

## Amplified geochemical imaging: an enhanced view to optimize outcomes

Harry S. Anderson\* of W. L. Gore & Associates describes the benefits of amplified geochemical imaging in a variety of context including environmental and oil and gas applications.

Before surgeons begin any delicate operation, they use state-of-the-art imaging to afford an enhanced view into the human body. Without question, the accuracy and detail of a CAT scan or MRI increases their chance of a successful surgical outcome. With a resource so precious, who wouldn't use the best technology? Likewise today's earth scientists have sophisticated imaging tools available that provide them with the enhanced view they need to focus their efforts, save time and money, and generate more reserves and profits. 3D seismic imaging is the tool we often think of first in petroleum exploration but recent advances have made possible a complementary technique: amplified geochemical imaging. This advanced geoscience tool is used in diverse applications such as environmental site assessment and pipeline integrity management, as well as petroleum and mineral exploration.

Since 1930, earth scientists have used surface geochemical techniques to explore for hydrocarbons. These techniques look for the effects of minute levels of hydrocarbons that migrate through the imperfect seals that cover every reservoir and migrate either as macroseepage via faults or as microseepage vertically through the reservoir overburden. (Klusman, 1993, Coleman et al., 1977)

Some of these early techniques were crude and included soil analysis, active soil gas analysis, iodine mapping, and microbial counting. Unfortunately, exploration results using these early geochemical techniques were often disappointing.

This is a direct result of several fundamental factors:

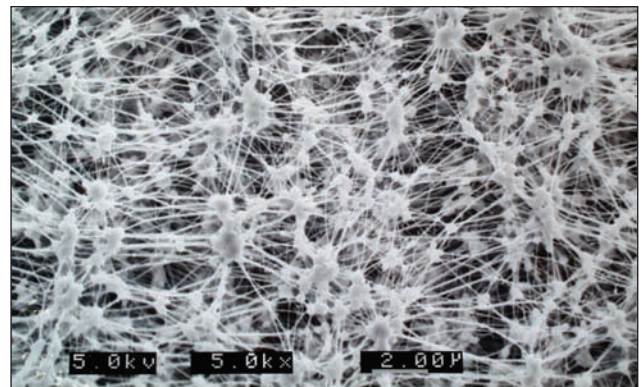
- Inability of the sampling method to cope with heterogeneous soil characteristics including permeability, moisture, and organic content
- Heavy losses in compounds due to sampling techniques (Hewitt and Lukash, 1996)
- Monitoring indirect effects (like microbes or iodine) rather than direct effects
- Poor sensitivity (ppm rather than ppb or ppt)
- Severely limited set of compounds not representative of the target (C<sub>1</sub>-C<sub>6</sub> only)
- Failure to use statistical tools to clearly differentiate noise from signal

Modern surface geochemical techniques, pioneered by Ronald W. Klusman of the Colorado School of Mines (1993) and W. L. Gore & Associates with their GORE Survey, have overcome these limitations resulting in a robust, sensitive tool for precise imaging of buried hydrocarbons and minerals whether deposited by natural earth processes or by manmade pollution.

To cope with many local and regional variations in soil character such as the amount of water saturation, and to improve sensitivity, a new passive adsorbent sampling system was developed. This passive sampler, the GORE Module, contains a specially engineered hydrophobic adsorbent encased in a microporous expanded polytetrafluoroethylene



GORE module.



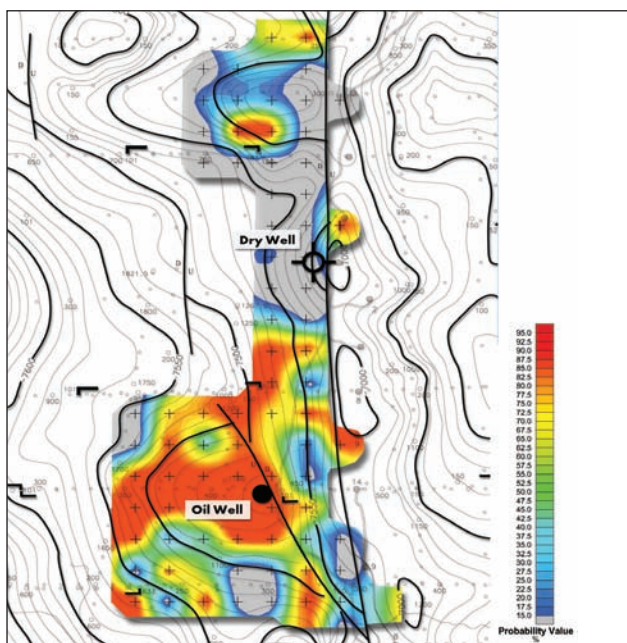
Microphotograph of ePTFE membrane showing engineered pores.

