbed}$ and C_{Water} represents the potentially mobile portion of C_{Total}; these will be discussed in detail in the next chapter.

There are four important facts that should be understood concerning the data listed in Table 3.1, the parameters listed in Equation 3.1, and the interrelationships of these parameters. First, C_{Total} should not be expected to be uniform with depth. Natural processes involved in the distribution of elements in the soil profile include:

TABLE 3.1 Native Soil Concentrations of Various Elements

Element	Concentration (ppm) Typical Range mg/Kg	Concentration (ppm) Extreme Limits
Ag	0.1 - 5.0	0.1 - 50
Al	10,000 - 300,000	—
As	1.0 - 40	0.1 - 500
B	2.0 - 130	0.1 - 3000
Ba	100 - 3500	10 - 10,000
Be	0.1 - 40	0.1 - 100
Br	1.0 - 10	—
Ca	100 - 400,000	—
Cd	0.01 - 7.0	0.01 - 45
Ce	30 - 50	—
Cl	10 - 100	—
Co	1.0 - 40	0.01 - 500
Cr	5.0 - 3000	0.5 - 10,000
Cs	0.3 - 25	—
Cu	2.0 - 100	0.1 - 14,000
F	30 - 300	—
Fe	7,000 - 550,000	—
Ga	0.4 - 300	—
Ge	1.0 - 50	—
Hg	0.01 - 0.08	—
I	0.1 - 40	—
K	400 - 30,000	—
La	1.0 - 5000	—
Li	7.0 - 200	1.0 - 3000
Mg	600 - 6000	—
Mn	100 - 4000	1.0 - 70,000
Mo	0.2 - 5.0	0.1 - 400
Na	750 - 7500	400 - 30,000
Ni	5.0 - 1000	0.8 - 6200
P	50 - 5000	—
Pb	2.0 - 200	0.1 - 3000
Ra	$10^{-6.5}$ - $10^{-5.7}$	—
Rb	20 - 600	3.0 - 3000
S	30 - 10,000	—
Sb	0.6 - 10	—
Sc	10 - 25	—
Se	0.1 - 2.0	0.01 - 400
Si	230,000 - 350,000	—
Sn	2.0 - 200	0.1 - 700
Sr	50 - 1000	10 - 5000
Th	0.1 - 12	—
Ti	1000 - 10,000	400 - >10,000
U	0.9 - 9.0	< 250
V	20 - 500	1.0 - 1000
Y	10 - 500	—
Zn	10 - 300	3.0 - 10,000
Zr	60 - 2000	10 - 8000

[a] Based on an Analysis of Data Presented in References 1,2,3,4,5, and 6.

- Leaching of mobilized elements such as calcium, boron, lithium, iron, magnesium, manganese, selenium, or sodium (a) out of the soil profile, or (b) into zones of accumulation.
- Translocation, in the course of soil-forming processes such as podzolization, of trace elements together with iron and aluminum.
- Mobilization of trace elements through breakdown of soil minerals as a result of alternate wetting and drying.
- Mechanical translocation of clay, which increases trace element concentrations in those soil horizons having higher amounts of clay particles.
- Surface accumulation of relatively soluble elements such as boron, calcium, and sodium in arid regions.
- Mobilization or fixation arising from chemical and/or microbiological activity.
- Surface enrichment due to trace element uptake by plants.

Second, analytical data derived from the chemical analysis of the total element content of a soil (i.e. C_{Total}) relays no information regarding C_{Fixed}, $C_{Adsorbed}$, and C_{Water} other than the magnitude of their combined concentrations. In other words, if a laboratory report states that a soil contains 125 ppm total Cu, this datum cannot reveal if 0.1 percent is potentially mobile (i.e. $C_{Adsorbed} + C_{Water}$) or if 99 percent is potentially mobile. At background concentrations, the relative magnitudes of the parameters listed in Equation 3.1 for cations generally are:

$$C_{Fixed} >> C_{Adsorbed} > C_{Water}$$

The greater part of C_{Total} exists as C_{Fixed} and is immobile. However, this relative ranking may or may not change as C_{Total} increases above the background concentration.

Third, the background concentrations listed in Table 3.1 represent the total concentration of an element present after the soil was formed and weathered. This concentration gives no information on the element-loading capacity of a soil. The element-loading capacity can be defined as the maximum amount of an element that can be added to soil which does not cause water migrating through this soil to contain a harmful concentration of that element. In other words, knowing that a soil contains 125 ppm total background Cu will not reveal if soil will or will not completely convert an additional loading of 500 ppm Cu into C_{Fixed}.

