#### ON THE GROUND

## Deep Groundwater Exploration Using Geophysics

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The current and continuing drought in many parts of the world, combined with everincreasing demands from both traditional and new water users, including municipal, industrial, agricultural and environmental needs, has impacted groundwater resources. Consequently, many groundwater exploration programs are increasingly focusing on deep (1,500 to 2,500 feet below ground surface) production zones. The financial investment in a new 2,500-foot deep groundwater production well can often approach \$1 million. Surface geophysical methods can reduce risk and unnecessary costs by assisting in the siting of wells in locations with the most potential to produce acceptable quantities of water.

Surface geophysical methods have been used for decades to successfully and economically explore for groundwater resources. For depths on the order of 200 feet or less, the electrical resistivity profiling and seismic refraction methods are generally useful and economic. For investigations to depths of about 500 feet, the time domain electromagnetic (TDEM) method has been successfully used; however, at greater depths TDEM becomes logistically difficult and less economic. For reconnaissance or regional basin-wide surveys, the gravity and/or magnetic methods have often been applied, but it is risky to select groundwater targets from those methods alone. For exploration depths of 1,500 to 2,500 feet, the seismic reflection and



controlled source audio magnetotellurics / magnetotellurics (CSAMT/MT) methods have proven to be successful. However, using high-resolution seismic at those depths is very expensive, and it is often difficult to interpret small faults or fractures zones within bedrock (typical groundwater targets) or to distinguish subtle changes in stratigraphy, such as the amount of clay. Therefore, in recent years, the CSAMT/MT method has become more widely used as it produces economic, structural, and stratigraphic detail to depths approaching 3,000 feet.

CSAMT/MT is a hybrid method that determines subsurface electrical resistivity distribution by measuring time-dependent variations of the earth's natural electric and magnetic fields (MT), as well as the electric and magnetic fields resulting from highfrequency, non-polarized, artificially transmitted electromagnetic waves (CSAMT). The method measures the resistivity of earth



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materials in two directions with perpendicular electric dipoles (Ex and Ey) and magnetometers (Hx and Hy) in the field setup shown above. In general, electric and magnetic fields are measured both parallel and perpendicular to geologic strike, thus giving CSAMT/MT a two-dimensional capability that is not achieved by other electrical or electromagnetic methods.

CSAMT/MT field data consist of sounding curves that are logarithmic plots of apparent resistivity versus frequency. Subsurface resistivities can be calculated with forward and inverse computer modeling software by converting the sounding curve data to computer modeled resistivity structure or layering below a given CSAMT/MT sounding. The resulting computer models are used for interpretation of subsurface materials and geologic structures related to groundwater flow, and can be presented as cross sections consisting of several soundings. From these cross sections, data can be presented as individual contour maps from selected depths or combined into a movie showing several depths or other slices. In general, CSAMT/MT data have shown a 10 to 15 percent variation between the actual depths to the anomalies, as verified by test hole drilling, and the depth predicted by the models. The nearby presence of conductors, such as buried metal pipes or drill stem, metal fences or electrical transmission lines, will result in electromagnetic noise that may affect the quality of the data.

The true resistivity of earth material is dependent upon composition, grain size, water content, and other physical characteristics. In general, fine-grained materials have lower resistivities than coarsegrained materials. Unweathered and unfractured hard rocks such as lithified sedimentary rocks, volcanic rocks, plutonic rocks, and some metamorphic rocks generally have high resistivities. The presence of fracturing and weathering lowers the resistivity of these rocks. Additionally, the occurrence of groundwater will greatly reduce the resistivity of all rocks and sedimentary materials through electrolytic conduction. Because of this effect, groundwater is a good target for electrical and electromagnetic geophysical methods that measure resistivity.

