ELSEVIER

Engineering Geology 52 (1999) 3–13

ENGINEERING GEOLOGY

Source-identification investigations of petroleum contaminated groundwater in the Missouri Ozarks

James B. Fels

Missouri Department of Natural Resources, Division of Geology and Land Survey, Rolla, MO 65402, USA

Abstract

The growing population in the Missouri Ozarks rely on the abundant supply of potable groundwater found in the fractured bedrock underlying the region. Protection of this valuable resource from surface, or near-surface contamination is essential to the health and safety of the citizens of Missouri. Petroleum products stored in underground storage tanks pose a threat to groundwater if a release occurs. "Pools" of free product of petroleum can become trapped in voids commonly found on the karst bedrock of the Ozarks. These pools become underground sources of contamination by slowly dissolving into the groundwater. Although the free product rarely travels far from the surface source, dissolved-phase contamination can migrate thousands of meters through underground conduits. Dissolved phase petroleum degasses and partitions out of the groundwater in these conduits. Consequently, contaminated groundwater is not commonly found more than a kilometer or two (few thousand feet) from the source.

The Missouri Department of Natural Resources, Division of Geology and Land Survey's Leaking Underground Storage Tank Unit (DGLS/LUST) investigates sites where petroleum-contaminated groundwater has been found in springs or private wells but a source of the contamination is unknown. These investigations start at the regional scale by determining the recharge area of the contaminated groundwater and by identifying the potentially responsible parties (PRPs). A review of DGLS documents and well logs supplemented by field measurements of water levels in private wells throughout the area is used to construct a potentiometric map and determine regional groundwater flow direction. Water tracing is used to confirm or deny the validity/accuracy of the potentiometric map and to establish hydrogeologic connections between the potential surface source of the contamination and the affected groundwater. Fluorescent dyes are injected into the subsurface, recovered in packets containing activated carbon and analyzed by a synchronously scanning spectrofluorometer. These results are compared to background fluorescence conditions established at the site prior to injection. The background conditions and dye recovery results must be submitted to the Missouri Water Trace Committee for approval as an independent quality assurance/quality control measure.

Each of the PRPs found to be within the recharge area of the contaminated groundwater are investigated to determine the source, or sources, of the contamination. Initial field screening techniques are followed up by confirmatory sampling of soil and groundwater. Geophysical methods such as resistivity and electromagnetic conductivity are used to locate the bedrock surface, fracture patterns and areas of extensive petroleum contamination. On-site drilling activities are performed at each of the PRPs with on-site contamination screening methods such as analyzing soil gas within the borehole with a photoionization detector (PID) and colorimetric tubes. Soil samples are collected and can be analyzed on-site with immunoassay kits with confirmatory samples sent to the lab. Temporary monitoring wells are installed in boreholes to collect on-site groundwater data. Depth-to-water levels are measured,

PII: S0013-7952(98)00049-0

and the relative elevations of the temporary wells are surveyed so that a more detailed potentiometric map can be constructed. Water samples are collected from the temporary wells, and the boreholes are abandoned per Missouri Law.

Petroleum fingerprinting by fluorescence is another tool used to investigate PRPs and determine the source of contamination. Petroleum is extracted from soil or water samples collected during on-site drilling and compared to the petroleum which is extracted from a sample collected at the contaminated spring or well.

Keywords: Hydrogeology; Site characterization; Dye trace; BTEX

1. Introduction

The Missouri Ozark region extends across the southern half of the state and the population is mainly rural. Almost every community, public water supply and individual homeowner in this area relies on groundwater for drinking water. The expansion of urban and recreational areas in the Ozark region has increased the need for water sources. Areas around St. Louis, the Lake of the Ozarks and the Springfield/Branson area are growing at a rapid rate, and the demand for a readily available source of potable water is often supplied from beneath the surface. An abundant supply of potable groundwater is found in the fractured rock underlying the region. The large areas of forest land and pasture in the Ozarks combined with relatively permeable soils allow the groundwater to be easily recharged by the nearly 112 cm (44 in) of annual precipitation (Missouri Department of Natural Resouces, 1986). However, these conditions also allow the rapid infiltration of surface, or near surface, contaminants such as septic tank effluent, landfill leachate, chemical spills or releases from Underground Storage Tanks (UST).

