



Simple techniques for assessing impacts of oil and gas operations on Federal Lands- a field evaluation at Big South Fork National River and Recreation Area, Scott County, Tennessee (online edition)

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ABSTRACT

Simple, cost-effective techniques are needed for land managers to assess the environmental impacts of oil and gas production activities on public lands so that sites may be prioritized for further, more formal assessment or remediation. These techniques should allow the field investigator to extend the assessment beyond the surface disturbances documented by simple observation and mapping using field-portable instruments and expendable materials that provide real-time data. The principal contaminants of current concern are hydrocarbons, produced water, and naturally occurring radioactive materials (NORM). Field investigators can examine sites for the impacts of hydrocarbon releases using a photoionization detector (PID) and a soil auger. Volatile organic carbon (VOC) in soil gases in an open auger hole or in the head space of a bagged and gently warmed auger soil sample can be measured by the PID. This allows detection of hydrocarbon movement in the shallow subsurface away from areas of obvious oil-stained soils or oil in pits at a production site. Similarly, a field conductivity meter and chloride titration strips can be used to measure salts in water and soil samples at distances well beyond areas of surface salt scarring. Use of a soil auger allows detection of saline subsoils in areas where salts may be flushed from the surface soil layers. Finally, a microRmeter detects the presence of naturally occurring radioactive materials (NORM) in equipment and soils. NORM often goes undetected at many sites although regulations limiting NORM in equipment and soils are being promulgated in several States and are being considered by the USEPA. With each technique, background sampling should be done for comparison with impacted areas.

The authors examined sites in the Big South Fork National River and Recreation Area in November of 1999. A pit at one site at the edge of the flood plain of a small stream had received crude oil releases from a nearby tank. Auger holes down gradient from the pit showed the presence of anomalous concentrations of VOCs at depths of 3 feet for a distance of about 50 feet. PID readings at other sites showed 1) one reclaimed site where hydrocarbon biodegradation was incomplete; 2) one reclaimed site where biodegradation had left no traces of VOCs; and 3) two sites where traces of substantial offsite migration of hydrocarbons occurred. Produced water salts at one site have migrated many 100s of feet downvalley from the area of salt scarring and tree death adjacent to the pits. Naturally occurring radioactivity (NORM) at most sites was at background. One site showed anomalous radioactivity related to NORM in a

small brine pit. Some of this NORM has moved downslope from the outlet pipe to the pit.

INTRODUCTION

Federal land managers have increasing responsibilities to assess the nature and extent of environmental impacts on Federal lands and to determine the associated risks to human health and ecosystems. Often, the land manager has a large number of sites to evaluate, limited resources to perform assessments, and limited guidance on how to evaluate and prioritize sites for more detailed assessments and remediation. Because formal site assessments are lengthy and expensive (see, for example, ASTM, 1999a), accurate prioritization is vital.

The generally remote location of oil and gas production sites on Federal lands has historically limited public concern regarding impacts on human health and ecosystems. More recently, oil and gas production sites on Federal and private lands have come under increased scrutiny as past production impacts are being noticed, impacts on fish and waterfowl are documented, use of surface and ground water supplies expands, rural areas are encroached upon by residential and commercial development, and recreational uses of producing areas increase.

For oil and gas production sites, the main sources of human health and ecosystem risk are hydrocarbons (especially that fraction that is dissolved in water), saline water co-produced with the hydrocarbons, and radionuclides, principally radium in the produced water or associated scale and sludge. The purpose of this study is to describe methods whereby field workers using relatively inexpensive, portable equipment and consumable supplies could rapidly evaluate oil and gas exploration and production sites for hydrocarbons, produced water salts, and naturally occurring radioactive materials (NORM). The techniques provide semiquantitative data that can be used to compare and prioritize sites for more formal site assessment efforts and remediation or to assess the effectiveness of remediation.

