AN OVERVIEW of Forensic Hydrology

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The term *forensic*, as applied to subdisciplines within the geosciences, first appeared during the late 1970s. At that time, concerns about contamination of soil and groundwater resources were coming to the forefront, and those of us working in this emerging arena coined terms such as *forensic geochemistry* and *forensic geology* to describe the use of geochemical or geological techniques to identify potential sources of contamination. By the 1990s, with concerns abounding about the impact of anthropogenic activities on the environment, a new, all-encompassing discipline appeared: *environmental forensics*. Today, environmental investigations of a forensic nature, including *forensic hydrology*, fall under the broad umbrella of environmental forensics.

Despite the terminology, the nature of any geoscience is forensic. Geoscientists were "geodetectives" long before the advent of environmental forensics; the Earth provides clues that we must decipher in order to tell its story. Whether we are interested in earth history 4.5 billion years ago, 450 million years ago, or environmental contamination that occurred 4.5 years ago, our approach has always been predicated on forensic earth sciences.

Tools for Forensic Hydrology

A variety of approaches can be used to trace groundwater and dissolved contaminants. Here, the more common methods are discussed in the context of contaminants of concern and issues encountered in hydrology.

Examining flowpaths: Forensic hydrologic investigations commence with flowpaths, both current and historic, and flow velocity. Contaminant migration on the surface or in the subsurface is a function of aqueous flow, particularly if the contaminant has a moderate level of solubility in aqueous media.

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In cases where surface hydrology may have controlled contaminant migration, examination of historic aerial photographs can provide significant insight into the migration and distribution of contaminants at the site. For example, imagine a site where contamination is identified in soil but located transverse to and isolated from the current surface water flow. Historic aerial photographs of the region could indicate the presence of flowpaths that were once present but subsequently destroyed, such as by development and grading. If, on the other hand, photography shows no such history, other offsite sources of the contamination may have to be considered and evaluated.

Once contaminants pass through the vadose zone and enter groundwater, the flow rate and direction of groundwater flow become critical to forensic investigations. Modeling subsurface flow sometimes can lead to estimates of when the contaminant was released, and if or when the contaminant could impact potable groundwater resources. Groundwater modeling is clearly one of, if not *the* most, important facets in forensic hydrology.

Geochemical analysis: General cation and anion analyses of groundwater are another means to evaluate genetic relationships among groundwaters. In addition to assessing changes in groundwater chemistry along flowpaths using Piper and Stiff diagrams, the results can provide information on hydrologic continuity, allowing forensic hydrologists to predict where contamination may migrate should an aquifer be impacted.

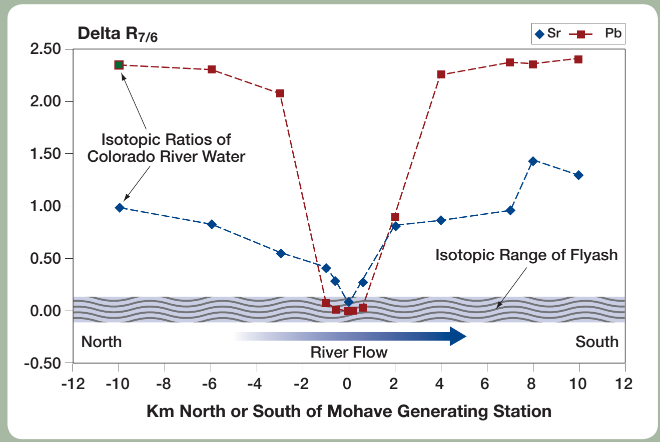
Examining stable isotopes of hydrogen and oxygen: Hydrogen and oxygen isotope analyses are both used routinely to discriminate among groundwater sources; similar isotopic ratios indicate genetically related groundwater (see page 18). Observed changes or trends in hydrogen/oxygen isotopic ratios provide information on water-rock interactions as well as evaporation. Tritium (^3H), a radioactive isotope of hydrogen, is an important tool for dating groundwater either in a semi-quantitative fashion using tritium units or via radiometric dating by measuring the abundances of tritium relative to its decay product, helium-3.

