

HOW DO YOU CLEAN UP 100 YEARS OF POLLUTION?

The authors interview two environmental experts to gain a better understanding of what really happens in the field with modern XRF analysis instruments.

By **JOHN PESCE** and **JIM MARTIN**,
Thermo Fisher Scientific

In 1980, Congress responded to a growing problem of abandoned factories and other polluted sites by passing the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), commonly known as “Superfund.” Its intent was to improve the environment and assist in the cleanup of sites that were contaminated by hazardous materials. It was reauthorized by the Superfund Amendments and Reauthorization Act (SARA) in 1986. The Resource Conservation and Recovery Act (RCRA) passed in 1976, and amended in 1984, delineated the priority heavy metal pollutants and defined regulations for site remediation. (see: <http://www.epa.gov/superfund>).

The EPA’s Office of Solid Waste publishes and updates SW-846, titled Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, which is the office’s official compendium of analytical and sampling methods that have been evaluated and approved for use in complying with RCRA regulations. Among these methods is EPA Method 6200 Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment. Originally published in 1998 and updated in 2007, this method standardized the use of field-portable x-ray fluorescence (FPXRF) technology.

Challenges of site screening

Sites can vary from less than an acre to hundreds or thousands of acres. Terrain can be flat, hilly, riverbeds, barren areas, in a remote area or an urban setting. Using FPXRF analyzers to delineate site contamination has become an invaluable tool. Modern instruments like Thermo Niton's helium-purged XRF units can read lighter elements such as sulfur.

To better understand how these instruments are used in the field, the authors interviewed two environmental experts, **Karl Ford** and **Dick Glanzman**. Ford is a remediation advisor/toxicologist for the Division of Resource Services, National Operations Center, Bureau of Land Management. Glanzman is an independent environmental consultant with more than 30 years of environmental experience.

What follows is a transcript of that interview.

AUTHORS: Can you tell me about your use of XRF for environmental analysis and your experiences?



Contaminated areas termed "slickens" found on the site and adjacent to Clark Fork River, as Evidenced by lack of vegetation



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An aerial view of the site project area. Portable sampling with an XRF can provide a much larger sample base and save a lot of money on large areas.

GLANZMAN: Some projects involved large sites with hundreds of acres of land to be investigated. The larger sites were former mine sites and ore processing facilities.

One of the larger mine-waste cleanups in the country is in what is known as the Clark Fork River Basin Superfund Complex in Montana, which includes the Butte porphyry copper pit. The river is about 120 miles long and includes the Milltown Dam. The sediments accumulated behind the dam are composed of tailings transported from mines as far away as Butte due to flooding. One part of the cleanup effort involves the sediment containing heavy metals captured behind this dam. XRF analysis was used to survey multiple sites and delineate where mine wastes were contained in the soil and river sediments. GPS was used in conjunction with the XRF data to create a comprehensive database.

Another site is in the Coeur d'Alene River watershed in Idaho, an area contain-

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ing the town of Kellogg. This location was known as the “Silver Valley” because of the large silver, zinc and lead deposits mined there.

The Bunker Hill Superfund site encompasses approximately 21 square miles in the Silver Valley of northern Idaho and includes a 365-acre abandoned lead/zinc mining and smelting industrial complex as well as numerous confined and unconfined waste deposits. FPXRF was used extensively to map sites and identify mine waste piles and tailings for lead, zinc, arsenic and other chemicals of concern, also called COCs.

FORD: One project involved the Saginaw and Palo Verde mine sites in Arizona. Saginaw Hill is located on a 540-acre parcel of BLM [Bureau of Land Management] land, which the local county was interested in acquiring as recreation land. Sulfide mining and smelting occurred at the sites from the late 1800s through the mid-1900s.

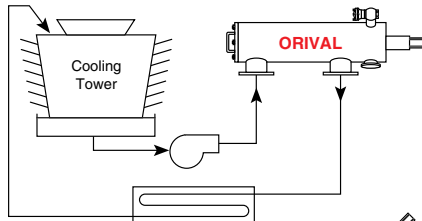


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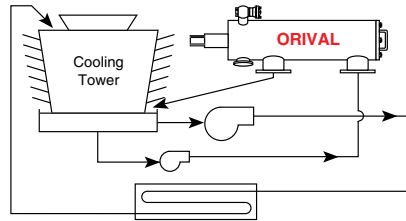
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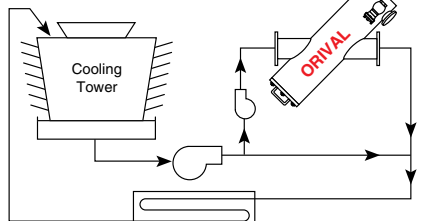
Typical **Full Flow** filtration using existing pump.