The methods used here to detect hydrocarbons, salts, and radionuclides have the advantage of being simple and cost-effective and extend the reach of the observer into the shallow subsurface. They provide real-time field data. Using these methods and simple site mapping, several locations a day may be assessed.

Knowledge of the site characteristics (geology, slope, drainage, topography, etc.) and site history enhances the ability to search for and recognize likely sites for

contamination. Thus, these techniques are best used by, or in company with, knowledgeable local personnel.

The main purpose of this reconnaissance study in the Big South Fork National River and Recreation Area (Fig. 1) is to test the simple techniques for site assessment in several different settings and not to perform extensive measurements at any one site or to generalize about the nature and extent of contamination throughout the park unit evaluated.

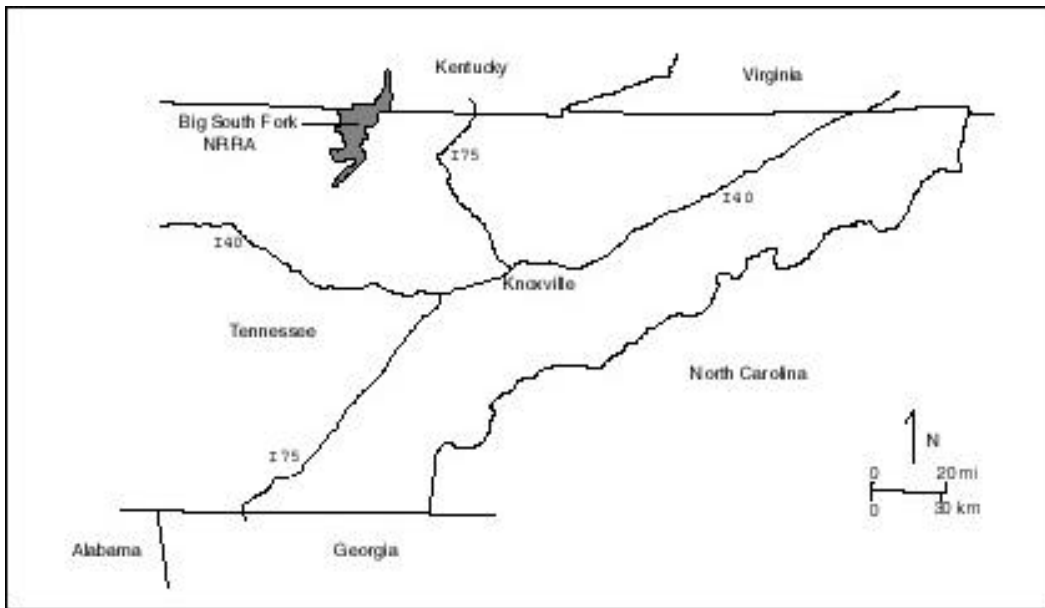


Figure 1- Location of the Big South Fork National River and Recreation Area in eastern Tennessee and southern Kentucky.

Hydrocarbons

Hydrocarbon releases can range from major, episodic, spill events or lesser, but more prolonged, seepage from pits, pipes, stuffing boxes, and tanks. Spills and seepage can be generated by equipment or containment failure, vandalism, lightning strikes, flood damage, and other natural phenomena. Released hydrocarbons can flow across the land surface or seep into the subsurface from pits and bermed areas designed to contain spills. Because most crude oils are less dense than water, they remain on the surface of the water table. The components of crude oil present will dissolve to some extent in ground water and volatilize to the soil gas in the unsaturated zone. The ratio of the partial pressure of a compound in air to its concentration in water at a given temperature is called the Henry's Law constant. Henry's law constants for pure phase components of crude oil can be used to predict dissolution in

water and volatilization to air, a critical step to an assessment of the toxicity (ASTM, 1999b; Yaws, Pan, and Lin, 1993). The water-soluble and volatile fractions often include those components of crude oil that have high toxicity (for example, benzene, toluene, ethylbenzene, and xylene- BTEX). Where a significant vapor-phase fraction is present, a subsurface hydrocarbon plume can be detected by measuring volatile organic compounds (VOCs) in soil gas above the hydrocarbon layer. Microbial degradation of hydrocarbons can contribute to detection of a plume because degradation products tend to be volatile.

