NATIONAL WATER QUALITY LABORATORY
NEWSLETTER
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Legion of Merit Award to Jose Andy Martinez

Sergeant Major Andy Martinez has received the Legion of Merit for exceptionally meritorious conduct for his 26 years of service to the U.S. Army in both active and reserve duty. Martinez has been a materials handler in the warehouse operations since his arrival at the National Water Quality Laboratory in 1991.

Martinez' career in the U.S. Army began as a radio telephone operator with the 1st Battalion, 5th Infantry Division in South Vietman. Martinez retired from the reserves in the 6th Brigade, 91st Division, where he provided leadership to the operations section and trained observer controllers.

Andy's commendation says that he served with devotion, integrity, and dedication. He continues to serve the customers of the NWQL with the same dedication that he gave to the U.S. Army.

LEGION OF MERIT-Jose Andy Martinez, materials handler in Laboratory Operations, receives merit award for active and reserve duty in the U.S. Army.

Ron Macklberg

FOOD FOR THOUGHT - Lisa Olsen, chemist in the Maryland District Office, Baltimore, takes a look at colorimetric analysis of nutrients during a recent visit to NWQL. Gary Cottrell, new supervisor of the Nutrients Unit in the Inorganic Chemistry Program, served as tour guide. Colorimetry is an analytical method based on measuring the color intensity of a substance or a color derivative of it. A nutrient is any element or compound that is essential to the life or growth of plants or animals.

Blank correction omitted for nitrogen, phosphorus

The National Water Quality Laboratory has notified the Water Resources Division that blank corrections were omitted for Kjeldahl nitrogen and Kjeldahl phosphorus for lab samples analyzed from April 20, 1999, to October 4. Samples analyzed at NWQL for nitrogen (lab codes 1985, 1986, and 1994) and phosphorus (lab codes 1983, 1984, and 1992) were not blank corrected, according to the November 16 notice from Merle Shockey, Acting Chief.

Shockey said the blank correction function was inadvertently omitted on April 20 when a new low concentration standard was added to the calibration curves for nitrogen and phosphorus. On October 4, 1999, the problem was identified and the blank correction was restored.

Between the dates of April 20 and October 4, results reported for these tests are biased high by about 0.05 milligram per liter (mg/L) for nitrogen and 0.01 mg/L for phosphorus on the basis of the average rise in blind blank concentrations for each analysis, according to the announcement. Customers were reminded that the laboratory reporting level for the nitrogen lab codes is 0.1 mg/L and for the phosphorus lab codes 0.05 mg/L.

Samples at or near the laboratory reporting level for nitrogen and phosphorus are most affected by this problem, said Shockey. The NWQL is currently analyzing the data to determine the best course of action. Guidance on corrections will be issued so that changes can be made for the annual data reports. For questions, contact Gary Cottrell (cottrell@usgs.gov), supervisor, Nutrients Unit, telephone (303) 236-3490, or Harold Ardourel (ardourel@usgs.gov), telephone (303) 236-3151.

Organic Blind Sample Project moves to Quality Systems Branch, keeps office in Lab

For several years, the National Water Quality Laboratory (NWQL) has operated an Organic Blind Sample Project (OBSP) to provide quality assurance for the determination of organic compounds. This project provides unbiased data on the performance of the entire analytical process for many organic methods. As of October 1, 1999, this project has been moved to the Branch of Quality Systems (BQS) to reinforce the independent nature of the evaluations. Two NWQL staff personnel, Kim Pirkey and Suranne Horodyski, have been detailed to BQS to work on the project.

The OBSP data from January 1996 through April 1999 have been summarized and are now posted to several new Internet Web pages. Blind sample spike recoveries, at several different concentrations, and blind blank data assessments are provided. Data tables, box plots, and time series charts, indicating long-term data quality, can be accessed directly by customers using their personal computers. Customers may link to these Web pages from either of the following locations: http://wwwnwql.cr.usgs.gov/USGS/OBSP/OBSPSplashPage.html or http://bqs.usgs.gov/

The Blind Blank Program, which is coordinated by Beth Kellogg (ekellogg@usgs.gov), will remain as part of the NWQL, and plans call for continued linking of blind blank data to the OBSP Web page. Questions or comments about the OBSP, quality-control data, or Web pages are welcomed. Contact either Kim Pirkey (kdpirkey@usgs.gov) or Suranne Horodyski (stineman@usgs.gov). The OBSP offices and lab will continue to be physically located at the NWQL in building 95 at the Denver Federal Center.