Soil cleanup standards that specify the excavation or treatment of soil containing concentrations of an element over a background concentration are usually based on an incorrect premise that the background concentration of an element in soil represents a maximum concentration of an element which the soil can immobilize. The background concentration represents the total concentration present after the soil was formed and undergone some degree

Element	Concentration: Typical Value	Concentration: Extreme Value
	Major Elements (ppm)	
Ca	1.0 - 150[b]	95,000[c]
	< 500[d]	
Cl	1.0 - 70[b]	200,000[c]
	< 1000[d]	
F	0.1 - 5.0	70
		1600[c]
Fe	0.01 - 10	> 1000[c,e]
K	1.0 - 10	25,000[c]
Mg	1.0 - 50[b]	52,000[c]
	< 400[d]	
Na	0.5 - 120[b]	120,000[c]
	< 1000[d]	
NO_3	0.2 - 20	70
SiO_2	5.0 - 100	4,000[c]
SO_4	3.0 - 150[b]	200,000[c]
	< 2000[d]	
Sr	0.1 - 4.0	50
	Trace Elements (ppb)	
Ag	< 5.0	
Al	< 5.0 - 1000	
As	< 1.0 - 30	4,000
B	20 - 1000	5,000
Ba	10 - 500	
Br	< 100 - 2000	
Be	< 10	
Bi	< 20	
Cd	< 1.0	
Co	< 10	
Cr	< 1.0 - 5.0	
Cu	< 1.0 - 30	
Ga	< 2.0	
Ge	< 20 - 50	
Hg	< 1.0	
I	< 1.0 - 1000	48,000[c]
Li	1.0 - 150	
Mn	< 1.0 - 1000	10,000[c]
Mo	< 1.0 - 30	10,000
Ni	< 10 - 50	
PO_4	< 100 - 1000	
Pb	< 15	
Ra	< 0.1 - 4.0[f]	720[c, f]
Rb	< 1.0	
Se	< 1.0 - 10	
Sn	< 200	
Ti	< 1.0 - 150	
U	0.1 - 40	
V	< 1.0 - 10	70
Zn	< 10 - 2000	
Zr	< 25	

[a] based on an analysis of data presented in references 7,8, and 9.
[b] in relatively humid regions.
[c] in brine.
[d] in relatively dry regions.
[e] in thermal springs and mine areas.
[f] picocuries/liter (i.e. 0.037 disintegrations/sec).

of weathering; it gives no indication of the maximum concentration of an element which a soil can immobilize, i.e., the element loading capacity of the soil.

Fourth, a number of established, accepted laboratory methods exist for determining the magnitude of C_{Total}, C_{Fixed}, $C_{Adsorbed}$, and C_{Water} in soil. C_{Total} is usually measured by dry ashing at 500 to 550°C for 3 to 4 hours or by wet ashing with a mixture of perchloric and nitric or sulfuric acids. $C_{Adsorbed}$ and C_{Water} are usually determined by using mineral acids (e.g. 0.1 N HCl), organic acids, and chelating agents (e.g. EDTA, DTPA); hot water extractions as usually utilized for elements that exist as anions (e.g. B, Mo, Se). It is most important to note that the test method employed is dependent upon the individual element to be tested, the parameter to be tested (e.g. C_{Fixed} versus $C_{Adsorbed}$), and the soil type. There is no "universal" analytical method which is applicable for all forms of an element in all soils.

It is most important to note that there are test methods, which are similar to the ones mentioned above, that are utilized to determine the amount of extractable chemical from wastes; these are used to determine if the waste should be classified as a hazardous waste and must be disposed in a Class I landfill. These test methods include the U.S. EPA's EP Toxicity, the TCLP test method, and the State of California's CAM-WET procedure (California Assessment Manual - Wet Extraction Procedure). These methods should not be utilized for soil cleanup criteria from spills of hazardous materials for two reasons. First, these methods, when applied to soils, provide a value, $C_{Extract}$, where:

$$C_{Extract} = a\,C_{Fixed} + bC_{Adsorbed} + C_{Water} \qquad (3.2)$$

where:

$C_{Extract}$ = concentration of an element extracted from a soil; $C_{Total} > C_{Extract}$

a, b = fractions

Since a and b are not determined, it is not possible to relate the parameters of Equation 3.2 to those of Equation 3.1. In other words, $C_{Extract}$ provides no information regarding the magnitude of C_{Fixed}, $C_{Adsorbed}$, and C_{Water}, information which is needed to determine the potential migration and transformation of an element in soil.

Second, when soils are exposed to the extractants utilized by these test methods (acid and citrate or acid and acetate), gross alterations can occur in soil mineralogy, in naturally occurring soil chemical reactions, and in soil physical and chemical properties. These gross alterations result from the fact

that the extractants can (a) selectively dissolve soil minerals, (b) impede crystallization and formation of aluminum hydroxides and other soil minerals while causing structural distortions in newly formed minerals, (c) perturb hydrolytic reactions of aluminum, and (d) desorb, via mass action, elements and organics from soil adsorption sites which may not normally be desorbed. Because the extractants cause gross alterations in the chemical and mineralogical properties of soil systems, the data derived from these test methods, when soil is utilized as the solid phase, cannot be extrapolated to actual field conditions. Therefore, they should not be used for soil cleanup criteria from spills of hazardous materials.