Hydrocarbon releases at a production site are typically visible at the surface in the form of stained soil, oil in pools on the soil surface or in pits, or oil sheen on the surface of nearby ponds and streams. These features are readily documented by observation and simple site mapping. What is typically not visible are hydrocarbons that have soaked into the soil surrounding a pit and are now moving downslope in the subsurface either dissolved in the groundwater or moving as a separate phase on the surface of the water table. Also not readily discerned are dissolved hydrocarbons that may be present in ground water seeps or surface water flows downgradient from the release site.

Leakage of refined petroleum products from underground storage tanks, seepage of chlorinated hydrocarbons from waste pits, and spills of petroleum products during refining and transport have required the development of detailed site assessment and remediation procedures for hydrocarbon-contaminated sites (ASTM, 1999c). A photoionization detector (PID, fig 2, appendix 1) is often used as a screening instrument at such sites to check for the presence of volatile organic carbons and to protect personnel from exposure to them.

The simple technique for site assessment described here uses a PID to detect volatile organic compounds in soil samples and soil gas at oil and gas production sites where spills are apparent. This simple approach has advantages in that readings are instantaneous and the sensitivity and range are excellent (0.1 to 10,000 ppm VOCs). The instrument can detect direct hydrocarbon contamination of soils, VOCs being given off by a non-aqueous phase hydrocarbon layer on top of the water table, or hydrocarbons dissolved in the water. It thus allows personnel to evaluate contamination beyond the immediate area of obvious contamination. Understanding how far and in which direction hydrocarbons may have migrated beyond the immediate site is critical to assessing and prioritizing the site, especially if potential receptors (i.e. stream, pond, water well) may exist downgradient from the site.



Figure 2- Photoionization detector (RAE Systems, appendix 1) used to determine the concentration of volatile organic carbons in air (either in soil gas in an auger hole or being given off by a soil sample to the headspace of a plastic sample bag).

There are some limitations to applicability of the method. The depth limits for augering holes by hand varies from site to site and, if the water table is deep, this limits the ability to detect the hydrocarbons. In other cases, there may be limited gas-phase transport of the VOCs, an intervening clay layer, or a deep water table, and a hydrocarbon plume may not be detected. Thus, this technique works best where the water table is relatively shallow and the soil and subsoil are easily augered.

Produced waters

Produced waters are generated at almost all oil production sites in the U.S., all coalbed methane production sites, and at many other gas production sites. The ratio of produced water to produced oil at a production site ranges from <1:1 to about 100:1. The average ratio is about 10 to 1 (Breit and others, 1997). The salinity (total dissolved solids, TDS) of these

waters can range from a few thousand to about 400,000 ppm. For comparison, seawater has 35,000 ppm TDS. Releases of these waters to streams are permitted where the waters meet certain standards; however, about 95 percent of all U.S. produced waters are presently being injected into subsurface formations to enhance oil recovery or to simply dispose of the water.

The salts typically found in produced waters (Na, Cl, SO₄) may cause waters to become contaminated and exceed secondary drinking water standards or standards for irrigation or livestock use. They may cause soil and ecosystem damage, but they are generally not known to cause human disease. However, loss of use of a ground or surface water supply because of taste, odor, damage to water systems, or related reasons has a significant economic cost for those impacted. Regardless of the salinity level, produced waters can contain significant levels of toxic trace elements including metals of concern under the Resource Conservation and Recovery Act (RCRA), however, there are only limited studies of trace elements at produced water release sites. Measurements for trace elements in waters and solids are beyond the scope of this field methodology study.