Kim Pirkey

Seminar calendar

"Global Warming Is Real: The Glaciers Tell Us So" Mark F. Meier, Professor Emeritus, Geological Sciences, Institute of Arctic and Alpine Research, University of Colorado, Boulder 1:30 p.m. Thursday, January 20 Foord Conference Room B1409, Building 20, Denver Federal Center Meier worked as a research glaciologist and hydrologist for USGS in Washington State for 30 years.

"The Floor of Yellowstone Lake Is Anything But Quiet: New Discoveries from Sonar Imaging, Seismic Reflection, and Magnetic Surveys" Lisa A. Morgan and Pat Shanks Mineral Resources Team U.S. Geological Survey 10:30 a.m. Thursday, February 24 Main Conference Room National Water Quality Laboratory Building 95, Denver Federal Center

The NWQL seminar entitled **"Large Rivers and Their Flood Plains as Conveyors and Storers of Sediment and Contaminants"** was presented December 1, 1999, by Robert H. Meade, U.S. Geological Survey. USGS visitors and guests are welcome to attend NWQL seminars.

STATE OF FLUX-Donald A. Goolsby, midcontinent project chief for the Central Region, addressed the Geological Society of America at its 1999 Annual Meetiing in Denver. Goolsby presented a talk October 28 entitled "Nitrogen Flux to the Gulf of Mexico," at a session on the occurrence and fate of agricultural chemicals in the hydrologic system. Goolsby was one of a number of U.S. Geological Survey members who made presentations during GSA's four-day meeting at the Colorado Convention Center.

Organic Chemistry adds new schedules for volatile compounds

The Volatile Organic Compound Unit of the Organic Chemistry Program added three new schedules last year to the NWQL Online Catalog. Lab Schedules (LS) 2022 and LS 2023 were created specifically for National Water-Quality Assessment Program (NAWQA) users who have previously sampled their study area and are interested in a small subset of volatile organic compounds (VOCs). Both of these schedules report VOCs at the laboratory reporting level, as do LS 2020 and LS 2021.

LS 2023 reports results for BTEX (benzene, toluene, ethylbenzene, and xylenes) and the oxygenated fuel ethers, including methyl-tert-butyl ether (MTBE), methyl-tert-pentyl ether (TAME), diisopropyl ether, and ethyl-tert-butyl ether. LS 2022 reports the same list of VOCs as LS 1307, including BTEX, the oxygenated fuel ethers, trihalomethanes, and the chlorinated solvents. LS 4054 was created for non-NAWQA users. LS 4054 contains the same compound list as LS 2020 but censors at a method reporting level. Analysis of nonselected compounds is also included.

LS 4054 replaces LS 1380 and LS 1392. For more details, all of these schedules can be viewed online in SPiN (the Internet version of Schedules, Parameters, Networks).

Current VOC method development includes a low-level selected-ion monitoring method for a subset of VOCs in water, including 1,2-dibromoethane (EDB), 1,2-dichloro-3-chloropropane (DBCP), MTBE, TAME, and BTEX. Laboratory reporting levels are in the low nanogram-per-liter range.

The laboratory reporting levels for EDB and DBCP are much lower than for LS 2020 and LS 1306 (hexane extraction, electron capture detection). The method will be fully validated and published. This analytical method is available only as a custom lab code at this time.

An analytical method is also being developed for U.S. Environmental Protection Agency (USEPA) Method 5035, which determines VOCs in soil samples. Five grams of soil is added in the field to a VOC vial that contains 5 milliliters of water and 1 gram of sodium bisulfate as a preservative. The sample then is shipped to the laboratory.

The NWQL Archon Autosamplers can be used to analyze soil or water samples. A vial is placed in the autosampler, which heats the sample to 40 degrees Celsius, while stirring and purging. Initial method detection limits, bias, and variability data indicate that this method performs within accepted guidelines. USEPA Method 5035 is available only as a custom lab code at this time.

Future plans include the possibility of fully validating the method, publishing an Open-File Report, and offering the analysis as a routine schedule if there is sufficient demand.