The cleanup of contaminated soil should be engineered on a case-by-case basis using published and appropriate soil testing methods; the scientific literature contains at least seven test methods addressing the leaching potential of chemicals in soils[10], and numerous methods addressing the biological, chemical, and physical properties of soils[11,12,13,14].

ELEMENT FIXATION IN CLAY AND SOIL MINERALS

The quantity C_{Fixed} in Equation 3.1 was defined as the concentration of fixed element which has been incorporated into the structure of clay and soil minerals. This section of Chapter 3 will discuss how an element that enters a soil system can be immobilized by fixation into the structure of clay and soil minerals.

Some chemicals such as HCl and water are miscible in all proportions. In other words, continual additions of HCl into a beaker filled with water will not result in the precipitation of a solid in a beaker nor the formation of a separate phase of HCl. For most chemicals, however, there is a limit to the amount that can be added before a solid will precipitate. For example, when a small amount of $MgCO_3$ is added to water, it dissolves. As more $MgCO_3$ is added, it dissolves. However, a point will be reached where additions of $MgCO_3$ will not dissolve but will settle at the bottom of the beaker as a crystalline solid. An equilibriuim is established in which the rate of precipitation of $MgCO_3$ (solid, s) equals the rate of dissolution of $MgCO_3$ (s) into dissolved Mg^{2+} and CO_3^{2-}:

$$Mg^{2+} + CO_3^{2-} \underset{\text{Dissolution}}{\overset{\text{Precipitation}}{\rightleftharpoons}} MgCO_3\ (s) \qquad (3.3)$$

Now suppose that in addition to Mg^{2+} and CO_3^{2-}, dissolved Ni^{2+} was also present in water at a concentration equal to that of dissolved Mg^{2+}. Ions such as Ni^{2+} which have the same valence and similar size as Mg^{2+} can replace Mg^{2+} in the crystal structure of the precipated structure. In other

where:

V_c = Velocity of the chemical at the point where $c/c_o = 0.5$.
V = Average linear velocity of groundwater.
K_d = Adsorption or distribution coefficient.
b = Soil bulk density.
P_T = Soil total porosity.

The term $[1 + K_d(b/P_T)]$ is known as the retardation factor. This term should not be confused with the soil TLC R_f (retardation factor) because they are not equivalent parameters.

Equation 4.42 can provide reasonable estimates of the velocity of an inorganic chemical; however, it is important to note that the reactions discussed in Chapter 3 are not directly accounted for in this equation.

Rapid Assessment Nomograph. This graphical technique was developed as an integrated methodology for assessing chemical movement through both the unsaturated and saturated zone[41]. Although the author has limited exposure to this method, it will be discussed because it appears to be a potentially useful tool. The technique was designed to allow emergency response personnel to make a first-cut, order-of-magnitude estimate of the potential extent of chemical migration/contamination from a waste site or chemical spill within a 24 hour emergency response time frame. The technique was not intended to provide a definitive, in-depth analysis of the complex fate and transport processes of chemicals in the subsurface environment.

This section will not discuss the use of this model or the input parameters needed to utilize the nomograph. However, the reader is encouraged to study and utilize it because it does provide reasonable estimates. The procedures developed in this model are based on a one-dimensional transport equation for flow through a porous medium. The equation considers dispersion, advection, equilibrium adsorption (linear isotherm) and degradation/decay (first order kinetics). Analytical solutions to the transport equation include both continuous (step function) and pulsed inputs of contaminants. The pulse solution was used to simulate short-term releases such as might occur from a spill or tank leak. The nomograph was developed from the continuous input solution but can also be used on pulse problems by subtracting the solutions to two continuous inputs lagged by the pulse duration.

Time and resource limitations expected during an emergency response have required a number of simplifying assumptions in the assessment nomograph; additional simplifications may be needed by the user due to limited data and information available at a particular emergency response site. The major assumptions incorporated into the assessment nomograph are as follows:

1. Homogenous and isotropic properties are assumed for both the unsaturated and saturated zones (or media).
2. Steady and uniform flow is assumed in both the unsaturated and saturated zones.
3. Flow and contaminant movement are considered only in the vertical direction in the unsaturated zone and the horizontal direction in the saturated zone.
4. All contaminants are assumed to be water soluble and exist in concentrations that do not significantly affect water movement.

The nomograph predicts contaminant concentrations as functions of both time and location in either the unsaturated or saturated zone. Separate computations, parameter estimates, and use of the nomograph are required for each zone. The prediction requires evaluation of four dimensionless quantities (A_1, A_2, B_1, and B_2) and subsequent evaluation of the result (C/C_o) through use of the nomograph. The parameters required for this procedure are: initial contaminant concentration, dispersion coefficient, average interstitial pore water velocity, degradation rate coefficient, soil bulk density, soil water content or effective porosity, and partition coefficient. Extensive guidelines for evaluation of these parameters are provided.

