Lead in Seawater

The reliability of many published analyses of lead in seawater was questioned at an International Decade of Ocean Exploration (IDOE) conference at Brookhaven National Laboratory in May 1972. The conference dealt with baseline studies of pollutants in the marine environment. Participants feared that many previously published lead concentrations in seawater are probably excessively high. It was recommended at the meeting that a workshop be established to carry out interlaboratory analyses of lead in seawater. Results of the workshop confirmed the organizers' suspicions of previous analyses of lead concentrations in seawater and it was discovered that even the published, lowest lead concentrations in deep ocean waters determined by isotope dilution techniques may be too high. The implications are that lead pollution effects in the marine environment may be more serious than had been previously thought, since the magnitude of industrial lead input to the oceans has not been diminished by these new findings.

A workshop on lead in seawater sponsored by the National Science Foundation (NSF) office for the IDOE was initiated in the fall of 1972. Samples of seawater standardized at one university by isotope dilution were circulated among participating oceanographic laboratories at seven universities in the United States and at one ministry in the United Kingdom during the next 6 months. None of the participants were aware of the standardized value of a sample until all of the results for that sample had been reported to the standardizing laboratory. A meeting of analysts from the participating laboratories and of five advisers from universities and government agencies was held in Pasadena, California, 16 to 20 September 1973. At this meeting the results of the workshop were discussed and interpreted, and a number of recommendations were made for improving the accuracy of atomic absorption and anodic stripping voltammetry methods for the analysis of lead in seawater.

None of the four surface coastal seawaters standardized by isotope dilution techniques in this workshop showed total dissolved plus adsorbed concentrations exceeding 80 ng of Pb per kilogram of seawater. These samples were taken in a region that was highly industrialized and heavily populated. The workshop group agreed that published measurements of thousands of nanograms of Pb per kilogram in coastal waters may be in gross error.

Two of the surface coastal waters studied in this workshop were found to contain about half as much lead as any deep water previously analyzed by isotope dilution methods. The surface waters were collected by special techniques to exclude contamination originating from the collecting boat. Deep waters analyzed prior to this workshop were collected by samplers that were subject to contamination from dirty waters emanating from the research ships because the cleaned samplers were lowered through dirty water in an unprotected condition. Even though the deepwater samples were analyzed by isotope dilution, erroneously high results may have been obtained as a consequence of the collection technique.

It was recommended that water samplers be devised which are contained within a protective covering. Such samplers could be lowered through contaminated waters in a clean condition until they reach the deeper waters that are to be sampled where they could be opened and lowered slightly while the water sample is collected.

Both atomic absorption and anodic stripping voltammetry techniques gave erroneously high results in the first sample of seawater standardized at a concentration of 14 ng of dissolved Pb per kilogram. Lead concentrations determined by four atomic absorption laboratories ranged from four to eight times higher than the standardized value, while those determined by three anodic stripping voltammetry laboratories ranged from 10 to 100 times higher. The amounts of seawater used for anodic stripping voltammetry analyses ranged from 10 to 90 g while those used for atomic absorption analyses ranged from 500 to 1200 g.

In a second standardized sample, which contained about four times as much lead as the first sample, three out of four lead concentrations determined by atomic absorption were about 1.6 times the standardized value while one of the two concentrations determined by anodic stripping voltammetry was 1.4 times the standardized value. Two other reported concentrations determined by these methods showed much greater error. An average concentration determined by pulse polarography was half as large as the standardized value.

A third standardized sample containing 17 ng of dissolved Pb per kilogram was sent to two laboratories for analysis by atomic absorption. One laboratory extracted all the dissolved lead from 23 kg of seawater for a single analysis, while the other laboratory extracted all the dissolved lead from only 175 g of seawater for analysis. The result reported by the analyst using the larger sample was 1.3 times higher than the standardized value, while the result reported by the analyst using the smaller sample was 5.0 times higher than the standardized value.

A fourth standardized sample of seawater containing 42 ng of dissolved Pb per kilogram was sent to the same laboratory that used the 23-kg aliquot of the third sample. The analyst used 1 kg and reported a result that was 3.8 times lower than the standardized value.

The standardizing laboratory found that the proportions of lead adsorbed on particles to dissolved lead were initially different among the four samples of seawater collected, and that the concentrations of these two species of lead changed in two of the samples upon aging in the shipping bottle.