Contact Donna Rose (telephone 303-236-3283; dlrose@usgs.gov) or Ralph White (telephone 303-236-3251; wrwhite@usgs.gov) with questions regarding any of these schedules or custom lab codes.

Donna Rose

VOLATILE COMMODITY-Chemist Donna Rose prepares samples for analysis of volatile organic compounds.

SAMPLE PREPARATION-Joy Arellano, student and part-time physical science aid, and Mars Harper, physical science technician, acidify water samples as part of the log-in process for the determination of herbicides. Concentrated sulfuric acid is added to water samples for two reasons: to preserve the herbicides and to assist in their extraction from the water.

New reporting levels released for high-use analytical methods

The National Water Quality Laboratory released new reporting levels October 1, 1999, for many high-use water methods. These new reporting levels were developed from long-term method detection levels (LTMDLs) and are termed "laboratory reporting levels" (LRLs).

The LT–MDLs and LRLs are used to develop statistically assured reporting levels at very low concentrations. The LT–MDLs ensure 99-percent confidence that if the constituent is present at the LT–MDL concentration, it would not be the result of blank contribution. The LRLs ensure 99-percent confidence that if the constituent is present at the LRL concentration, it would be detected and reported. LT–MDLs, therefore, control the risk of false positives, and LRLs control the risk of false negatives. The new LRLs can be viewed at http://wwwnwql.cr.usgs.gov/Public/ltmdl/ltmdlsplash.html.

The water year* 2000 LRLs were implemented for high-use water methods last October 1, and will be valid through September 30, 2000. Methods not included in the water year 2000 assessment were either eliminated because of insufficient data or were not amenable to the LRL reporting convention (that is, gravimetric, nonwater matrices and gross-measurement methods). The implemented procedures are listed at the following Web site: http://wwwnwql.cr.usgs.gov/Public/ltmdl/ltmdlstatus.html. For a detailed account of the LRL reporting convention, refer to Childress and others (1999).

Methods included in the water year 2000 assessment will be continually retested. Ongoing yearly assessments are necessary to determine if method performance has changed enough to warrant a change in reporting capability. Newly calculated LT–MDLs are compared to existing LTMDLs to determine if they are statistically different from one another. Generally, most LRLs should remain unchanged from year to year.

This water year, 147 methods will be assessed and will include the 80 previously assessed methods plus any remaining high- and medium-use methods. Key additions for water year 2000 are cyanide, silver, many filtered inductively coupled plasma (ICP) constituents, many unfiltered ICP mass spectrometer methods, most nitrogen and phosphorous (nutrients) methods, organic herbicides (schedule 0079), and pesticides (schedules 1398 and 2001).

All methods are now being assessed with a few noted exceptions that include the following: wrong spike concentration, backlog of results, poor recovery, insufficient digits for statistical assessment, nonwater methods (sediment or tissue), radiochemical methods, gross- and physical measurement methods (weighing, color comparison, field-preferred measurements), and discontinued or replaced methods.

For questions regarding the LRL reporting convention, or the LT–MDL assessment process, contact any of the following people: Bill Foreman, Methods Research and Development, (303) 236-3942; Brooke Connor, Quality Assurance Unit, (303) 236-3280; and Tom Maloney, Quality Management Program, (303) 236-3460.

Reference

Childress, C.J.O., Foreman, W.T., Connor, B.F., and Maloney, T.J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Open-File Report 99-193, 19 p.

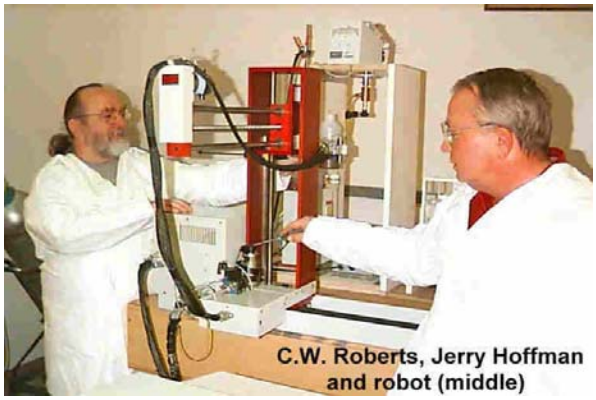
***** The 12-month period ending September 30 each year is called the "water year." The water year is designated by the calendar year in which it ends. Thus the year that ended September 30, 1999, is called "the 1999 water year."