Example: The Case of the Flyash

A study of the Mohave Generating Station, a 1,580-megawatt coal-fired power plant located in Laughlin, Nevada, aimed to determine if heavy metals present in flyash generated by coal combustion were being transported to local surface waters and water in embayments along the Colorado River.

Isotopes of strontium and lead were used in the study because: 1) abundances of these elements in flyash far exceed those of local background soils and groundwater; and 2) the strontium and lead isotope ratios ($^{87}Sr/^{86}Sr$ and $^{206}Pb/^{207}Pb$) of flyash differed significantly from those of Colorado River water. Results are shown at right.

The data showed that within about 1 km of the Mohave Generating Station, surface waters were severely impacted by metals leached from flyash. The impact decreased with distance, such that lead isotope ratios return to those of pristine Colorado River water at distances about 4 km from the facility, while strontium isotope ratios exhibited impacts to about 6 to 8 km away. The Mohave Generating Station ceased operation in 2005.



Strontium (Sr) and lead (Pb) isotopic ratios measured in samples relative to those of flyash (Delta $R_{7/6}$ notation) shown with distance from the generating station. The magnitude of the differences are shown as percentages for lead and per mil (thousand) for strontium isotopic ratios.

Fingerprinting Techniques

Element/element ratios, stable isotopes, and organic/inorganic geochemistry can be used to trace specific contaminants of concern (CoCs). The discussion below focuses on isotopes, each of which may be integrated with appropriate element/element ratios or organic/inorganic analyses.

Hydrocarbons: Evaluating sources of hydrocarbons in soil and groundwater can involve many fingerprinting techniques (see page 26). PIANO (paraffins, isoparaffins, aromatics, napthenes, olefins), light stable isotopes (carbon, hydrogen, oxygen, nitrogen, sulfur), and lead isotope analyses of hydrocarbons can be used to assess genetic relationships among fugitive releases. Light stable isotopes and organic compound ratios can also be used to monitor degradation. And lead isotope ratios have been effective in estimating the year of leaded gasoline releases.

Sewage, industrial, and agricultural leachate: Nitrates, perchlorates, saline waters, and metals are prime CoCs for groundwater resources exposed to sewage or to industrial or agricultural waste streams. Given the present-day proximity of urban environments to agricultural resources in some areas, the CoCs can be quite diverse, as are the forensic techniques to assess impacts to such resources.

When dealing with nitrate or perchlorate contamination, light stable isotopes of nitrogen and chlorine, respectively, have been integrated with oxygen isotopes to evaluate contaminant sources as well as degradation pathways (see page 22). Heavier isotopes, such as those of strontium, can also help to discriminate among sources of nitrate and perchlorate. Likewise, saline waters associated with seawater intrusion, oilfield brines, and agricultural runoff often can be traced using hydrogen/oxygen, chlorine, or strontium isotopes.

Heavy metal contamination is primarily related to industrial activities and mining. Lead is undoubtedly the most notorious heavy metal, but contamination associated with chromium VI, mercury, and arsenic is becoming more prevalent. With the exception of arsenic, tracing these metals has relied upon utilizing isotopes of each specific CoC. Lead isotopes have played an important role in assessing sources of both arsenic and lead (see box above).

Choose the Right Mix

To say that the issues within forensic hydrology are diverse is an understatement. As urbanization encroaches upon rural areas, groundwater resources may be impacted by contaminants derived from a multitude of sources. As a result, the forensic hydrologist must now employ a wide variety of techniques, some of which have been discussed here. Our ability to protect and preserve groundwater resources lies in our ability to choose the right combination of forensic techniques that can be integrated with a sound sampling strategy, are economically feasible, and can expedite the solution to the problem at hand. The articles presented in this issue provide several examples of studies that do just that.

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