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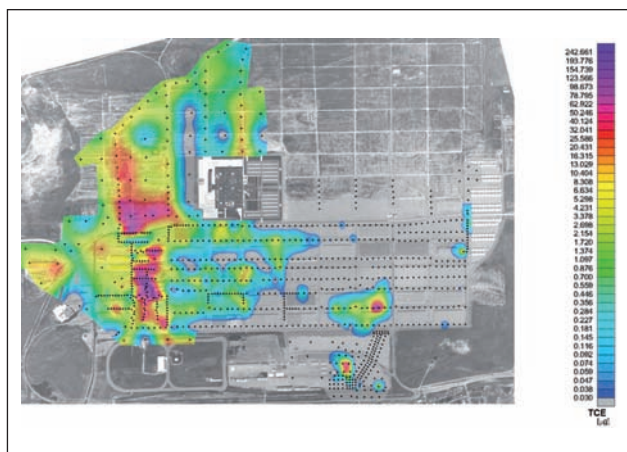
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Installation of module in soil.



Typical site map showing results of survey, colour-coded for probability of charge.



Map of TCE contamination from LaPlant, 2002.

(ePTFE) membrane. This centre dash known as GORE-TEX - has pores engineered small enough to keep soil particles and water from entering, but are about 1000 times larger than the molecules of interest. As a result, the molecules of interest are unimpeded in their path to the adsorbent. This allows the module to be placed directly in dry or saturated soils and even in water up to a depth of about 10 m. The modules are manufactured in a cleanroom to eliminate ambient contamination and include a duplicate sorbent to be used if complications arise in the analysis. These modules uptake about 3-4 litres/hr in free air and, by placing them in the soil for weeks or months, they collect an integrated chemical signal. This boosts the mass collected by two to three orders of magnitude over an active sample and smoothes temporal variations due to barometric pressure, rainfall, and temperature variations.

When combined with a very sensitive state-of-the-art analytical method incorporating thermal desorption, gas chromatography, and mass spectroscopy, nanogram (10E-9 gram) levels of compounds can be detected relating to concentrations as low as 1 ppt. This high sensitivity allows detection in any soil type including saturated clays and sands, cemented rock, or even through thousands of feet of evaporates or volcanic rock. Over 150 volatile compounds can be measured as needed for the application. These can be volatile gases like ethane, volatile liquids like benzene or low volatility liquids, and solids like pyrene, TNT, or sulfur as long as their vapour pressure is above 2E-6 mm Hg. In very moist environments it is also desirable for the compounds to have Henry's Law constants >10E-7 atm/ cu m/mole. A few compounds of environmental interest, such as pentachlorophenol, 135TNB, VX, and RDX, fall outside this range. Molecules smaller than ethane are not adequately retained by the adsorbent, but natural gas with >99% methane can still be mapped by looking for the higher MW alkanes always associated with this gas.

Installation is easy and inexpensive using simple hand tools in soil or hand drills in concrete, rock, or permafrost. A 15mm diameter hole is placed 60-100 cm into the surface and after attaching a retrieval string, the module is inserted into the hole. The hole is then sealed with a cork or simply caved in to isolate it from the atmosphere. Exposure time depends on the application and can vary from 15 minutes in water to two months in rock over buried ore deposits. Typical soil exposure time is 10-17 days.

The final technical advancement necessary for amplified geochemical imaging is interpretation of the data using multivariate statistical tools. After removing compounds which don't pass signal/noise, statistical tools including principle components analysis (PCA), discriminant analysis (DA), and hierarchical cluster analysis (HCA) are used. These identify the chemical fingerprint of interest and the model factors to generate interpretations. Finally the data are mapped using

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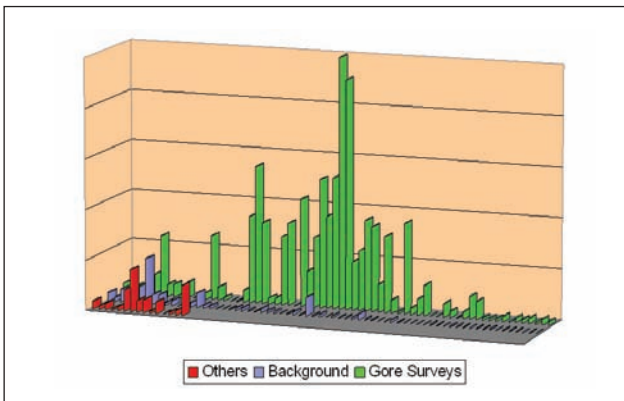


Chart of background versus oil-indicative distribution.

industry standard geographical mapping tools and reported in one of several formats tailored to the client.