Brooke Connor

MARLAP manual placed on Web

The Multi-Agency Radiological Laboratory Protocols (MARLAP) manual will be available for agency review by mid-January, 2000. The manual will include, but not be limited to, project planning, determination of data-quality objectives and measurement-quality objectives, method evaluation, instrumentation, statistics, quality assurance/quality control, and data verification and validation.

The manual can be accessed through the Department of Energy National Analytical Management Program (NAMP) Web site at http://www.em.doe.gov/namp. For further information or to receive a password to download the document and make comments, contact Ann Mullin (ahmullin@usgs.gov).



C.W. Roberts, Jerry Hoffman and robot (middle)

STAFFERS RETIRE - Gerald L. (Jerry) Hoffman (right), research chemist, and C.W. Roberts, physical science technician, are shown in the robotics lab last year prior to their retirement in September. Both worked for the Methods Research and Development Program. Hoffman, a project chief, specialized in surface-water chemistry, trace metal contamination control, ultratrace metal analysis techniques, automation by using robotics, and tissue analysis. Roberts worked in robotics and sample preparations.

Treseder detailed to Central Region

Debi Treseder, NWQL administrative officer, started a 120-day detail December 6 as the Central Region administrative officer for the Water Resources Division. Treseder's temporary office is in building 53 at the Denver Federal Center. In her absence, Merilee Bennett is serving as acting administrative officer for the Laboratory. Bennett can be contacted at 303-236-3531 or via Geomail (mbennett).

New publications by Laboratory authors

Garbarino, J.R., 1999, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of dissolved arsenic, boron, lithium, selenium, strontium, thallium, and vanadium using inductively coupled plasma–mass spectrometry: U.S. Geological Survey Open-File Report 99-093, 31 p.

The following seven papers were published in Morganwalp, D.W., and Buxton, H.T., eds., 1999, U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8–12, 1999: U.S. Geological Survey Water-Resources Investigations Report 99-4018B, volume 2 of 3—Contamination of hydrologic systems and related ecosystems, 482 p.

Occurrence of sulfonylurea, sulfonamide, imidazolinone, and other herbicides in midwestern rivers, reservoirs, and ground water, 1998, by Battaglin, W.A., **Furlong, E.T., Burkhardt, M.R.,** and Peter, C.J.: p. 215–225.

Wastewater analysis by gas chromatography/mass spectrometry, by Brown, G.K., **Zaugg, S.D.,** and Barber, L.B.: p. 431–435.

Occurrence of pesticides in rain and air in urban and agricultural areas of Mississippi, April–September 1995, by Coupe, R.H., Manning, M.A., **Foreman, W.T.,** Goolsby, D.A., and Majewski, M.S.: p. 301–312.

Pesticides in the atmosphere of the Mississippi River Valley, Part II—Air, by **Foreman, W.T.,** Majewski, M.S., Goolsby, D.A., **Wiebe, F.W.,** and Coupe, R.H.: p. 263–274.

Routine determination of sulfonylurea, imidazolinone, and sulfonamide herbicides at nanogram-per-liter concentrations by solid-phase extraction and liquid chromatography/mass spectrometry, by **Furlong, E.T.,** Burkhardt, M.R., Gates, P.M., Werner, S.L., and Battaglin, W.A.: p. 275–288.

Halogenated organic compounds in endocrine-disrupted male carp from Las Vegas Wash and Lake Mead, Nevada, by **Leiker, T.J.,** Bevans, H.E., and Goodbred, S.L.: p. 415–421.

Pesticides in the atmosphere of the Mississippi River Valley, Part I—Rain, by Majewski, M.S., **Foreman, W.T.,** and Goolsby, D.A.: p. 255–261

Determining significance from noise

The Office of Water Quality and the National Water Quality Laboratory (NWQL) are developing a policy for reporting analytical results with an appropriate number of significant digits. In the past, data users have noticed that variability is missing in the result for data analysis, particularly for results near the reporting limit.