In 1984, Subtitle I of the Resource Conservation and Recovery Act was signed into law, requiring the regulation of all USTs. In 1988, regulations became effective which mandated new performance standards and installation requirements (40 CFR part 280). Missouri passed legislation in 1989 (HB 78) to develop an Underground Storage Tank program within the Department of Natural Resources (MDNR). There are an estimated 22 000 registered UST's in Missouri with ca 16 000 of these actively storing petroleum products. The remainder of the tanks have been closed or abandoned. To address the concern for abandoned tanks, which pose a potential threat to human health and the environment, the US Congress established the Leaking Underground Storage Tank (LUST) Trust Fund as section 205 of the Superfund Amendments and Reauthorization Act (SARA). This one-tenth of 1% per gallon fuel tax provides funds for immediate corrective action of petroleum releases which are not eligible for cleanup under Superfund. Missouri receives an allocation of the Trust Fund to oversee and regulate the cleanup of petroleum releases from USTs. There are close to 5000 known LUST sites in Missouri with ca 2400 sites currently undergoing review or investigation. A portion of Missouri's allocation from the LUST Trust Fund is used to investigate sites with petroleum contamination in soil and/or groundwater where a responsible party is not known.

The MDNR Division of Geology and Land Survey (DGLS) began an interagency arrangement in 1991 to perform detailed hydrogeologic investigations on selected LUST sites across the state where petroleum contamination has been found in groundwater and the source of the contamination is not known. DGLS is tasked to gather hydrogeologic data, interpret the data and present the material in a report which is used for enforcement and/or litigation, if necessary. In 1991, DGLS had two employees dedicated to these investigations — a geologist and a geologic technician. Because of the success of DGLS in determining the responsible party at these sites, we received funding for four full time employees, two geologists and two geologic technicians, in 1994 and formed a LUST Unit at DGLS in 1995. The majority of the sites DGLS/LUST works on are in the Ozarks due to the large dependence on the groundwater resource and the vulnerable geology of the region.

2. Geology/hydrogeology

2.1. General

The Missouri Ozarks are underlain by predominantly Paleozoic carbonates with a few sandstone and shale formations throughout the strata. The Ordovician and older carbonates are generally dolomitized with the younger Mississippian carbonates remaining as limestone. Most of the carbonate formations contain chert as nodules and as beds with some Mississippian age formations containing up to 80% chert. Therefore, the residual soils that form from the bedrock are cherty and clay-rich but with a residual structure. Relict beds of chert or sandstone are present within the residuum where the parent rock once contained beds of chert or sandstone. A relatively high iron content colors most of the residual soils in the Ozarks red and causes the clay minerals present in the residuum to flocculate and form blocky aggregates. Joints and fractures which are present in the bedrock also influence the characteristics of the residuum. Deeply weathered rock and/or a pinnacled bedrock surface are found where joints intersect or where vertical fractures extend to the surface.

The bedrock throughout the Ozarks is generally flat-lying with a slight dip away from the Ozark dome which is located in southeast Missouri. Major fracture patterns are oriented northwest–southeast with secondary fractures trending northeast–southwest. Most of the major faults are oriented in the same direction and are generally normal faults or a combination of normal faulting and strike-slip faulting. Displacement along faults in the Missouri Ozarks varies widely with an average throw of ca 30–40 m. Synclinal and anticlinal folding also follows the same trends which result in localized bedrock dips which may differ from the dip related to the Ozark dome.

Due to the soluble nature of carbonate bedrock and the lack of a confining layer in the residual soils, the bedrock throughout most of the Ozarks is impacted to some degree by solution ranging from localized solution-enlarged bedding planes and fractures to extensive networks of voids, caves and other underground conduits. Sinkholes and sinkhole plains are common sights throughout the southern half of Missouri, as are springs, losing streams and surface entrances to caves, all of which are indicators of the bedrock dissolution that has occurred and that is still occurring in the Ozarks.

Groundwater is recharged rapidly due to the high permeability of the residual soils and the fractured and karst nature of the bedrock. The high chert content of the soil combined with the flocculated clay structure results in relatively high permeability and allows precipitation to enter the subsurface rather easily. In areas of sinkholes, precipitation is concentrated into the sinkholes resulting in a direct connection to the subsurface water. Losing streams are also sources for groundwater recharge. Discharge of groundwater in the Ozarks is attributed to private wells, community wells, springs and gaining streams. Groundwater flow is predominantly in bedrock fractures, bedding planes and voids. Therefore, velocities and yields vary greatly between and within the different formations that comprise the aquifers.