Compared to traditional surface geochemical techniques, amplified geochemical imaging incorporates the combined advantages of improved sampler design, higher sensitivity, robust data set, and multivariate statistical interpretation. This technique has proven its value for over a decade in a number of applications including environmental pollution mapping, pipeline leak assessment, petroleum exploration, and mineral exploration.

### Environmental site assessment

The most difficult part of any environmental programme for characterizing and remediating pollution in the soil or groundwater is obtaining an accurate site assessment and map of the plume. Because many polluted sites have supported multiple industries over the years, unknown sources often exist which will complicate monitoring and remediation. In one case, the use of amplified geochemical imaging found an unknown TCE separator at a military site that, once identified, reduced the remediation time using soil vapour extraction by dozens of years and reduced costs by several million dollars (LaPlant, 2002). This tool has been used successfully

on industrial sites, airports, gas stations, dry cleaners, landfills, pipelines and terminals, and manufactured gas plants.

Amplified geochemical imaging using a passive soil-gas survey will not only accurately map intensity of pollution but will also screen for indicators of natural attenuation pointing toward potential low-cost remediation solutions. This accurate map can in turn focus subsequent soil and water matrix sampling, monitoring well placement, layout, and design of remediation chemical injection, and monitoring and verification of site clean-up. In all cases using this tool to generate a an enhanced view saves costs in the overall programme. A series of analytical techniques including thermal desorption, gas chromatography, and mass spectroscopy generate a quantitative measurement of most volatile compounds including chlorinated solvents, fuels, polyaromatic hydrocarbons, pesticides, water soluble compounds, explosive and chemical warfare agent breakdown products, and even mercury. Another use of this imaging tool is to document site status for property transfers to limit future seller liability for clean-up costs related to new spills.

More recently, the compound specific sampling rates of GORE Modules are being characterized in both air and water allowing direct measurement of concentration. This allows their use in applications such as long term monitoring as well as vapour intrusion and human health risk assessment. Detection limits in air are typically about 1 ppb, but can be extended to ppt if necessary. Such sensitivity suggests possible application in monitoring sentinel wells and drinking water quality.

When placed in water, the unique hydrophobic ePTFE membrane of this sampler allows volatile compounds, dissolved in water, to partition from the water into the airspace inside according to Henry's Law, and be captured by the hydrophobic adsorbent. It is essentially an in-situ purge and trap without all the lab work-up. This process is very fast allowing water exposure times of minutes for most applications to a few hours for low concentrations and measurement of a wide variety of compounds including VOC's, SVOC's, and water soluble compounds. Because it is a very



Deployment of survey offshore.

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simple passive approach, long-term well monitoring costs are slashed by dramatically reduced fieldwork costs, reduced sample handling, and eliminating costs to process purge water or to ship on ice.

### Pipeline integrity management

Throughout the world, nations are requiring routine monitoring of buried gas and hydrocarbon pipelines to avoid explosion and environmental risks. Leak monitoring frequency is often proportional to the level of public risk. Taking lines out of service for this inspection is very costly and may not always pinpoint small leaks. The sensitivity of modern passive geochemical surveys combined with a multivariate statistical analysis allows one to identify even very small leaks both odourized and non-odourized in liquid and gas lines. This technique is particularly economical and beneficial for short run, small diameter pipelines with many bends. If leaks are located, it also will focus subsequent remediation activities.

### Oil and gas exploration

Seismic imaging is a powerful tool that has helped increase success in petroleum exploration. However seismic does have some limitations including its inability to image thin or obscured deep reservoirs, difficulty seeing through volcanic layers or thick salt sequences, difficulty imaging steeply dipping strata, high cost per unit area, and general inability to determine reservoir charge. The current worldwide restricted supply of acquisition capacity makes alternative non-seismic tools of greater interest and importance. Using amplified geochemical imaging where seismic is ineffective, or combining seismic with this technique can dramatically increase exploration productivity. Hydrocarbon charge in reservoirs as deep as 7500 m, and as shallow as 300 m, have been confirmed using amplified geochemical imaging even through thousands of feet of volcanic deposits or evaporites.

With petroleum exploration, it is critical to look for nanogram quantities ( $10^{-9}$  gram) of about 80 hydrocarbons and sulfur compounds ranging from ethane ( $C_2$ ), to Phytane, ( $C_{20}$ ). This range, broader than all other geochemical techniques, combined with its very high sensitivity allows chemical fingerprinting of near surface microseepage of petrochemicals ranging from dry gas to moderate/heavy oil (Viforeanu). Plotting of pristane/phytane ratios,  $C_{17}$ /phytane ratios, and alkane/alkene ratios can also provide insight to the reservoir character and petroleum phase. Amplified geochemical imaging has been used in over 130 basins in more than 50 countries in all terrains including desert, jungle, plains, tundra, and offshore. Applications include frontier exploration, prospect evaluation, in-field development, and looking for by-passed pay.