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Background Levels of Polycyclic Aromatic Hydrocarbons (PAH) and Selected Metals in New England Urban Soils

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ABSTRACT: Polycyclic aromatic hydrocarbons (PAH) are byproducts of combustion and are ubiquitous in the urban environment. They are also present in industrial chemical wastes, such as coal tar, petroleum refinery sludges, waste oils and fuels, and wood-treating residues. Thus, PAHs are chemicals of concern at many waste sites. Risk assessment methods will yield risk-based cleanup levels for PAHs that range from 0.1 to 0.7 mg/kg. Given their universal presence in the urban environment, it is important to compare risk-based cleanup levels with typical urban background levels before utilizing unrealistically low cleanup targets. However, little data exist on PAH levels in urban, nonindustrial soils. In this study, 60 samples of surficial soils from urban locations in three New England cities were analyzed for PAH compounds. In addition, all samples were analyzed for total petroleum hydrocarbons (TPH) and seven metals. The upper 95% confidence interval on the mean was 3 mg/kg for benzo(*a*)pyrene toxic equivalents, 12 mg/kg for total potentially carcinogenic PAH, and 25 mg/kg for total PAH. The upper 95% confidence interval was 373 mg/kg for TPH, which exceeds the target level of 100 mg/kg used by many state regulatory agencies. Metal concentrations were similar to published background levels for all metals except lead. The upper 95% confidence interval for lead was 737 mg/kg in Boston, 463 mg/kg in Providence, and 378 mg/kg in Springfield.

KEY WORDS: background, PAH, metals, urban, anthropogenic, soil.

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are byproducts of combustion and are naturally occurring chemicals in the environment. Forest fires and volcanoes are major natural sources of PAHs, but there are anthropogenic sources as well due to burning of fossil fuels, including automobile and industrial emissions. PAHs are chemicals of concern in many waste site investigations that are undertaken pursuant to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the Resource Conservation and Recovery Act (RCRA), and state

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hazardous waste programs. Risk assessments performed according to federal guidance for former manufactured gas plant sites, wood treating facilities, petroleum refineries, and other sites generally conclude that PAHs pose unreasonable risks to human health and that remedial actions must be taken to reduce risks to acceptable levels. The majority of the risk posed by PAHs is generally due to benzo(*a*)pyrene and the other PAHs that have been shown to cause cancer in laboratory animals after repeated dosings. The U.S. EPA (1993a) currently identifies seven PAHs as "probable human (B2) carcinogens": benzo(*a*)pyrene, benzo(*a*)anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, chrysene, dibenz(*a,h*)anthracene, and indeno(1,2,3-c,d)pyrene.

Because of the very health-protective assumptions used in regulatory risk assessments, very low risk-based clean-up levels for PAHs are derived for such sites. In Michigan, residential soil cleanup levels of 0.33 mg/kg for each carcinogenic PAH have been set (MDNR, 1993). In New Jersey, proposed residential soil cleanup levels are 0.66 mg/kg for benzo(*a*)pyrene (New Jersey *Register*, 1992). The use of standard CERCLA risk assessment guidance (U.S. EPA, 1993b) results in the derivation of a risk-based cleanup level for benzo(*a*)pyrene of 0.1 mg/kg.

All of these risk-based soil cleanup levels are below the urban, nonindustrial background soil concentrations presently reported in the literature. However, the availability of such data is very limited. Blumer (1961) reports that benzo(*a*)pyrene concentrations in Cape Cod, MA, soils range from 0.04 to 1.3 mg/kg. Menzie et al. (1992) report that urban background soil levels of total carcinogenic PAH range from 0.06 to 5.8 mg/kg. Butler et al. (1984) report that total PAH levels in soils alongside roadways in England range from 4 to 20 mg/kg, and potentially carcinogenic PAH range from 0.8 to 11.5 mg/kg. Blumer et al. (1977) report that total PAH levels in soils in a Swiss town range from 6 to 300 mg/kg.

It is very difficult to compare the data from these studies to the results of site risk assessments due to the limited dataset and the nonuniformity of the PAH compounds evaluated. Clearly, more data are required from nonindustrial urban locations to define the urban background level for PAH and to critically evaluate the role of risk assessment in setting remedial goals for PAH in soils. Accordingly, we have collected 60 samples of surficial soils from urban locations in three New England cities and analyzed them for all 17 PAH compounds present on the EPA's Target Compound List, which is used in the Superfund program. In addition, all samples were analyzed for total petroleum hydrocarbons (TPH) and for seven metals: arsenic, barium, cadmium, chromium, lead, mercury, and selenium.

II. METHODS

A. Sample Collection

Samples of surficial soils from urban locations in three New England cities were collected: Boston, MA; Providence, RI; and Springfield, MA. Twenty independent

samples and duplicates of two samples were collected in each city. The samples were collected on July 21, 22, and 23, 1992, respectively. The samples were taken at a depth of 0 to 6 in. in areas considered to be not directly affected by industrial sites. Generally, the locations were along roads and sidewalks, and in parks and open lots. Each location was characterized in writing, including a soil description, and photographically documented. The samples were collected following standard environmental sampling protocols (U.S. EPA, 1986).