2.2. Hydrogeology that affects petroleum migration

The potential for groundwater contamination from surface, or near surface sources is extremely high due to the rapid recharge of the area and the channelized flow of groundwater within the subsurface. A release of petroleum can find its way to the groundwater very quickly, especially if a sinkhole is nearby. Like many other organic solvents, petroleum products act as desiccants as they descend through the soil, enhancing migratory pathways already in place. Residual petroleum adsorbed to the soil can be a long-term source of groundwater contamination if not removed or remediated. Precipitation descending through the soil column leaches out water-soluble petroleum constituents in the soil and carries them into the groundwater as dissolved-phase contamination. If free-phase petroleum products enter the subsurface in quantities large enough to reach the saturated zone, there are a number of areas where the free product could accumulate and become a subsurface source for long-term dissolved-phase contamination of the groundwater. Relict chert or sandstone beds within the residuum are common places for perched water to accumulate and cascade down through fractures or discontinuities in the beds. Since petroleum products are less dense than water, they will accumulate on top of the perched water and often displace the water while concentrating the product. The water which is displaced contains dissolved-phase contamination and migrates downward to the next saturated zone, which could be the regional water table. Water tends to perch at the base of the weathered zone a few meters below the top of the bedrock surface in some formations. Below the weathered zone within these formations, the horizontal component of flow is much greater than the vertical. Perched water tends to flow within this weathered zone. In this situation, floating free product will travel with the perched water or become trapped, causing dissolved-phase contamination which could discharge at a spring or descend into the regional groundwater. In areas of irregular bedrock surfaces, such as pinnacles and cutters, free-phase petroleum product flows along the bedrock surface to the low points, and accumulating in cutters or valleys. The pool of free product slowly contributes water soluble petroleum constituents into the water migrating below this pool and serves as a source of dissolved-phase contamination for a long period of time. In areas of karst bedrock containing voids above the regional water table, perched water tends to accumulate and flow rapidly toward a discrete discharge location. In areas where the voids are below the regional water table, conduits provide migratory pathways, but the gradients are generally not as great, resulting in slightly lower flow rates. In either case, free product can become trapped in the top of voids, since it is less dense and will float to the highest point in the void, while water below continues to migrate. The water flowing past the pool of product trapped in the void becomes contaminated with dissolved-phase petroleum. Therefore, free-phase petroleum does not tend to travel far from the surface source when released into the subsurface. If the release is small, the soil may adsorb the bulk of the material and serve as a near-surface source of dissolved-phase groundwater contamination. However, if the release is large enough to pass through the soil, free-phase petroleum descends until reaching the first saturated zone. The petroleum usually becomes trapped as described above and becomes an additional subsurface source for dissolved groundwater contamination.

The most water soluble constituents in common refined petroleum (gasoline, diesel, etc.) are aromatic compounds and oxygenation additives which together comprise $<20\%$ of the total material. Benzene, toluene, ethylbenzene and total xylenes (BTEX) are the common indicators of dissolved-phase petroleum contamination. Methyl-tertiary butyl ether (MTBE) is a common oxygenation agent which has been added to certain gasoline blends since the early 1980s. All of these compounds are volatile and, with the exception of MTBE, tend to partition into the gaseous phase as opposed to being dissolved in water. All of the BTEX components and MTBE have relatively high vapor pressures, which is a measure of a compound's tendency to evaporate, but MTBE has a low partitioning coefficient (Henry's law constant) for volatilizing out of water and into the vapor phase. The BTEX components have high Henry's law constants. Due to these physical properties, dissolved-phase groundwater contamination does not travel extremely long distances in a conduit flow regime. High groundwater velocities often found in karst aquifers result in turbulent groundwater flow. The turbulence essentially strips the dissolved-phase contamination (at least the strippable components) while the water is in motion. In addition, groundwater which enters voids, wells or springs decreases in pressure causing degassing of the water as it reaches equilibration with the new pressure. By definition, the water table is the surface at which groundwater is at atmospheric pressure. Water below this level is under greater pressure, or head. It is this same head which causes groundwater to flow. Therefore, groundwater flowing under a pool of free phase petroleum is under pressure. Once this water comes into contact with the atmosphere, degassing occurs, and if turbulent water flow is present, partitioning into the vapor phase is enhanced. In the Missouri Ozarks, dissolved-phase petroleum contamination is not commonly found >1–2 km (a few thousand feet) away from the surface source of the contamination.