Saline produced waters can adversely impact ecosystems. Most produced waters contain concentrations of sodium and chloride sufficient to kill vegetation outright or prevent germination of seeds. They also contain some minor elements, such as boron and lithium, that inhibit plant growth. In streams and estuaries, excess salinity contributed by produced waters may limit growth or reproduction of aquatic organisms (Andreasen and Spears, 1983). Produced water releases are often accompanied by excessive soil erosion near the source because the added sodium causes dispersion of clays, disruption of soil texture, and loss of cohesion. Dispersion of clays reduces soil permeability and further inhibits plant growth. Siltation of waterways may further alter habitat for aquatic organisms and limit the life of reservoirs. Soils and water more removed from sites of obvious soil salinization and erosion may have salt impacts that are less obvious, but still are deleterious to ecosystems.

An extensive literature has developed for assessing and remediating saline soils in agricultural lands (U. S. Department of Agriculture, 1954; Tanji, 1990). Subsurface drainage systems and addition of amendments such as gypsum and organic matter are the principal means for soil remediation in affected agricultural lands. Saline soils at oil and gas production sites share some features with saline soils in agricultural areas such as poor support of vegetation, destruction of soil texture and enhanced erosion, but typically differ in the composition of the added salts (see below).

Several studies have attempted to discriminate salts derived from produced waters from those derived from natural or other industrial sources, including studies of water salinization (Whittemore, 1995; Davis and others, 1998; Abbott, 1998; Spangler and others, 1996) and studies of soil salinization (Otton and Zielinski, 1998). These studies document differences in the total amount of salts or compositional differences between salinity sources (chloride content, bromide to chloride ratio, or isotopic differences). Assessment and remediation techniques specifically tailored for known produced-water release sites have been developed by the American Petroleum Institute (Carty and others, 1997).

The initial assessment approach described here is an extension of methodology developed by the authors at some produced-water contaminated sites in Colorado (Otton and Zielinski, 1998; Zielinski, Otton, and Rice, 2000). The method uses a field conductivity meter (fig. 3, appendix 1) to measure the conductivity of waters or soils sampled at the site. The method is improved by the recent availability of chloride titration strips (fig. 4, appendix 1) that can provide reliable field data for chloride concentrations in waters or soil leachates.



Figure 3- Field conductivity meter (Markson Science, appendix 1) used to determine conductivity of water samples and soil leachates.



Figure 4- Chloride titration strips (HACH Company, appendix 1) provide measurement of chloride ion concentrations in sampled waters or in soil leachates.

The soil samples can be retrieved either from the surface or from an auger hole. The conductivity values serve as a surrogate for salinity. The conductance and chloride values observed at suspected contaminated sites are compared to values for samples of water from the contaminant source (produced water tank or brine pit) or from impacted soils immediately downslope from the source and to background values for soils and waters measured at uncontaminated sites.

Naturally Occurring Radioactive Materials (NORM)

The USEPA estimates that about 30 percent of oil and gas production sites have radionuclide levels of regulatory concern (SC&A, 1997). NORM (mostly ^{226}Ra and ^{228}Ra in approximately equal radioactivity) is dissolved in saline waters associated with the oil or gas in the producing horizon. As water is produced with oil or gas, temperature and pressure drop, and gases exsolve from solution. As a result, minerals often precipitate from the water forming scale in downhole tubulars, surface flow lines, and tanks, sludge in tanks, or precipitates in holding ponds. When barite (BaSO_4) and other minerals precipitate from the water, radium is incorporated as a coprecipitate. The American Petroleum Institute conducted a survey of NORM contamination at

oil and gas production sites across the U.S. documenting many areas with significantly elevated levels of NORM (Otto, 1989). The authors have documented NORM contamination and measured radium isotopes at sites in Oklahoma, Illinois, Kentucky, Wyoming, and Michigan (Otton and others, 1997a,b,c; Zielinski, Otton, and Budahn, 1997; Zielinski, White, and Otton, 1998; Zielinski, Otton, and Budahn, 2000). The approach used here is based on this experience.