B. Sample Analysis

Chemical analysis of the samples was performed by AnalytiKEM, Inc. (Cherry Hill, NJ). The samples were analyzed by GC-MS for the 17 PAH compounds present on the EPA's Target Compound List using the methods required by EPA Method 8270 for the analysis of semivolatile compounds. In addition, the samples were analyzed for the eight RCRA metals, total petroleum hydrocarbons (TPH; EPA Method 418.1), and total solids. The complete analyte list is given in Table 1.

C. Data Validation

Validation of the data received from AnalytiKEM was performed according to U.S. EPA (1991) guidelines. The data were reviewed for completeness, holding times, GC-MS tuning and system performance, initial and continuing calibrations, laboratory method blank analysis, surrogate recoveries, matrix spike and matrix spike duplicate analysis, field duplication precision, and compound quantitation and detection limits.

D. Data Analysis

The analytical data were summarized in accordance with U.S. EPA (1989) risk assessment guidance. If a compound was detected at least once in surface soil, one half the sample quantitation limit (SQL) was used as a proxy concentration for all samples reported as "below detection limit" in the estimation of exposure point concentrations. However, if a compound was not detected in any sample, that compound was omitted from further consideration. In addition, when a proxy concentration (i.e., one half the detection limit) was greater than the highest actual detected value for a compound in any sample, that concentration was considered to be an aberration and was omitted from the database. This is consistent with U.S. EPA (1989) guidance, which recognizes that high sample quantitation limits can lead to unrealistic concentration estimates.

TABLE 1
Chemical Analyses of Urban Soils

Semivolatile Organics, EPA Target Compound List
Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(*a*)anthracene
Chrysene
Benzo(*b*)fluoranthene
Benzo(*k*)fluoranthene
Benzo(*a*)pyrene
Indeno(1,2,3-cd)pyrene
Dibenzo(*a,h*)anthracene
Benzo(*g,h,i*)perylene
2-Methylnaphthalene
Metals
Arsenic, total
Barium, total
Cadmium, total
Chromium, total
Lead, total
Mercury, total
Selenium, total
Silver, total
Other
Total petroleum hydrocarbons
Solids

A slightly different method of analysis was used to evaluate PAH. Because PAH are generally found in groups, it was conservatively assumed that if one PAH was detected in a sample, other compounds in that class might also be present in that sample. Therefore, if one PAH was detected in a sample, all undetected PAH were assigned a proxy concentration equal to one half the SQL. If a sample had no detected PAH, no PAH were assumed to be present in the sample, and a concentration of zero was used for all nondetects.

Summary statistics (minimum, maximum, arithmetic mean, upper 95% confidence limit on the arithmetic mean, and frequency of detection) were generated for each compound for each city and for all three cities combined.

The data for PAH were summarized in several different ways. Of the 17 PAH analyzed in each sample, seven are considered to be probable human carcinogens (Group B2) by the U.S. EPA (1993a). The U.S. EPA has derived a cancer slope factor, which is a measure of the carcinogenic potency of a compound, only for benzo(*a*)pyrene (B(*a*)P) (U.S. EPA, 1993a). Review of the literature indicates that not all PAH are equally potent with respect to tumor induction. Several researchers have proposed toxic equivalency schemes that relate the tumorigenic potency of each PAH to that of B(*a*)P (ICF-Clement Associates, 1988; Woo, 1989). B(*a*)P toxic equivalency factors (B(*a*)P-TEFs) can be used to adjust either the B(*a*)P dose-response value to provide a compound-specific dose-response value, or the concentration of each PAH in a sample to be expressed in terms of B(*a*)P toxic equivalents (B(*a*)P-TE). The latter method was used here. B(*a*)P-TE were calculated using the B(*a*)P toxic equivalency factors recommended for use by the U.S. EPA (1993c), as shown in Table 2. For each sample, PAH concentrations were reported for each of the 17 PAH on the analyte list, for total PAH (tPAH), for total carcinogenic PAH (cPAH), and for B(*a*)P-TE, and these values were used to generate the summary statistics for each group of samples.

III. RESULTS

Analysis of the laboratory results for the PAH indicates that quality control criteria were acceptable. The data were analyzed to determine if any statistically significant differences existed between the datasets for the three cities. A Hartley test for homogeneity of variances (Mendenhall, 1979) and a one-factor analysis of variance to test for equality of the means (Mendenhall, 1979) indicated no statistically significant differences. The results indicate that the PAH data can be pooled and treated as one dataset for further statistical analyses.