3. Investigation methods — regional information

3.1. Background data acquisition

When DGLS/LUST receives notice of a site needing investigation, it is usually due to a private well or spring becoming contaminated with petroleum products from an unknown source. An initial site visit is made to locate the well or spring and to do a preliminary survey of the geology, hydrogeology and potential magnitude of the problem. Field reconnaissance consists of inspecting rock outcrops and paying particular attention to the degree of and orientation of fracturing and looking for karst features. Streams are also an important part of the field reconnaissance. Determining if the streams are gaining or losing flow, checking for the presence of springs and/or seeps and looking for signs of contamination are parts of the initial field visit. Background information is also researched in the office. The DGLS has an extensive library of files relating to geology and hydrogeology of the state including detailed geologic maps and publications, cave maps, isopach maps, well logs, potentiometric data, groundwater tracing data and maps, losing stream data and maps and detailed environmental reports on various types of sites throughout the state. Once all this information is compiled and reviewed, an initial conceptual model of the site hydrogeology is made.

Field data is collected to supplement the information gathered in the office. A door-to-door survey of local residents is performed to locate all private and community wells, both active and abandoned, in an area that is proportionate to the magnitude of the contamination problem. Well information is gathered such as depth of well, depth of casing, odor or discoloration of water and static water level. Once a sufficient number of comparable wells are measured, a potentiometric map can be produced to determine the direction of regional groundwater flow and locate any groundwater divides or other recharge boundaries. Potentiometric data and water trace maps found during the DGLS file search are also used to determine recharge boundaries. Once the preliminary boundaries of the recharge area for the contaminated groundwater are found, a field search for PRPs can begin within these boundaries. The owners and/or operators are interviewed to inform them of the investigation and to gain access to their property for gathering site specific data.

3.2. Groundwater tracing

Groundwater tracing is usually performed at all of the PRP's facilities which were initially identified to determine if they are hydrologically connected to the contaminated well or spring and to provide data for evaluating the accuracy of the potentiometric map. The reliability of a water trace for simulating the contaminants' flow paths is dependant upon several factors, such as the placement and depth of the tracer injection, hydrologic conditions at time of release and at time of injection, and type and amount of tracer. Fortunately, DGLS has a long history of water tracing in the Missouri Ozarks and has gained decades of experience in completing water traces. Early water traces relied on injecting large quantities of fluorescent dye and visually identifying the results, perhaps with the assistance of a black light or a high intensity, focused incandescent light. The need to eliminate the subjectivity of this method was partially answered with the purchase of a filter fluorometer. This machine allowed for quantitative analysis of fluorescent dyes but did not separate green dye (which are some of the best fluorescent tracers available) from background fluorescence. A synchronously scanning spectrofluorometer has proven to meet the detection level needs and the ability to quantitatively analyze fluorescent tracers. DGLS has been using a synchronously scanning spectrofluorometer since 1983 combined with a computer program that is set up for fluorescent tracer analysis. This program controls the spectrofluorometer and produces printouts of scan-specific data. This system aids in distinguishing naturally occurring background fluorescence from fluorescent tracers. Because of this increase in technology and the experience gained over the years, smaller amounts of the tracer can be injected and detected. The use of the synchronously scanning spectrofluorometer and computer program allows for the simultaneous detection of different dyes.

Prior to the injection of tracers, a study of background fluorescence is performed. This determines the amount and wavelengths of naturally occurring fluorescence at all of the monitoring locations used for the water trace. All known locations at which the tracer could be detected are monitored for the resurgence of the tracer. Fluorescent dyes and optical brighteners are recovered at these monitoring locations with packets containing either activated carbon or cotton. These packets are placed at springs, creeks, private well and other locations at which the tracer may be found. The packets are placed in the water for a period of one week, at which time they are retrieved and replaced with new packets. The packets are brought back to the lab where any dye present is eluted from the activated carbon and/or the cotton with a solution of ethanol and ammonium hydroxide. This solution is pipetted into cuvettes, which are placed into the spectrofluorometer for analysis. The background study is usually performed for a period of at least 4 weeks or until steady background conditions exist.

After the background study has been finalized, the types of tracers suitable for use can be determined. The four most commonly used fluorescent tracers used at DGLS/LUST are Fluorescein, Rhodamine-WT, Tinopal CBS-X and Pyranine. Two or more tracers can be used concurrently from different injection locations. When injections are made at multiple locations, a different tracer is used for each. The tracer must be injected in an area and at a depth which would best represent the location at which the release may have occurred in order to mimic the flow paths as closely as possible. This becomes more critical the shorter the distance of the intended trace. Most UST pits are backfilled with porous sand and gravel so the tracer may be poured directly into the tank pit from the surface and flushed with potable water. This must be done with caution, however, due to the buoyancy of tanks once water is injected into the tank pit. If monitoring wells are present on-site, they can be used for injection points depending on their depths and construction. As a last resort, a backhoe pit is dug on-site at a strategic location and depth and the tracer is injected and flushed with potable water. After the water has soaked into the subsurface, the pit is backfilled and patched. The monitoring packets continue to be collected and replaced on a weekly basis and analyzed with a spectrofluorometer throughout the tracer study. A report is generated consisting of the background study and the tracer study recovery results and submitted to the Missouri Water Trace Committee for approval. This requirement serves as an excellent QA/QC measure for later enforcement and/or litigation, if necessary. After the results of the tracer study have identified which PRPs are within the recharge zone of the contaminated groundwater site, intrusive, site-specific investigations of those PRPs can begin.