The CSAMT/MT method has been used to identify groundwater exploration targets and to site wells in a variety of geologic conditions. A water-filled fracture example is shown in the figure at the top of page 6 from an area with clastics on the surface and weathered-to-unweathered carbonate bedrock at depth. Note that similar results would be obtained from an area with sediments over granitic or metamorphic bedrock. Station spacing for this example is 50 feet, which is considered a detailed survey. Calculated resistivities in ohmmeters are shown in a logarithmic range with colors ranging from red for conductive or low resistivity zones to blue for higher resistivity areas. Clastics in this area

generally have lower resistivities and are interpreted with values of less than about 500 ohm-meters (primarily the red to yellow colors on the section). Hard, relatively unweathered and unfractured carbonates are interpreted as much higher resistivities with values from around 1,000 to more than 4,000 ohm-meters (darker blue colors). Resistivity values between about 500 and 1,000 ohm-meters are interpreted as weathered zones, fractures zones, or faults within the hard carbonates. Clastics are interpreted to extend to about 200 to 400 feet depth in the example, weathered bedrock beneath the clastics is interpreted to have thicknesses on the order of 100 to perhaps 200 feet, while carbonate bedrock extends beyond 1600 feet depth. Within the high resistivity bedrock at depths ranging from about 400 to 900 feet, as identified on the figure, are low resistivity water-filled fractures that have been drilled and found to be good groundwater producers.

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# Water Rights: How Much Do They Cost in the West?

**Philip Ganderton, Ph.D.** – The University of New Mexico

The average annual prices paid for an acrefoot water right in selected states in the western United States over the period 1990 to 2001 are shown below. The data are taken from research to be published in an upcoming issue of Southwest Hydrology that will focus on water as a commodity. The research was performed by Professors David Brookshire, Bonnie Colby, Philip Ganderton and Ph.D. student, and Mary Ewers from the economics departments of The University of New Mexico and The University of Arizona. Even though conditions in water markets vary considerably across the region, and the amount of data contributing to these summary statistics varies from two trades (Wyoming) to 490 trades (Colorado), some general observations can be made. By far

the most developed water market of those represented here covers the Colorado Big Thompson (CBT) project area, and with 490 observed transactions, the trend in water rights prices is undeniably upward. Average prices in 1990 for trades in this basin were \$1,730, but they had risen to over \$11,000 per acre-foot by 2000. Other basins show prices for an acre-foot of water ranging from \$500 to \$2,500. Prices in New Mexico's Middle Rio Grande Basin have recently moved from a fairly constant \$1,000 to more than \$4,000, and many buy offers at that price go unanswered. According to the researchers, the successful development of water markets depends on many economic and institutional factors, which both encourage markets and hinder their expansion. Variations in these factors help to explain the number of trades in each state and the prices at which water rights trade. Contact Philip Ganderton at gandini@nmu.edu

#### Mean Water Right Prices (\$/acre-foot) by Year for Selected Western States

State (obs)	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001
AZ (53)	770	38		1025	960	383	550	100	663	559	950	876
CA (49)	38		290		50	1856	1000	944	1000	1011	1629	943
CO (490)	1730	2043	2083	1922	2048	2262	2676	3500	2927	4314	11286	11207
NM (28)	1000	795	1063	1513	2669		2989	2300		1984	4000	4250
NV (14)	2000	2500	2860						1951	1120	1888	2975
TX (36)	558	544	324	761	531	1331	597	640	710	150		585
UT (18)	109	2000	2264	1153	2500	802	322			1672	654	1000
WY (2)				155							75	



## Estimating Ages of Hydrocarbon Releases Using Stable Isotopes of Lead

#### **Richard W. Hurst, Ph.D.** – Hurst & Associates, Inc. and Department of Geological Sciences, California State University

Estimating the year gasoline was released into the environment has been a difficult task. Most methods, relying upon gasoline additive chronologies or presumed rates of biodegradation, do not provide adequate age resolution and the type of data needed to correlate releases to a specific hydrocarbon source.

In 1982, Ng and Patterson published results of stable lead isotope analyses (<sup>206</sup>Pb/<sup>207</sup>Pb) from leaded gasoline-impacted Southern California marine sediments that indicated <sup>206</sup>Pb/<sup>207</sup>Pb ratios of lead in gasoline increased from about 1.15 in 1965 to about 1.20 in 1978. This variation was attributed to the increased utilization of Mississippi Valley Type (MVT) lead ores in the production of tetraethyllead; MVT ores are known to have extremely high or radiogenic <sup>206</sup>Pb/<sup>207</sup>Pb ratios, ranging from about 1.3 to 1.35.