TABLE 2
Benzo(*a*)Pyrene Toxic Equivalent Factors (BAP-TEF)

Compound	EPA TEF
Benzo(*a*)pyrene	1.0
Benz(*a*)anthracene	0.1
Benzo(*b*)fluoranthene	0.1
Benzo(*k*)fluoranthene	0.1
Chrysene	0.001
Dibenzo(*a,h*)anthracene	1.0
Indeno(1,2,3-c,d)pyrene	0.1

The results of the PAH analyses are presented in Table 3 for all cities combined. A summary of the PAH results by city and for all cities combined is presented in Table 4, which reports for each: tPAH, total cPAH, and total B(*a*)P-TE. The arithmetic mean and the upper 95% confidence limit concentration are reported for each. Table 4 provides a summary of the data by city, and the results are graphically presented in Figure 1.

Table 5 presents a summary of the metals, TPH, and solids data by city. A Hartley test for homogeneity of variances and a one-factor analysis of variance to test for equality of the means indicated that the metals and TPH data from the three cities cannot be combined. This is due to the fact that the concentrations in each city are not normally distributed and did not have equal variances. The concentrations of the metals are compared to the arithmetic mean concentrations in the eastern U.S. (ATSDR, 1992) in Table 5. Most notably, lead concentrations are much higher than background concentrations. This is most likely due to the effects of automobile exhaust.

In order to determine if sample location significantly affected PAH concentration results, individual samples were classified based on the sample location's

TABLE 3
Summary Statistics for PAH — All Areas Combined

Compound	Minimum detect (mg/kg)	Maximum detect (mg/kg)	Arithmetic mean	Upper 95% interval (mg/kg)	Frequency of detection[a]	
2-Methylnaphthalene	0.017	0.64	0.151	0.173	19	62
Acenaphthene	0.024	0.34	0.201	0.306	30	62
Acenaphthylene	0.018	1.10	0.173	0.208	24	62
Anthracene	0.029	5.70	0.351	0.535	54	62
Benzo(*a*)anthracene	0.048	15.00	1.319	1.858	58	62
Benzo(*a*)pyrene	0.040	13.00	1.323	1.816	57	62
Benzo(*b*)fluoranthene	0.049	12.00	1.435	1.973	55	62
Benzo(*g,h,i*)perylene	0.200	5.90	0.891	1.195	36	62
Benzo(*k*)fluoranthene	0.043	25.00	1.681	2.522	59	62
Chrysene	0.038	21.00	1.841	2.693	60	62
Dibenzo(*a,h*)anthracene	0.020	2.90	0.388	0.521	32	62
Fluoranthene	0.110	39.00	3.047	4.444	60	62
Fluorene	0.022	3.30	0.214	0.317	35	62
Indeno(1,2,3-c,d)pyrene	0.093	6.00	0.987	1.293	43	62
Naphthalene	0.018	0.66	0.125	0.149	35	62
Phenanthrene	0.071	36.00	1.838	2.982	61	62
Pyrene	0.082	11.00	2.398	2.945	61	62
Total BAP-TE	0.257	21.31	2.437	3.324	62	62
Total carcinogenic PAH	0.680	77.70	8.973	12.423	62	62
Total PAH	2.292	166.65	18.361	24.819	62	62

[a] Frequency of detection = number detected: number samples.

TABLE 4
Background PAH Concentrations in Urban Surface Soils[a]

Compound	Boston (n = 20)		Providence (n = 20)		Springfield (n = 20)		All cities (n = 60)	
	Arithmetic mean (ppm)	Upper 95% CI (ppm)	Arithmetic mean (ppm)	Upper 95% CI (ppm)	Arithmetic mean (ppm)	Upper 95% CI (ppm)	Arithmetic mean (ppm)	Upper 95% CI (ppm)
Total B(*a*)P-TE	2.4	4.6	2.1	2.9	2.8	4.5	2.4	3.3
Total cPAH	8.4	16.0	7.8	11.0	10.6	18.3	9.0	12.4
Total PAH	18.7	35.9	16.8	23.5	19.1	29.9	18.4	24.8
TPH	474.9	652.6	267.4	338.2	184.4	233.3	306.2	372.8

[a] 0 to 6 in.