4. Investigation methods — site specific information

4.1. Borehole advancement

In an effort to determine the source, or sources, of groundwater contamination, each PRP found to be within the recharge area of the contaminated well or spring is investigated equally. Field screening methods such as soil gas surveys, temporary wells, geophysical surveys and petroleum fingerprinting are used to gather a rather large amount of hydrogeological and chemical data very quickly. This data can be used to eliminate some of the PRPs from further investigation and/or to show areas where more sampling is required. The DGLS has two drill rigs which are used to advance boreholes at each of the PRP locations. Both rigs are pickup-truck mounted so physical access to most sites is not a problem for the equipment. Boreholes are ca 3 cm (2 in) in diameter and are advanced in 1.5 m (5 ft) increments. Boreholes are advanced using direct-push technology by hydraulically pushing a continuous sample tube through the soil column or by auger drilling. All boreholes are advanced to the of bedrock surface or first saturated zone, whichever is encountered first. Boreholes are placed in locations where contamination is expected to be found, such as surrounding the tank pit, the pump islands and the supply lines from the tanks to the pumps, especially at any elbows or “Ts” in the piping. The boreholes are drilled by permitted monitoring-well drillers and logged by registered geologists. Soil gas is analyzed every 1.5-m in the borehole by inserting a rigid copper tube with tygon tubing inside it. The end of the copper tube is plugged so that it can be pushed through any soil that may have collapsed in the borehole and slots are cut in the side of the copper tube near the end. A vacuum pump is attached to the tygon tubing to purge the borehole prior to sampling the soil gas. A PID is used to quantify volatile organic compounds within the ionization potential of the detector lamp. A 10.6 eV lamp is used in the PID which is capable of detecting all of the BTEX compounds. The PID is not a chemical-specific detector and cannot differentiate among compounds, so colorimetric tubes are used to analyze for specific compounds or suites of compounds. These tubes are calibrated to give qualitative and quantitative analysis of the gaseous-phase material being pulled through the tube. Soil-gas samples are collected throughout the total depth of each of the boreholes advanced at each of the sites. Soil samples are also collected throughout the borehole for confirmatory analysis. Immunoassay kits, which can produce quick results in the field, are used to give a semi-quantitative range of contaminant concentrations. Duplicate samples are sent to the lab for confirmation by GC/MS.

If the boreholes encounter groundwater, temporary wells are installed and allowed to equilibrate overnight. Slotted PVC screen is attached to a well point and inserted into the borehole; soil cuttings are placed around the top of the well at the surface; and the PVC riser is capped. The next morning water levels are measured; groundwater samples are collected; and well locations and elevations are surveyed. The samples can be analyzed in the field with the immunoassay kits or sent to the lab for GC/MS analysis. All of the boreholes are abandoned according to Missouri state regulations, and registration forms for the drilling activities are filled out and sent to the Missouri Wellhead Protection Section of DGLS.

Data collected during the drilling activities are compiled and presented on site maps to illustrate the findings. Borehole locations are plotted on a base map with numbers which correspond to the boring logs. Depth-to-rock or depth-to-water measurements from the boreholes can be used to construct a cross section of the area. This can reveal migratory flow paths such as buried valleys