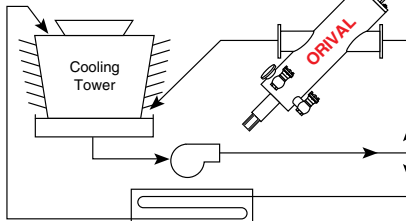
Typical **Side Stream** filtration of basin using a recirculating pump.



Typical **Side Stream** filtration using a booster pump.



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Aerial view of dam and power house before removal

We performed an assessment, using contractors, to determine the extent of elevated metal levels in soils and sediment. This confirmed the expectation that elevated metal levels in surface soils were present. Other testing indicated elevated levels of arsenic- and lead-contaminating ground water. We not only found elevated levels of arsenic and lead, which are primary COCs, but also copper, antimony, mercury, and thallium, which are secondary COCs. The levels were from one to 100 times the site's health risk management criteria.

Another BLM project was in Utah, about 40 miles south of Salt Lake City, called the Manning Canyon Mill Site. This is an abandoned gold milling facility that was active from the 1800s until 1937. The site covers approximately 1,470 acres or 2.30 square miles. There are six defined tailings areas covering about 66 acres. The tailings piles were sampled extensively on the surface and soil borings were used to characterize the metals concentrations



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Topography Affects Contamination

According to a recent *New York Times* article: "Since the 1860s, when mining began, mineral- and arsenic-laden waste from the Butte mines 120 miles south, atop the Continental Divide, has flowed into the headwaters of the Clark Fork. (The waste comes from naturally occurring arsenic in the ore minerals that have been mined in the area over the years.)

Flooding, especially a ferocious incident months after the dam was completed in 1908, sent tons of arsenic, copper and other heavy metals into the river.

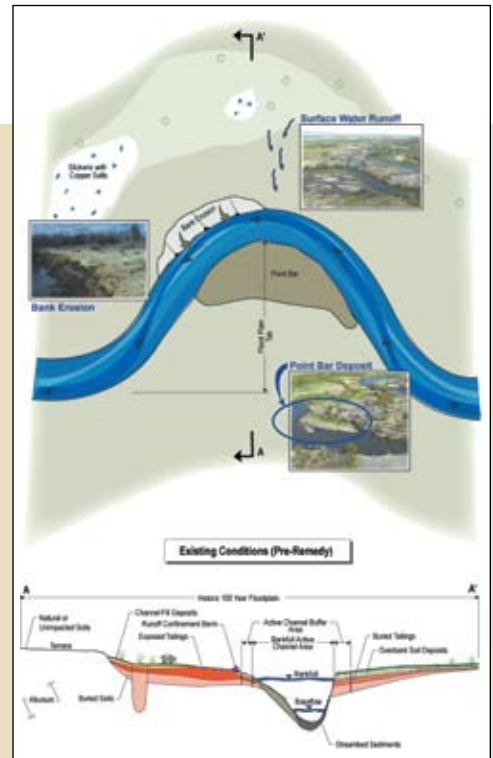
The last stop for most of the waste, though, was at this dam. Six million cubic yards of mine waste gathered behind it and backed up on the flood plain.

In 1981, officials discovered that water backed up behind the dam had forced the arsenic into nearby groundwater and contaminated wells in the settlement of Milltown, home to several dozen residents. The area was listed as a federal Superfund site in 1983.

Although the sediment has very low levels of arsenic, the arsenic has leached into the groundwater over decades. Since last October, workers have been loading waste on a 45-car train, hauling it 90 miles up river each day to a small town called Opportunity and dumping it into an existing waste site."

Jim Robbins, *Montana Dam Is Breached, Slowly, to Restore a Superfund Site*, *The New York Times*, May 27, 2008.

http://www.nytimes.com/2008/05/27/science/27dam.html?pagewanted=1&_r=2&sq=Milltown%20Dam&st=nyt&scp=1&adxnlnx=1213729892-Ryej5lXs14pcU3FV0mlmIQ



Aerial view of Clark Fork river showing contaminated slickens with artist rendition of the river showing pollution from bank erosion and runoff.