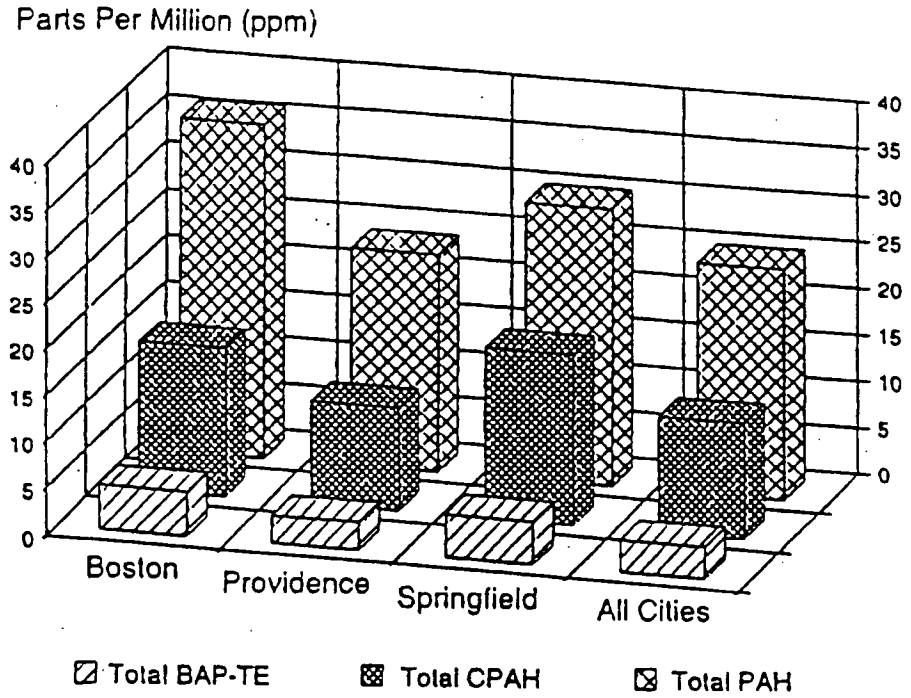

FIGURE 1. Background concentrations of PAH in urban soils. Data presented are the upper 95% confidence interval on the arithmetic mean. Data are presented numerically in Table 4.

proximity to asphalt pavement, based on both written and photographic documentation of sample location. Generally, samples collected within 4 to 6 ft of a road were considered to be near pavement. Of the 60 separate locations, 42 were considered to be near pavement and 18 were not. When tested for equality of variance and means as above, the two populations were determined to be significantly different. The mean total PAH concentration near pavement was 22 ppm compared to 8 ppm not near pavement. These results are shown in Table 6.

Similar analyses were performed to see if TPH or total organic carbon concentrations could be used as surrogates for PAH concentrations. The results showed that there is no correlation between PAH and TPH concentrations, nor between PAH and total organic carbon concentrations (data not shown).

The highest total PAH concentration detected was 166 mg/kg, taken from a street corner in Boston. The next highest PAH concentration was 109 mg/kg, taken at the base of a telephone pole. Four of the 60 samples were taken at the bases of telephone poles, with widely varying results. The total PAH concentrations in the other three locations were 62, 4, and 45 mg/kg.

TABLE 5
Summary Statistics for Metals, TPH, and Soils by City

Compound	Boston (n = 20) Arithmetic mean (mg/kg)	Boston (n = 20) Upper 95% interval (mg/kg)	Providence (n = 20) Arithmetic mean (mg/kg)	Providence (n = 20) Upper 95% interval (mg/kg)	Springfield (n = 20) Arithmetic mean (mg/kg)	Springfield (n = 20) Upper 95% interval (mg/kg)	Arithmetic mean in U.S. soils[a] (mg/kg)
Arsenic, total	4.20	5.59	3.53	4.27	5.63	9.23	7.4
Barium, total	53.95	66.25	45.29	59.43	45.17	51.03	420
Cadmium, total	1.55	2.79	ND	ND	ND	ND	0.25[b]
Chromium, total	23.00	27.69	12.08	14.35	12.62	14.45	52
Lead, total	398.70	737.44	305.76	462.98	261.69	377.76	17
Mercury, total	0.29	0.39	0.19	0.24	0.20	0.25	0.12
Selenium, total	0.51	0.57	0.39	0.48	0.53	0.55	0.45
Total petroleum hydrocarbons	474.90	652.62	267.43	338.19	184.38	233.27	—
Total solids	90%	93%	93%	95%	90%	92%	—

[a] ATSDR. 1992. *Public Health Assessment Guidance Manual.* PB92-147164. U.S. Department of Health and Human Services.
[b] ATSDR. 1991. *Toxicological Profile for Cadmium.* PB92-147164. Draft. U.S. Department of Health and Human Services.

TABLE 6
Comparison of Background PAH Concentrations in Urban Soils: The Effects of Proximity to Pavement

					Results of statistical analysis					
					Test for homogeneity of variances			Test of equality of means		
	Near pavement		Not near pavement							
Compound	Arithmetic mean (ppm)	Standard deviation	Arithmetic mean (ppm)	Standard deviation	Sample F-statistics	Associated degrees of freedom	Statistically significant at 0.05 level of significance	Sample Student's *t*	Associated degrees of freedom	Statistically significant at 0.05 level of significance
Total B(*a*)P-TE	2.9	4.2	1.1	0.92	21.3	41, 17	Yes	2.69	50	Yes
Total PAH	21.9	30.7	8.3	7.2	18.4	41, 17	Yes	2.69	50	Yes

IV. CONCLUSION

In this study, 20 surface soil samples were collected from each of three New England cities and analyzed for PAH, TPH, and metals. The results of the statistical analyses described in the previous section show that, with respect to PAH, the three datasets are not significantly different and can be considered as one dataset representative of urban environments. The samples were taken in typical urban areas but not near known industrial sites. Therefore, these data are considered to be representative of the generalized effects of urban activities.