If temporal variations in gasoline lead isotope ratios could be calibrated, an improved method of age-dating gasoline releases might result (Hurst 2000, 2002). Such a method would have advantages over other gasoline age-dating models because: (1) lead does not biodegrade, so it provides a long-term record of a release in soil and groundwater; (2) its isotopes do not fractionate; and (3) lead isotope ratios can be analyzed accurately by thermal ionization mass spectrometry.

#### Development of the ALAS Model

Samples of archived leaded gasoline (with lead concentration ranging from about 30 to 1,000 parts per million) and gasolineimpacted soils were acquired and analyzed; for each sample, the year the gasoline was produced or released into soil was accurately known. More than 100 samples from the United States have been analyzed to produce a well-defined calibration curve termed the ALAS model (Anthropogenic Lead ArchaeoStratigraphy; Figure 1). As observed by Ng and Patterson (1982), the increases in gasoline <sup>206</sup>Pb/<sup>207</sup>Pb ratios as a function of time are directly related to the increased use of radiogenic MVT ores in the production of tetraethyllead by gasoline additive manufacturers, such as Ethyl Corporation and DuPont. Increases in gasoline lead isotopic ratios continued through the end of the leaded gasoline era in about 1990, as documented by <sup>206</sup>Pb/<sup>207</sup>Pb ratios measured in ALAS model calibration samples and as calculated from U.S. Bureau of Mines lead production figures (Figure 1, Hurst, 2002). Since 1992, there have been numerous applications of the ALAS model to site remediation investigations involving leaded gasoline and heavier distillates contaminated by accidental additions of tetraethyllead through common transfer lines during refining. The correlation between ALAS model ages and release ages *See Lead isotopes, page 30* 



Figure 1. Variation in <sup>206</sup>Pb/<sup>207</sup>Pb ratios and corresponding  $\delta^{206}$ Pb of the ALAS model (1923-1990). Two ALAS models are shown for comparison: one as calculated from U.S. Bureau of Mines lead production figures (1920-1990) (curve) and the other as measured using free product and soils (individual data points; only 37 of about 125 measured calibration samples can be resolved at this scale).



Figure 2. Relationship between ALAS model ages and gasoline releases with documented age at U.S. sites. In each case, ALAS model ages were determined independently, prior to review of documents identifying the known age of a release at each site.

*Lead isotopes, continued from page 9* determined from site-related documents is excellent ( $R^2 = 0.95$ ; Figure 2).

#### Case Study

Free product, gasoline, was discovered seeping into the lower level of a parking structure that resulted in three operating service stations being identified as potentially responsible parties. Lead isotopic ratios were measured on samples of free product, impacted groundwater, and dispensed gasoline from each service station for comparison. Results are plotted on a lead isotope discrimination diagram (Figure 3); samples with similar lead isotopic ratios define clusters on such plots that indicate a common source of origin.

The <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>206</sup>Pb/<sup>204</sup>Pb ratios of unleaded gasoline (for which the lead concentration ranges from about 10 to 300 parts per billion (ppb)) from each service station differ significantly from those of the free product seeping into the parking structure, indicating that none of the service stations was the source of the free product.





ALAS model ages, determined from lead isotope ratios of free product and BTEXimpacted groundwater (BTEX = benzene, toluene, ethylbenzene, xylenes) indicated older releases that dated back to 1968-1973. Documents produced during the discovery phase of the ensuing lawsuit provided evidence of gasoline releases between 1970 and 1975, prior to the construction of the parking structure. Subsequent investigations focused on mapping the heretofore unknown, early-1970s plume and identifying the site's former property owners.

#### Summary

Lead isotope ratios and the ALAS model have significantly advanced the capability to estimate the year of a leaded gasoline release into the environment. In the era of unleaded gasoline (gasoline with ppb-range concentrations of lead derived from crude oil), lead isotopes are used to correlate unleaded product releases and/or dissolved phase gasoline constituents, such as MTBE, to their source.

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