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and depth of the tailings. Arsenic averaged 7,107 ppm in *Tailings Area 1*; 4,866 ppm in *Tailings Area 2*, 7, 436 ppm in *Tailings Area 3*, 5, 580 ppm in *Tailings Area 5*; and 3,601 ppm in *Tailings Area 6*. We also found lead and mercury, which are CERCLA hazardous substances, but they did not exceed the risk management criteria for the site.

AUTHORS: Can you describe some of your practices in field work using XRF?

GLANZMAN: After doing a reconnaissance of the site, we typically gather soil samples to look at likely areas of contaminants. Our goal is to do the site survey as fast and as completely as possible, consistent with the requirements. We may fly over an area to gather remote sensing data covering the site. Remote sensing processing produces a map of surface mineralogy that is then used to guide work to site locations containing mine wastes that are leaching metals and metalloids into the stream and river. A ground FPXRF survey is used to document these locations and gather representative confirmation samples for laboratory

“ The FPXRF allows the mapping of specific COCs and associated indicator elements across the site in one sampling event, increasing efficiency while reducing mobilization costs. ”

analysis and further testing.

The COCs we look for are generally very site-specific; copper, arsenic, lead and other elemental concentrations can differ significantly in grain size, with lead, copper and other metals commonly concentrated in fine grains.

We also have confirmatory laboratory testing performed on selected soil samples, as typically 5 percent of the total is required by EPA Method 6200. However, the lab needs to be instructed to thoroughly homogenize the samples prior to sample preparation, (which also needs to be specified) before taking a sample for digestion because fine-grains and dense sample particles tend to settle toward the bottom of the sample container during transit. These are the particles that typically contain the higher metals and metalloid concentrations and if not homogenized can result in inaccurate and biased analytical data. We also need complete digestion for comparison with the total concentrations analyzed by the FPXRF. These factors can make a huge difference in the results.

FORD: Our site-sampling experience is similar. We do a



Demolition of the power house.

reconnaissance of the site and select areas of interest. Then using a standard grid pattern, we collect samples in plastic bags. Sometimes we take a surface sample, and other times we use a hand auger or Geoprobe. Using the bags lets us identify the site location and split samples for XRF and for lab correlation testing. We typically use a No. 60 mesh sieve for XRF field testing, but we can often get better correlation using a No. 10 sieve. In my experience over the years, this gives us the results we require without further sample preparation. We follow the CERCLA or Superfund process on BLM land. We typically use EPA Method 6200 and evaluate abandoned mines, processing areas, and waste (tailings) for heavy metals and other contaminants. We can run thousands of tests depending on the size of the site.

The elements we look for vary by the nature of different sites. We routinely look for most heavy metals as primary chemicals of concern: arsenic, cadmium, copper, lead, mercury, cobalt, chromium, iron, manganese, nickel and zinc. In some areas thallium and antimony are also of interest as secondary COCs. We measure total metals by using XRF methods. For lab testing we follow standard EPA-CLP methods (SOW 787).

AUTHORS: Can you explain further how FPXRF helps the field work?

FORD: We typically use XRF data in conjunction with GPS readings to characterize a site. It is fairly easy to download the XRF results, so we put all the data into an Excel spreadsheet. The new field-portable XRF x-ray tube has higher intensity x-rays, which help eliminate some interference issues we had with lead and arsenic in earlier units. Also, the extension pole accessory with its tripod adapter lets us test in-situ and walk away to perform other tasks.

GLANZMAN: The current FPXRF instrumentation produces data acceptable to EPA standards for “data of known quality” when adhering to Method 6200 during its use on a site.

Some say using the FPXRF is “like taking a lab to the field” to reduce analytical costs. When properly used in the field, FPXRF

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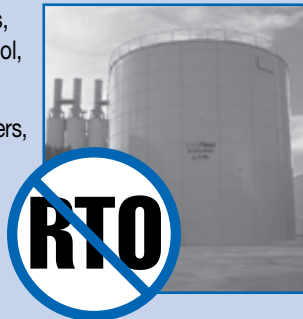


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allows the collection of samples documented as representative to be sent to the laboratory for analysis. These “samples of known importance” best characterize the nature and extent of site contamination” are sent to the laboratory for analysis and further tests. This is a new paradigm for environmental projects.