It is clear from the results presented here that common regulatory target cleanup levels for cPAH and B(*a*)P-TE (0.1 to 0.66 mg/kg) are much below the background concentrations of these compounds in urban surface soils (upper 95% confidence interval of 3.3 and 12.4 mg/kg for total B(*a*)P-TE and total cPAH, respectively). Figure 2 graphically compares the "bright line" target cleanup level for B(*a*)P of 0.1 mg/kg with the total B(*a*)P-TE (upper 95% confidence interval on the arithmetic mean) measured in urban environments.

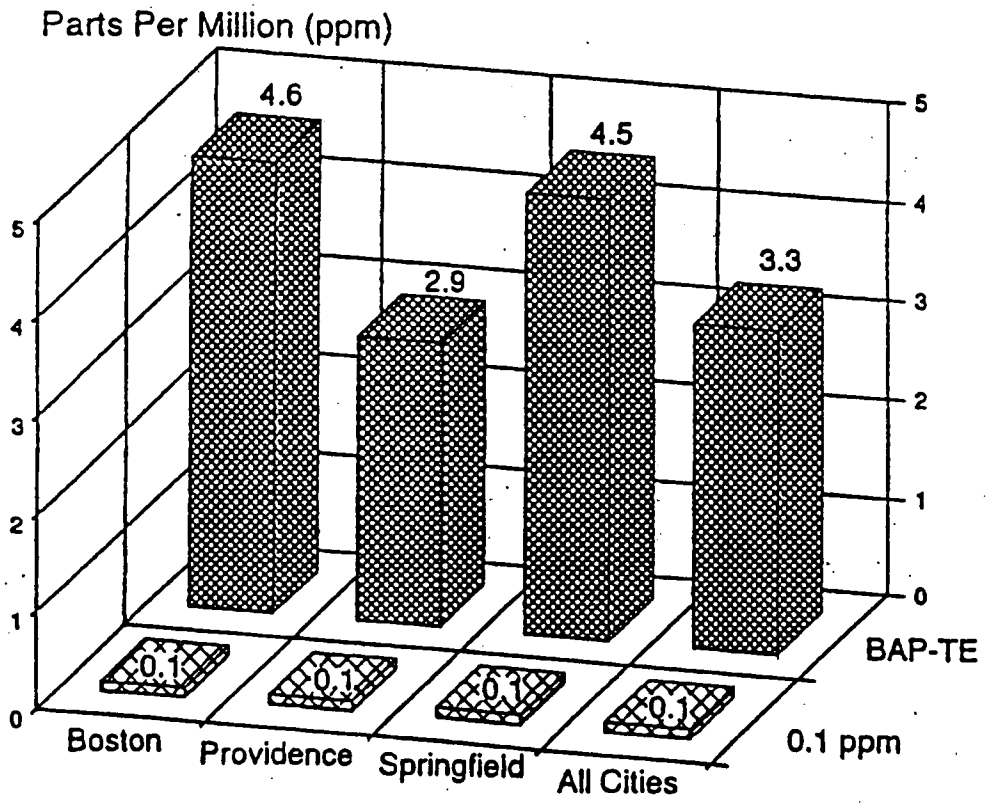

FIGURE 2. Comparison of B(*a*)P-TE with U.S. EPA Region III[4] risk-based concentration for B(*a*)P. B(*a*)P data presented are the upper 95% confidence interval on the arithmetic mean.

Upper 95% confidence intervals are compared because this is the statistic preferred by EPA and many states for risk assessment. Moreover, the State of Massachusetts defines its background concentrations of metals based on the upper 95% confidence limit on the arithmetic mean concentration (Massachusetts Department of Environmental Protection, 1992). For all cities combined, the background level of B(*a*)P-TE of 3.3 mg/kg is approximately ten times greater than the target cleanup level of 0.33 mg/kg and approximately 30 times higher than the target cleanup level of 0.1 mg/kg. For those regulatory situations in which the use of B(*a*)P-TEFs in determining site risk is not allowed, the background level of cPAH is approximately 40 to 100 times greater than these target cleanup levels.

An analysis of the data comparing samples taken near pavement with those determined to be not near pavement indicated that those samples designated near pavement had significantly higher, approximately threefold higher, PAH concentrations for both total PAH and total B(*a*)P-TE. This is most likely due to the presence of diesel and automobile exhaust particles, perhaps influenced by the presence of asphalt and runoff of vehicular oil from the roads.

Total petroleum hydrocarbons (TPH) were also found at consistently high levels in each city. The commonly applied regulatory cleanup level for TPH is 100 mg/kg. This cleanup level is not risk based and is three times lower than the background concentration of TPH found in this study (arithmetic mean of 306 mg/kg and upper 95% confidence interval on the mean of 373 mg/kg).

It is incumbent upon the regulatory agencies to recognize that substantial background levels of PAH and TPH exist in our urban environments and to acknowledge this information in the development of realistic target cleanup levels. The use of these background data in setting more realistic target cleanup levels may result in better allocation of remedial and regulatory dollars in site investigations.

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