This method uses a microRmeter to measure radioactivity from gamma-ray sources at the site (fig. 5, appendix 1). The instrument is sensitive to gamma rays from decay products of ^{226}Ra (principally ^{214}Bi) and ^{228}Ra (principally ^{208}Tl), but also measures gamma rays from ^{40}K . Measurements on equipment and suspect soils at a site are compared to background readings for uncontaminated equipment and soils nearby. The ability of the instrument to detect anomalous radioactivity is limited by the gamma-shielding effects of soil (about 40 cm of soil reduces the gamma signature of a source by 90 percent) and the metals and other materials in equipment. Thus radium-bearing sludge inside tanks or pipes or radium-bearing soils buried by uncontaminated soils may not be consistently detected or may be measured at levels less than that of unshielded material.



Figure 5- MicroRmeter (Ludlum Measurements, Inc., appendix 1) used to measure gamma activity associated with naturally occurring radioactive materials at an oil and gas production site.

Although several States have established radioactivity limits for equipment and radium activity limits for soils at oil and gas production sites, Federal limits are not yet established (Gray, 2000). Site remediation requirements are usually given in microRem/hour ($\mu\text{R/hr}$) for equipment and picoCuries/gram (pCi/g) radium for soils. This technique provides data directly applicable to requirements for equipment, but does not yield information relative for existing standards for soil remediation. The radium content of soils must be established by laboratory radiochemical analyses. Some remedial companies use a microRmeter as a screening tool for cleanup of soils based on their experience with soils in some areas. For example, they may cleanup all soils more than 50 percent above background as measured with a microRmeter, having established from previous studies that those soils exceed the applicable standard.

Big South Fork field study

As a result of discussions with personnel of the Geologic Resources Division of the National Park Service, the authors visited the Big South Fork National River and Recreation Area in northeastern Tennessee in early November 1999 (fig. 1). A Geographic Information System (GIS) study of the Big South Fork National River and Recreation Area (T.J. Mercier and J.K. Otton, U.S. Geological Survey, unpub. map, 1999) shows that 314 oil and gas wells exist within the unit boundary and 3453 wells exist within the watershed. The Big South Fork boundary file and the watershed boundary file were supplied by Ron Cornelius (National Park Service, written commun., 1999). The oil and gas well location data were derived from proprietary files (Information Handling Systems, Inc.) leased by the U.S. Geological Survey.

A review of the published literature for the oil fields in the Big South Fork area suggests that oil and gas production in this area yields little produced water (Glenn, 1915; Winston and others, 1974). Onsite discussion with Big South Fork National River and Recreation Area personnel and site visits showed that selected fields had some water produced and that condensates were being produced at other sites. In this area, oil fields producing from sandstone units tend to have coproduced water, whereas those producing from carbonate reservoirs yield little or no produced water (Steve Bakaletz, National Park Service, oral commun., 1999).

PROCEDURES

Hydrocarbons in soils

This technique relies on detecting VOCs (1) present in soil pore gas derived from a nearby hydrocarbon source; and (2) derived from gently heating hydrocarbons present in a soil sample, where the hydrocarbon can either occur as a free phase in pore spaces or be sorbed to mineral grains. Volatile hydrocarbons in soil gas or in headspace above a bagged soil sample are detected using the PID discussed above. A PID can detect concentrations of low molecular weight (C1-C10, excluding methane) VOCs in air down to 0.1 ppm. The PID has an internal pump that draws air through a charcoal filter and a moisture filter to a photoionization chamber where hydrocarbons are ionized by UV light. Ejected electrons are detected as a current. Gas VOC concentrations are calculated based on calibration of the PID to a known standard gas. Reliable readings require the use of filters and careful operation to limit access of dust and moisture to the measuring chamber. Reported precision for measurement of a single standard gas is ± 2 ppm or 10 percent of reading.