The missing variability often contributes misleading statistical significance when testing a hypothesis. Providing too few digits for data often gives graphs a grainy or "quantized" appearance, with data lining up in discrete rows, as in figure 1. However, by providing an "appropriate" number of digits, we can remove the graininess, reveal relations, and increase power in the hypothesis testing, as in figure 2.

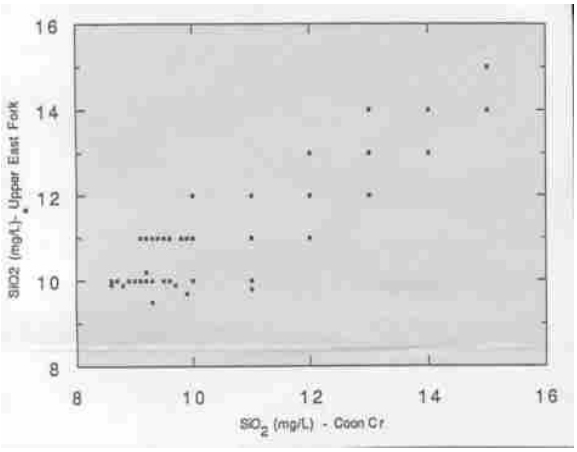


figure 1

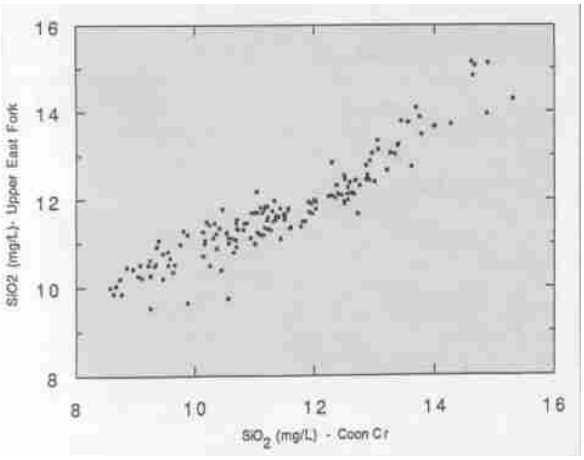


figure 2

The Office of Water Quality is developing a policy for reporting results with enough digits so as not to lose the method precision. The policy is based on the standard textbook notion that significant figures can be determined from precision information. The procedure we will use is based on an ASTM standard (American Society for Testing and Materials, 1999).

For example, 23.45214 could be unprocessed data from a chemical analysis. Because this number is a calculated result from an instrument response modified by a calibration, the calculation does not recognize which digits are significant and which are not. But if a standard deviation of 0.076 is provided, then 23.45 should be the digits reported in the final result. In practice, it is usual to say 2, 3, and 4 are certain digits and 5 is the first uncertain digit, based on the standard deviation. All are considered significant figures. For simplicity, we call the 5 in this example the least significant digit (LSD) in the series. The LSD is always the rightmost digit in a result.

When it comes to applying this practice, the real significance will always vary based on the decadal position of the LSD. To understand this problem, consider the results 89.1 and 12.1. Both show three significant figures, yet there is more implied precision in the 89.1 than in the 12.1, based on the ratio of the LSD to the result. There is a ratio of 0.1/89.1 or 0.11 percent and 0.1/12.1 or 0.89 percent. The uncertainty represented by the LSD will rarely describe the exact precision in the result.

The policy of the NWQL and the Office of Water Quality is to maintain all significant digits down to the LSD and one additional digit to the right (LSD+1). By maintaining this policy, there will never be an underreporting of significance in any chemical result.

There will, however, be an error towards maintaining too many digits for the real precision of the method. This additional digit benefits data users who compile large data sets for statistical testing.

The NWQL is in the process of defining procedures for determining the precision for each method. The Laboratory is also providing the rules for determining the LSD+1 digit to round the unprocessed results to the appropriate number of significant digits for the customer.

The Laboratory data base will store the unrounded result and the correctly rounded result. The new data reporting is planned to start this month and should be completed by April 2000, with the release of the new version of the National Water Information System. For information, contact Pritt at jwpritt@mailnwql.cr.usgs.gov.

Reference

American Society for Testing and Materials, 1999, Annual book of ASTM standards, Section 14, General methods and instrumentation (E 29, Standard practice for using significant digits in test data to determine conformance with specifications): Philadelphia, v. 14.02, p. 18.

Jeff Pritt

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