#### Frontier

The use of amplified geochemical imaging in frontier applications allows evaluation of very large blocks (8000-plus  $km^2$ )

in a relatively short time for costs as low as \$350/ $km^2$ , or less than 10% of 3D seismic costs. In this application, it is used to validate the petroleum system, make decisions on areas of the block to keep or drop, evaluate leads, and to focus a seismic programme to areas of identified charge. In focusing a seismic programme it could lower total finding costs as much as 40%.

#### Prospect evaluation

Amplified geochemical imaging can be used to validate and map charge, making it useful in setting drilling priorities. Where relatively fresh productive or dry wells are available in the basin, it is preferable to place 10-15 samplers around them to collect a chemical fingerprint to be used as models for the statistical analysis. This improves the accuracy of prediction especially in more complicated settings with multiple sources. The phase type can be differentiated between dry gas, condensate and oil and, with adequate modelling, differentiate oils with substantially different composition or specific gravity. With hundreds of wells drilled, amplified geochemical imaging is 95% accurate in predicting dry holes (Potter et al., 1996). When combined with other G&G, routine users claim it doubles their overall success rate. This technique generally can't determine the thickness of a reservoir or its permeability and hence can't determine economic attractiveness of a prospect. But, it is about 90% accurate in defining some level of charge, which can substantially raise POS calculations and reduce risk.

When used extensively in a given basin with many wells, such as the Woodbine Trend of Polk County, Texas, the Anadarko basin in Oklahoma, USA, and the San Jorge basin in Argentina, it has been shown to correlate to initial production rates or the product of reservoir thickness and permeability, helping to determine prospect economics. With proper sample spacing amplified geochemical imaging can often locate offset faults or fracture swarms, so critical in unconventional gas plays or compartmentalized reservoirs. Amplified geochemical imaging has also been used by explorers to choose the better seismic depth conversion methodology: bottom up, direct, or top down (Lee, et al., 2005).

#### Field development

As older fields come on the market, building reserves by finding by-passed pay is on the increase. Defining charged channel sands, difficult to find by seismic alone, is an easy task for amplified geochemical imaging. This is a major untapped opportunity for start-up companies who need early cash flow.

#### Offshore

The unique design of Gore's geochemical module allows it to be placed in swamps or in shallow bays to a depth of about 10 m. This may be the only tool which can image a charged

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reservoir extending from dry land through a tidal area into a shallow bay. For deeper offshore exploration, a sample from an ocean bottom core is commingled with the sampler in a sealed glass jar and processed like any other field sample. Successful programmes have been completed in the GOM, South China Sea, Offshore Peru, North Sea, and the Black Sea at water depths from 30 to 1000 m. Frozen stored cores can also be very effectively used if properly sampled.

The same analytical and statistical techniques are used offshore as onshore with equivalent or better success rates due to the lower background noise in offshore sediments.

Also in development for offshore exploration, is a special device used to sample slicks to determine if they are natural or man-made and to characterize their composition. These can be analyzed using TD/GC/MS for semi-volatile compounds or solvent extracted to test for higher molecular weight compounds.

### Mineral exploration

The search for buried ore deposits is accelerating now that most of the near surface mines have been found or produced. Conventional geochemical techniques looking for metals in the soil, for example by inductively coupled plasma (ICP), are not effective for buried ore deposits. Buried ore bodies, with depositional environments that create oxidation, reduction, or electrochemical processes, can be imaged using GORE Surveys. Such ores include gold, copper, and polymetallic ores. Methylated organic and inorganic compounds as well as other volatile compounds are often found directly over the mineralized areas with sulfur compounds either over the ore body or as a halo around the deposit depending on the state of oxidation of the ore. This advanced technique opens a whole new world of opportunity to the mineral exploration geologist.

### Summary

Modern advances in geochemical sampling, analysis, and interpretation, have led to the robust tool of amplified geochemical imaging. This technique uses a passive signal collection device that can work in dry, saturated soils, or directly in water. It is sensitive enough to work in areas with overburden that are relatively impermeable and have extremely low ppt concentrations. It can report about 150 different compounds with high accuracy. By combining the use of multivariate statistical techniques with this very sensitive and rich compound data set this tool has broad application in the environmental, energy, and mineral industries. It gives the earth scientist another tool to save time, improve analysis and success, and reduce costs by generating an enhanced view.

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