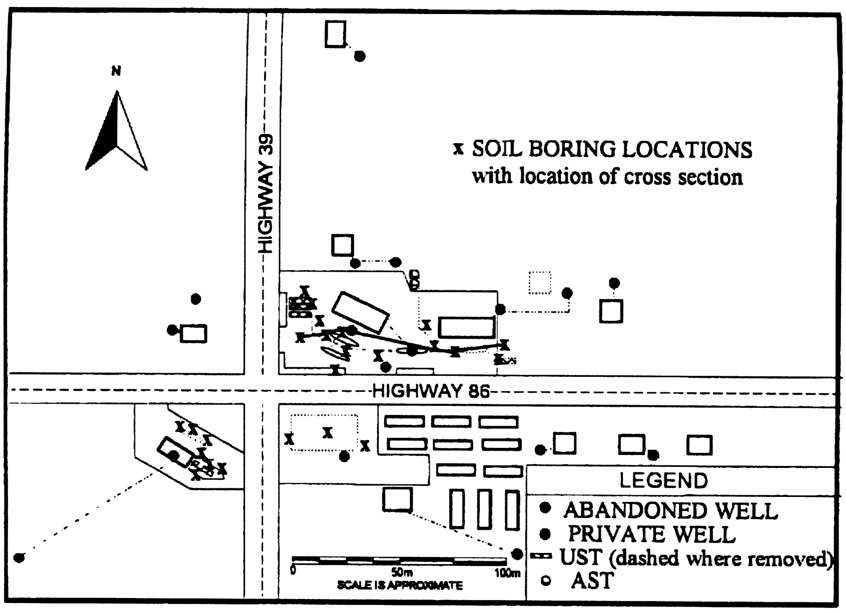

Fig. 1. Site map showing location of boreholes and the boreholes which were used to construct a cross-section.

or areas of depressed water table suggesting fractures or descending perched water. Figs. 1 and 2 are examples from a site investigation in southwest Missouri where boreholes were advanced to the bedrock surface, passing through a relict chert bed which we were able to drill through. Some of the boreholes encountered perched water on top of the irregular bedrock surface. The cross section shows the relationship between the relict structure of the residuum and the bedrock surface, accumulation of groundwater in valleys in the bedrock surface and the distribution of contamination in these bedrock lows.

The groundwater elevations are also used to make a site-specific potentiometric map. This is used in conjunction with the regional potentiometric map developed at the beginning of the investigation. A better understanding of flow from the area of potential release can reveal data gaps, or areas where more investigation is needed. Fig. 3 is a potentiometric map of another site in southwest Missouri where several abandoned shallow water wells were converted into monitoring wells. An air rotary drill rig was contracted to drill two additional boreholes for monitoring wells to complete the network. This figure is an example of how a potentiometric map can reveal fracture-induced flow. In the vicinity of this site, a small east–northeast and west–southwest trending fault was found, but it was not known how far the fault extended in the direction of the site. This map shows two important discoveries with regard to PRP identification. First, a roughly north–south groundwater divide separates two different groundwater basins and secondly, a trough exists which controls the flow on both sides of the divide. This trough trends east–northeast to west–southwest and is in line with the strike of the mapped fault which is exposed ca 3 km away. The fault and/or fractures associated with it control the flow of groundwater and the transport of contamination to one well, but not other nearby wells.

4.2. Geophysical surveys

Surface geophysical investigations are used in some investigations to locate anomalies which could direct future drilling activities. The DGLS has a surface resistivity unit which can be used to determine depth to water, depth to rock, deep bedrock weathering, fracturing and possibly areas with high levels of petroleum contamination. Electromagnetic conductivity equipment is also rented for similar determinations. Both of these geophysical methods operate on the same principal by sending a current into the subsurface while a

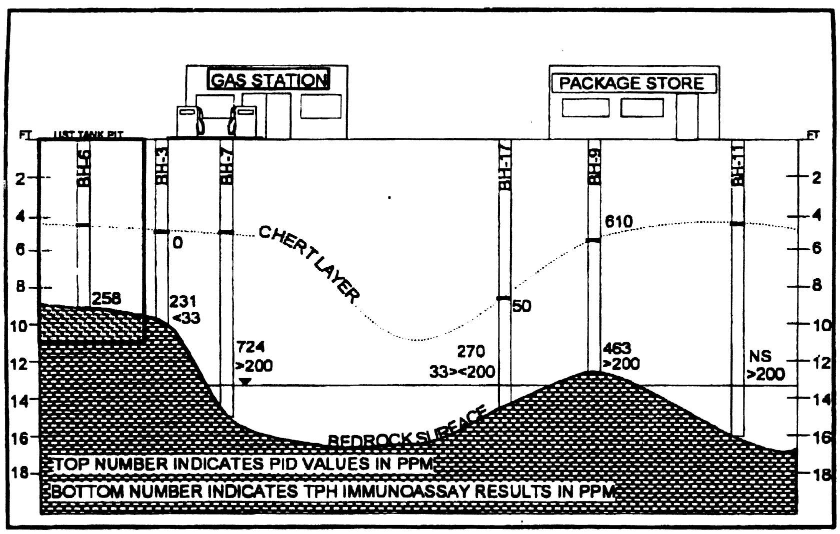

Fig. 2. Cross-section made from borehole data. Soil gas and soil sample results show contamination concentrating in bedrock lows.