It is believed that samples of seawater had been accurately analyzed for lead by isotope dilution, but that, unfortunately, the concentrations were similar to those of the procedural blanks used at the beginning of the workshop in atomic absorption and anodic stripping voltammetry. It was agreed that neither the atomic absorp-

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See the Preconvention Issue (11 January 1974, pages 105–114) for details of lectures and symposia. On pages 562 and 563 of this issue there are Advance Registration and Hotel Reservation forms.

tion nor the anodic stripping voltammetry techniques were used to analyze the first seawater sample in a manner that gave reliable results. Although concentrations reported for the second sample were closer to standardized values, it was agreed that this reflected an increase in the ratio of analyzed sample lead to procedural blank lead. Results obtained in the third and fourth standardized samples substantiated this interpretation. Material balance considerations showed that the amounts of lead in the analyzed sample were of the same order as the amounts of lead in the blanks. Total errors of analyses were of the same order of magnitude as reported concentrations.

A most significant and encouraging outcome of the workshop was that analysts and advisers attending the meeting made a number of recommendations for improving the accuracy of atomic absorption and anodic stripping voltammetry methods of analyzing lead in seawater, which they agreed to use in their own future work. These recommendations included ways of increasing the amount of analyzed sample lead, together with directions for reducing procedural blank lead.

A valuable result of the workshop was the development of a reliable method for cleaning containers used for shipping standardized samples of seawater.

The group agreed that the workshop should be continued until some of the participants demonstrated an ability to determine lead in seawater reliably with either atomic absorption or anodic stripping voltammetry techniques.

The difficulties that have been revealed in this study regarding the analysis of lead in seawater by atomic absorption and anodic stripping voltammetry may not apply uniquely to lead. Similar difficulties may exist for other metals in seawater, such as copper and cadmium. It was recommended that all analysts consider whether the adoption of clean laboratory techniques and procedural modifications that would improve the sample to blank metal ratio for other heavy metals might produce more reliable results for these other trace metals as well.

A detailed report containing results and recommendations, which will be submitted to a journal for publication, was prepared by those attending this meeting.

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Forthcoming Events

March

7–8. **Dyssocial Behavior Control** (Psychosurgery), 5th cerebral function symp., Coronado, Calif. (L. Smith, Porter Memorial Hospital, 2525 S. Downing St., Denver, Colo. 80210)

8–11. **Environmental Mutagen** Soc., 4th annual, Washington, D.C. (R. J. Burk, Jr., EMS, 4211 39th St., NW, Washington, D.C. 20016)

8–11. **Acupuncture and Chinese Medicine**, 2nd world symp., San Francisco, Calif. (J. Kao, Managing Editor, *American Journal of Chinese Medicine*, P.O. Box 555, Garden City, N.Y. 11530)

9–12. American Assoc. of **Pathologists and Bacteriologists**, San Francisco, Calif. (A. J. French, 1335 E. Catherine St., Ann Arbor, Mich. 48104)

9–16. International Acad. of **Pathology**, San Francisco, Calif. (L. D. Stoddard, Medical College of Georgia, Augusta 30902)

10–14. International **Anesthesia Research** Soc., 48th congr., San Francisco, Calif. (B. B. Sankey, 3645 Warrensville Center Rd., Cleveland, Ohio 44122)

10–14. Society of **Toxicology**, Washington, D.C. (R. A. Scala, Medical Research Div., Esso Research and Engineering Co., Linden, N.J. 07036)

10–15. American Soc. of **Photogrammetry**, St. Louis, Mo. (L. P. Jacobs, 105 N. Virginia Ave., Falls Church, Va. 22046)

11–14. American Soc. of **Neurochemistry**, 5th annual, New Orleans, La. (S. H. Appel, Duke Univ. Medical Center, Durham, N.C. 27706)

11–15. National Assoc. of **Corrosion Engineers**, 30th annual conf., Chicago, Ill. (NACE, 2400 West Loop S, Houston, Tex. 77027)

11–15. Symposium on **Isotope Techniques in Groundwater Hydrology**, Intern. Atomic Energy Agency, Vienna, Austria. (J. H. Kane, Office of Information Services, U.S. Atomic Energy Commission, Washington, D.C. 20545)

12–14. National Federation of **Abstracting and Indexing** Services, Chicago, Ill. (S. Keenan, NFAIS, 3401 Market St., Philadelphia, Pa. 19104)

13. Symposium on **Sickle Cell Anemia and Other Hemoglobinopathies**—Teaching Day in Hematology, Research Foundation of the State Univ. of New York, Brooklyn, N.Y. (B. Kearney, Box 20, Downstate Medical Center, 450 Clarkson Ave., Brooklyn 11203)