We used a 2-inch diameter soil auger (appendix 1) to create entry for soil-gas sampling and to retrieve soil samples from various depths (depths checked with a ruler or tape). Soil augering typically involves multiple entries into a hole with withdrawals to pull soil from the auger bit. We measured soil-gas VOC concentrations at one or more depths as augering progressed. Soil-gas measurements in the open auger hole are made by sampling through attached Teflon tubing that is lowered down the hole to the desired depth (typically less than one inch above the bottom of the hole). Teflon tubing is recommended by the PID manufacturer to minimize VOC sorption losses to the tube walls. The internal pump of the PID draws the soil gas sample through the tube and into the ionization chamber. Care must be taken to avoid plugging the end of the tube with dirt and to avoid drawing water into the PID. The PID values typically drop through time as air from the atmosphere slowly dilutes the VOCs in the open hole, so the maximum value is recorded.

Retrieved soil samples were placed in sealable plastic bags and set aside for several minutes in a place somewhat warmer than ambient conditions in the ground. This allows the soil sample to degas volatile hydrocarbons that may occur as a fraction of hydrocarbons present as a free phase in the soil or sorbed to the soil minerals. All samples at a given site should be warmed similarly. Later, the tip of the PID inlet tube is carefully inserted into the partially opened plastic bag and

measurements made. The values typically start high and drop quickly as ambient air is drawn rapidly into the plastic bag. The maximum value is recorded.

Background measurements should be made at a site to determine the range of natural VOC levels in local soils. Organic matter in soils generates measurable VOCs, including many that are common to petroleum-contaminant sites (Dragun and Barkach, 1993). The Teflon tubing used to make downhole measurements may sorb VOCs from soil gas in a contaminated auger hole and then release them during subsequent measurements. Flushing of the tube with ambient air should be performed between soil gas measurements, especially after measuring high VOC samples. Ambient air may also yield slightly elevated VOC readings if volatile hydrocarbons are contributed from a nearby pit or tank or from aromatic plants at the site.

For an overview of hydrocarbon sampling in petroleum-contaminated soils see various papers in Calabrese and Kostecky (1993).

Although not attempted in this field study, our lab experiments suggest that volatile organic phases dissolved in water can be detected by collecting 750ml of water in a 1-liter glass container. A piece of plastic film is placed over the container opening, then the lid is screwed on. The sample is shaken for two minutes and then allowed to sit for two additional minutes to allow all of the bubbles entrained in the water to reach the headspace (a stop watch should be used). The jar is then carefully opened and the PID input port inserted in the jar headspace by poking a hole through the plastic film. The maximum value observed should be recorded. As with the soil gas sampling, readings to measure background hydrocarbon levels in waters should be made and sample bottle contamination should be monitored, perhaps using distilled water as a blank.

Evaluation of salts from produced water releases

This approach relies on field estimates of total dissolved ion concentration with a conductivity meter (fig. 3, appendix 1) and measurements of dissolved chloride concentration using chemical titrator strips (fig. 4, appendix 1). These measurements are made directly on water samples or on 1:1 (by volume) aqueous extracts of soils. We compared measurements of chloride in field samples using the chloride titrator strips to measurements of chloride of the same samples by ion chromatography and found excellent agreement (fig. 6).