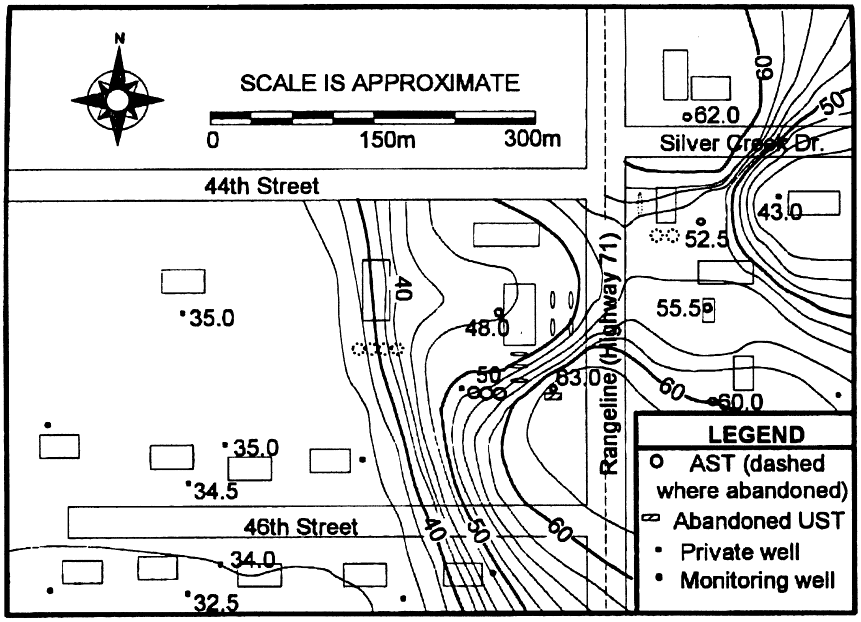

Fig. 3. Potentiometric map showing fracture induced flow. An east–northeast fracture forms a trough in the water table on both sides of the groundwater divide.

detector measures the resistance or the conductance of the current returning to the surface. The numbers can be plotted on a site map and contoured or plugged into equations to determine depths of various media. Like most other geophysical methods, several assumptions must be made, introducing subjectivity into the interpretation of resistivity and conductivity data. Water is conductive, and organic compounds such as petroleum are resistive. Soil is conductive, and rock is resistive. Interpreting what the numbers mean and how to reduce field data into specific, legally sound intervals can be very difficult. The most practical application that can be supported for enforcement and/or litigation is to contour the data and intrusively determine what is causing any anomalies. Fig. 4 is an example of resistivity contours from a site investigation in south-central Missouri. Resistivity contour lines were drawn by a computer contouring program, and trends were identified. These trends suggest possible migration pathways from an abandoned gas station to two contaminated private water wells. These anomalies could represent buried valleys or fractures which the contaminated groundwater may be following. Pump tests performed with monitoring wells also showed the same trend and connection. Subsequent drilling in the areas of these trends indicated that the depth to bedrock was greater, but the borings did not encounter water. The bedrock lows could be due to increased weathering around fracture zones which control the flow of groundwater below the bedrock surface.

4.3. Petroleum fingerprinting by fluorescence

Fingerprinting of petroleum products can be helpful when there are multiple PRPs which have soil contamination and are hydrologically upgradient of the contaminated groundwater. There are various analytical techniques and instruments capable of performing petroleum fingerprinting. There are also pros and cons to each of these techniques. The method we use at DGLS is one first described by Pharr et al. (1992) in which a synchronously scanning spectrofluorometer is used to analyze the various samples containing petroleum. The oil industry has used fluorescence for

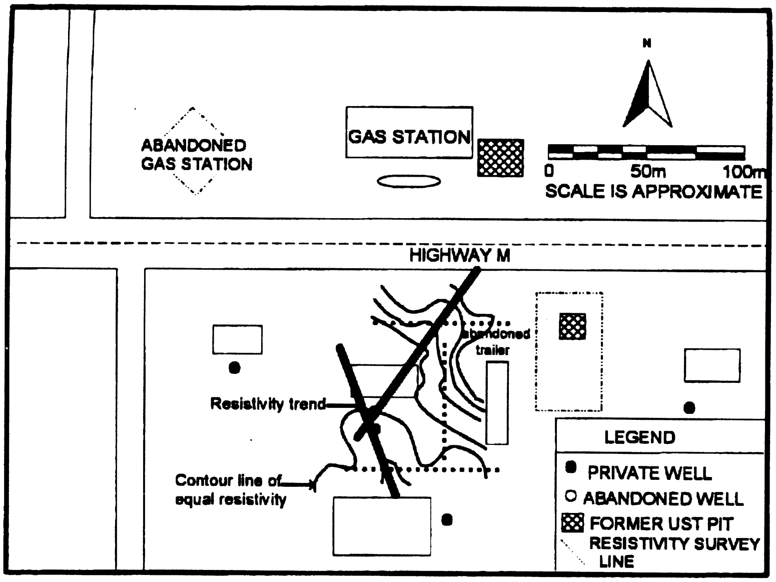

Fig. 4. Resistivity trends found in a surface resistivity geophysical survey. Subsequent drilling found the trends to be related to bedrock lows, or valleys.