13–14. **Environmental Research** Symp., 5th annual, Chemical and Biological Div., American Defense Preparedness Assoc., Washington, D.C. (ADPA, Suite 819, 740 15th St., NW, Washington, D.C. 20005)

13–15. American Acad. of **Occupational Medicine**, San Francisco, Calif. (J. M. MacMillan, Reynolds Metals Co., P.O. Box 27003, Richmond, Va. 23261)

15–19. National **Science Teachers** Assoc., Chicago, Ill. (R. H. Carleton, NSTA, 1201 16th St., NW, Washington, D.C. 20036)

17–20. American Assoc. of **Dental Schools**, Atlanta, Ga. (B. F. Miller, AADS, 1625 Massachusetts Ave., NW, Washington, D.C. 20036)

18–20. International Symp. on **Physiological and Toxicological Aspects of Combustion Products.** Committee on Fire Research, Natl. Acad. of Sciences, and the Flammability Research Center, Univ. of Utah, Salt Lake City. (I. N. Einhorn, Div. of Materials Science and Engineering, Univ. of Utah, 2020 Merrill Engineering Bldg., Salt Lake City 84112)

18–22. **Lunar Science** Conf. 5th, NASA Johnson Space Center and Lunar Science Inst., Houston, Tex. (LSI, 3303 NASA Rd. 1, Houston 77058)

20–22. International Topical Conf. on **Tetrahedrally Bonded Amorphous Semiconductors**, Yorktown Heights, N.Y. (M. H. Brodsky, IBM Corp., T. J. Watson Research Center, Yorktown Heights, 10598)

21–22. Symposium on the **Preventability of Perinatal Injury**, Natl. Foundation–March of Dimes, New York, N.Y. (Coordinator, SPPI, NF–MD, 315 Park Ave., S., New York 10010)

21–23. Florida **Acad. of Sciences**, Orlando. (I. Foster, Eckert College, St. Petersburg, Fla.)

21–23. Mississippi **Acad. of Sciences**, Biloxi. (C. L. Dodgen, University Medical Center, Jackson, Miss. 39216)

21–24. International Assoc. for **Dental Research**, North American Div., Atlanta, Ga. (A. R. Frechette, IADR, 211 E. Chicago Ave., Chicago, Ill. 60611)

22–23. Michigan **Acad. of Science, Arts and Letters**, East Lansing. (D. Stokes, 1006 Rackham Bldg., Univ. of Michigan, Ann Arbor 48104)

25–26. State **Medical** Soc. of Wisconsin, Milwaukee. (E. R. Thayer, Box 1109, Madison, Wis. 53701)

25–26. **Theory and Use of the Scanning Electron Microscope** Conf., Rockville, Md. (J. M. Wehrung, EMventions Microanalysis Lab., 2351 Shady Grove Rd., Rockville 20850)

25–28. American **Physical Soc.**, Philadelphia, Pa. (W. W. Havens, Jr., APS, 335 E. 45 St., New York 10017)

25–28. American College of **Surgeons**, Houston, Tex. (E. W. Gerrish, ACS, 55 E. Erie St., Chicago, Ill. 60611)

25–28. Institute of **Electrical and Electronics Engineers**, New York, N.Y. (D. G. Fink, IEEE, 345 E. 47 St., New York 10017)

25–29. **Molecular Biology and Mechanisms of Virus Disease**, winter confs., Intern. Chemical and Nuclear Corp. and the Univ. of California at Los Angeles, Squaw Valley, Calif. (Conf. Office, Virus Research, c/o Dept. of Bacteriology, Univ. of California, Los Angeles 90024)

26–27. **Reducing Fuel Consumption and Emissions by Combustion Modifications**, Central States Section, Combustion Inst., Madison, Wis. (G. Borman, Univ. of Wisconsin, 1513 University Ave., Madison 53706)

26–29. American **Astronomical** Soc., Lincoln, Neb. (H. M. Gurin, AAS, 211 FitzRandolph Rd., Princeton, N.J. 08540)

26–29. National **Atomic and Molecular Physics** Conf., 6th, Inst. of Physics, Swansea, England. (Meetings Officer, IP, 47 Belgrave Sq., London, SW1X 8QX, England)

26–29. Institute of **Electrical and Electronic Engineers**, intern. conv., New York, N.Y. (D. Larson, IEEE INTERCON,