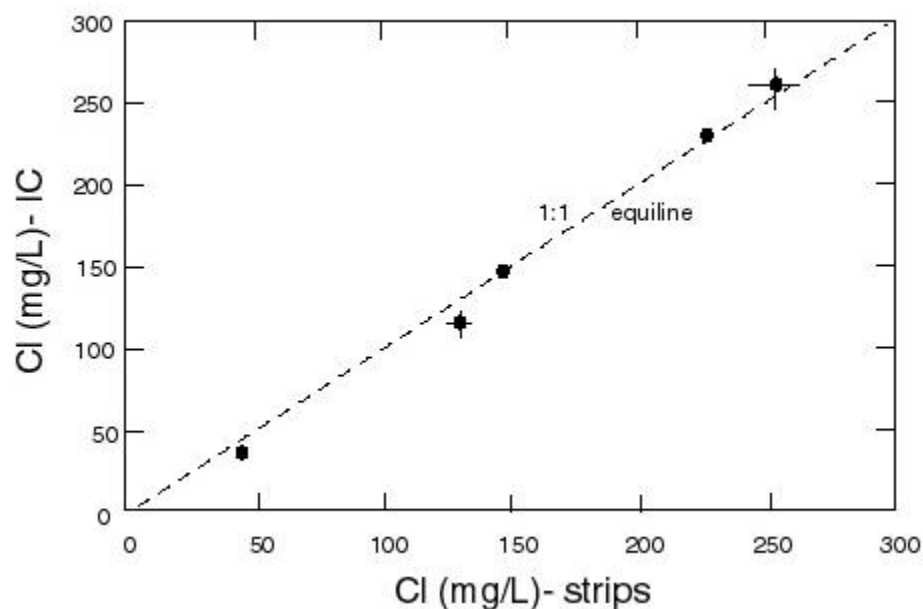


Figure 6- A comparison of chloride measurements of field samples by the chloride titration strips (x-axis) after filtering in the lab to chloride measurements by ion chromatography (IC, Y-axis).

If an active produced water source (pit water, flowing or leaky pipe, or other) is available, conductivity and chloride measurements should be made directly on these waters to establish reference chloride/conductivity ratios for the source. If the produced water is not available, water extracts of soils directly impacted by produced water releases, as indicated by visual inspection, can be measured instead. Waters and soils upslope from the produced water source should be measured to establish local baseline values, however, care must be taken to identify other possible sources of salts upslope from the studied site. At inactive sites, produced water remaining in brine ponds or other possible sources may be substantially diluted by rain or shallow ground water inflow.

For soil samples, a surface grab sample or subsurface auger sample is loosely packed into a small plastic jar and then transferred to a larger, screwtop, plastic jar. The small plastic jar is then filled with distilled water and the water poured in the larger jar. The mixture of soil and water in the larger jar is shaken for one minute and set aside for several minutes to allow the coarser particles of soil to settle out of the water column. Conductivity and chloride measurements are made on the liquid.

Evaluation for radioactivity (NORM)

The microRmeter (fig. 5, appendix 1) is a sensitive measuring device for gamma-rays. At oil and gas sites, it can be used to detect gamma rays from radium-bearing barite that is commonly precipitated from produced waters (Otto, 1989). It cannot detect radioactivity in the produced waters. It can also be used to detect the presence of radioactivity as ^{210}Pb and associated decay products that have plated out on the interior surfaces of gas production and processing equipment. Valves and elbows in gas gathering and processing equipment are typical places for accumulation of ^{210}Pb .

Since soils contain varying amounts of naturally radioactive isotopes of uranium, thorium, and their decay products including radium and radon, the background for the local site should be determined by making several measurements around the perimeter of the disturbed site. In making these background measurements, care should be taken to avoid other disturbed sites nearby, and to avoid making measurements downslope from the disturbed site where radioactive soil contamination may have moved. These background readings are noted in the site description. Equipment and soils at the site are then surveyed.

Since precipitates often fall to the bottom of tanks, the bases of all oil and water tanks are measured and information is recorded. Note that the tank wall will attenuate some of the gamma-ray intensity. The composition of the tank should be noted (i.e. steel, fiberglass, wood). A simple annotated sketch map in field notes allows these measurements to be documented systematically. Soils in pit bottoms (if dry), soils adjacent to water in pits, soils in and near places where water has been released from overflow pipes, and where water has moved downslope from a pit or tank are places to examine. Since water-saturated soils attenuate gamma-ray intensity compared to dry soils, water saturation should be noted, if present. Discolored soils, often indicators of oily sludge discarded on the surface, should be examined. Substantial areas of anomalous soil (greater than 50 percent above background) should be sketched. Bottoms of washes draining the site should be checked to detect radioactivity moving offsite in particulate matter.