petroleum identification for a long time. Many of the compounds in crude oil, as well as refined products, fluoresce under an energy source, such as an ultraviolet light. The spectrum of fluorescence for petroleum is much wider than for tracer dyes because of the numerous chemical compounds that make up petroleum products and the different blends of those products. Therefore, a program has been prepared to allow the DGLS computer-driven spectrofluorometer to be used for analysis of petroleum samples.

The method used is based on identifying water-soluble petroleum constituents, since they are of primary concern in dissolved-phase groundwater contamination. A contaminated groundwater sample is collected in sufficient quantity (usually a few liters) to allow for concentration. This amount of contaminated water is mixed with a few milliliters of hexane in a separatory funnel. The petroleum in the water is extracted by and concentrated into the hexane which can be pipetted into a quartz cuvette and scanned by the spectrofluorometer. This analysis is graphed by comparing fluorescent intensity to wavelength. Samples from each of the PRPs are compared with each other. Samples from the PRP's can be from onsite groundwater contamination or soil contamination. On-site groundwater contamination would be extracted into the hexane as described above. Soil samples must undergo an intermediate step to eliminate naturally occurring fluorescent organic material in the soil from entering the hexane extraction. The petroleum in the contaminated soil sample is extracted with distilled water; then the dissolved-phase contamination undergoes the hexane extraction. Fig. 5 shows the

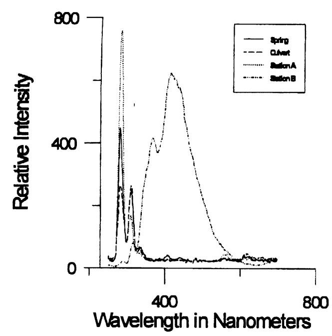

Fig. 5. Results of petrolium fingerprinting analysis performed on a synchronously scanning spectroflourometer. The scan from contamination at Station A is similar to the scan from a contaminated spring and nearby culvert. The scan from Station B is drastically different.

results from a site in Springfield where fingerprinting was used to determine if a difference could be distinguished in soil contamination found at various PRPs. In this case, one PRP which was upgradient of the contaminated groundwater could be eliminated. The fingerprinting results show the soil contamination to be significantly different from the contaminated groundwater and from soil contamination found at other PRPs. This method of fingerprinting has been useful as a screening tool, but it should be used with caution. If contamination is recent with very high levels of contamination or even free product present or if the comparison is of gasoline versus diesel, the fingerprinting method has been found to be fairly successful. However, if the contamination is from an old release, or if the contamination levels are minor, or if the release occurred from petroleum products supplied by the same distributer, the method is not reliable.

5. Conclusion

The ultimate goal of these hydrogeological investigation performed by DGLS/LUST is to restore one of the natural resources that the Missouri Ozarks is known for — a good and plentiful groundwater supply. Once the responsible party (RP) is identified, they are contacted by the regulatory division of the MDNR and are required to remediate the source area and the groundwater problem. Groundwater cleanups are never easy, especially in fractured or karst rock. With petroleum contamination, however, there are a few physical and chemical characteristics which allow it to be cleaned up more easily than a soluble, dense nonaqueous-phase liquid or metal contamination. Petroleum products accumulate and float at the first saturated zone with the resulting dissolved-phase contamination rarely migrating >1–2 km, especially in the Missouri Ozarks.

Since 1991, when DGLS started performing these investigations, >50 site investigations have been completed with a success rate of $>92\%$ in identifying the source of contamination. The depth of groundwater and/or the limitations of available equipment prevented source identification at the remaining sites. DGLS is constantly striving to improve its techniques and expertise with a goal of achieving a 100% success rate in identifying the contaminant sources and restoring the aquifers to near original quality.

References

Missouri Department of Natural Resouces, 1986. Missouri Water Atlas. Missouri Department of Natural Resouces, Missouri.

Pharr, D.Y., McKenzie, J.K., Hickman, A.B., 1992. Fingerprinting petroleum contamination using synchronously scanning fluorescence spectroscopy. Ground Water 3 (4), 484