Broader sampling possible

GLANZMAN: We also use XRF to test other media, such as stained walls and foundations, residential soils, vegetation and trees. Each of these media can be analyzed for their total concentration of COCs, such as vegetation for arsenic, mercury and antimony. Using XRF, we can analyze any site media. These analyses are then used to determine what needs remediation at a particular site.

“ The FPXRF analyzer can be used to sample all the solid media: soils, stream sediments, coatings on large rocks and very coarse grained cobbles and boulders... ”

Soil samples typically have A, B and C layers. A is the organic horizon, usually fine-grain loam, but also can include peat. The B horizon is fine-grain soil. The C horizon is usually disaggregated and weathering bedrock. The COCs can have significantly different concentrations in each of these layers, which determine not only their nature and extent, but also their fate and transport.

The FPXRF analyzer can be used to sample all the solid media: soils, stream sediments, coatings on large rocks and very coarse grained cobbles and boulders within stream sediments, foundations and structures within the site boundaries, vegetation and even trees. Samples can be sieved in the field to determine what grain sizes are most important in defining the nature and extent of each COC. The instrument allows real time documentation of COC concentrations in media that are difficult to sample. In other words, properly used, the FPXRF allows essentially a full documentation of the nature and extent of COCs while at the site during the first sampling event. As with any high technology tool, staff using the FPXRF needs training to use it correctly and effectively.

New site screening methods

AUTHORS: Can you expand on that point?

GLANZMAN: The relatively new Triad approach recognizes and responds to some of the flaws in the earlier conventional approach, particularly when an FPXRF analyzer is introduced into

the sampling plan from the very beginning of the investigation at an environmental site. The FPXRF allows the mapping of specific COCs and associated indicator elements across the site in one sampling event, increasing efficiency while reducing mobilization costs. It allows a more intense sampling where the COCs are concentrated, delineating both the source(s) and the dispersion from source(s). Using EPA Method 6200 and these COC maps, truly representative samples are collected from both the delineated anthropogenic and natural background areas within the site. Since XRF is a non-destructive analytical method, the representative samples sent to the laboratory are the same samples analyzed by the FPXRF, documenting the quality of the FPXRF analytical data. Both the laboratory and the FPXRF data can then be used for the statistical methods and for risk analysis. Adding in the FPXRF data significantly increases the number of samples used in the statistical methods, so the confidence levels are higher than the significantly fewer poorly

“...the FPXRF still achieves a relatively low cost budget because most of the extensive sampling plan development occurs in the field, not in offices remote from the site.”

defined samples available using the conventional sampling method.

Teams make a difference

GLANZMAN: The new paradigm can now include some senior staff with a group of more junior people that can do a reconnaissance with an XRF analyzer and then develop a sampling plan with known objec-

tives. This is in contrast to taking only a few samples, then using costly laboratory tests to get very accurate readings. Under conventional sampling plans, this is followed by multiple rounds of looking at the site and more lab testing could be avoided with the new approach by carefully sampling in-situ with XRF tests and selecting the bagged soil samples for lab testing. The junior staff uses the FPXRF to analyze, collect and bag samples on a grid pattern, noting locations frequently augmented by GPS.

For statistical significance, you need many samples to achieve appropriately high confidence levels needed for risk assessment. For this, you need data of known quality to add to the lab results and the FPXRF still achieves a relatively low cost budget because most of the extensive sampling plan development occurs in the field, not in offices remote from the site. This is where XRF field tests let you fill in with data of known quality.

Summary and conclusions

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“Sampling can be adjusted to more accurately determine the site-specific nature and extent issues”

using the FPXRF is that senior professionals who will be interpreting the data can be interpreting the data in the field where changes and additions to the sampling grids can be added to answer questions about the nature and extent of distribution of COCs at the site. These changes can be made in real time to answer nature and extent questions as they arise, rather than weeks to months after receiving the validated laboratory analytical results under the conventional sampling process. Junior staff receives real-time training and mentoring by senior professionals when and where site characteristics are being determined. Sampling can be adjusted to more accurately determine the site-specific nature and extent issues and the collection of truly representative samples are clearly documented. **PE**

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Acknowledgements: Photographs and illustrations of the Clark Fork River CERCLA site were provided by Diana Hammer & Kristine Knutson of EPA Region 8 Office in Helena, Mont., and Dennis Smith of CH2M Hill. Jim Martin of Armada Consulting Group contributed materials to the article. Geoprobe is a registered trademark of Geoprobe Systems.