A reclaimed site provides few visual clues as to where to investigate for anomalous radioactivity. The site should be crisscrossed systematically with the instrument held at hip level. An instrument with an audible signal is useful for this type of surveying. Soils with anomalous readings (greater than

50 percent above background) should be investigated closely. A trowel or small shovel should be used to remove the surface layers to determine if the radioactivity is coming from a more intense source below the soil surface.

BIG SOUTH FORK SITE STUDIES

In early November of 1999, the authors visited several sites in and adjacent to the Big South Fork National River and Recreation Area in northeastern Tennessee to test the assessment procedures described above (figs. 1 and 7). The Big South Fork National River and Recreation Area is on the Cumberland Plateau where it is deeply dissected by the Big South Fork of the Cumberland River and its tributaries. The area is underlain by generally flat-lying sandstone, shale, and limestone. Thick residual soils form on the ridge crests, thin soils on hillslopes, and colluvial and alluvial deposits of varying thickness occur on the toe of the valley slopes and on valley floors. Rainfall for the area is about 60 inches per year. Our visit was preceded by an extended period of below-normal precipitation and stream flows were at 60-year record lows.

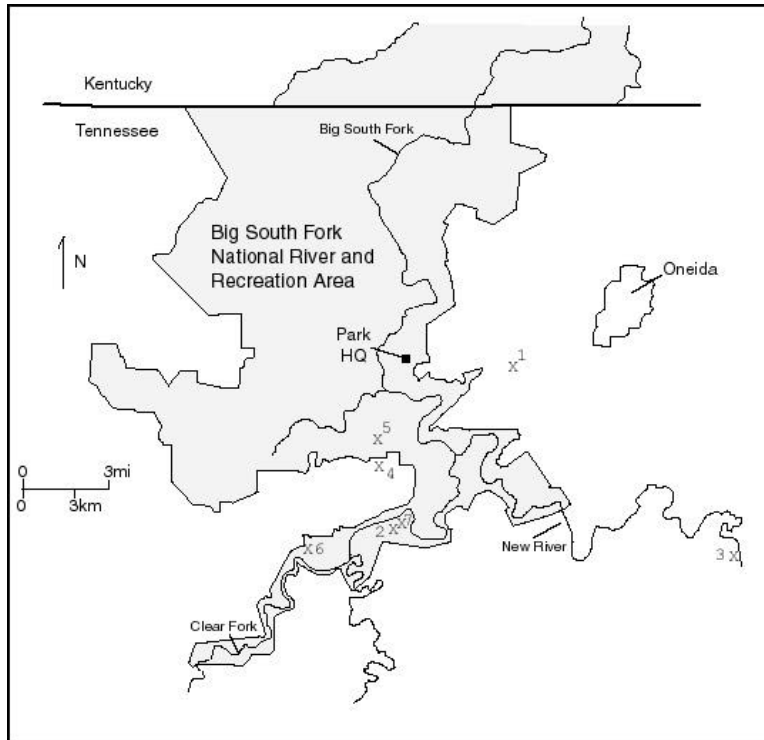


Figure 7- Detailed map of Big South Fork National River and Recreation Area showing some cultural features and study site locations (1 to 7) in and near the park unit.

Site BSF 99-1

This site lies along Pine Creek adjacent to a dirt road that follows an old railroad grade (fig. 7). It is in the Oneida South 7.5-minute quadrangle at latitude $36^{\circ}28'5.68''N$ and longitude $84^{\circ}35'17.11''W$. The site is about 1 mile upstream (east) of the Big South Fork National River and Recreation Area boundary. There is an active oil storage tank, an older pumping unit, and two abandoned tanks at the site (fig. 8A). Adjacent to the oil storage tank is a small pit about 12 feet by 23 feet formed by constructing a berm on the downslope side of the pit. During our visit we observed spilled oil on the soil surface extending from a valve at the base of the tank to the pit (fig. 8B). The pit had oil in it and, based on oil staining on the pit walls and a tree trunk, the oil level was about 12-16 inches below its apparent maximum after the spill event (fig. 8C). The pit had not overflowed.

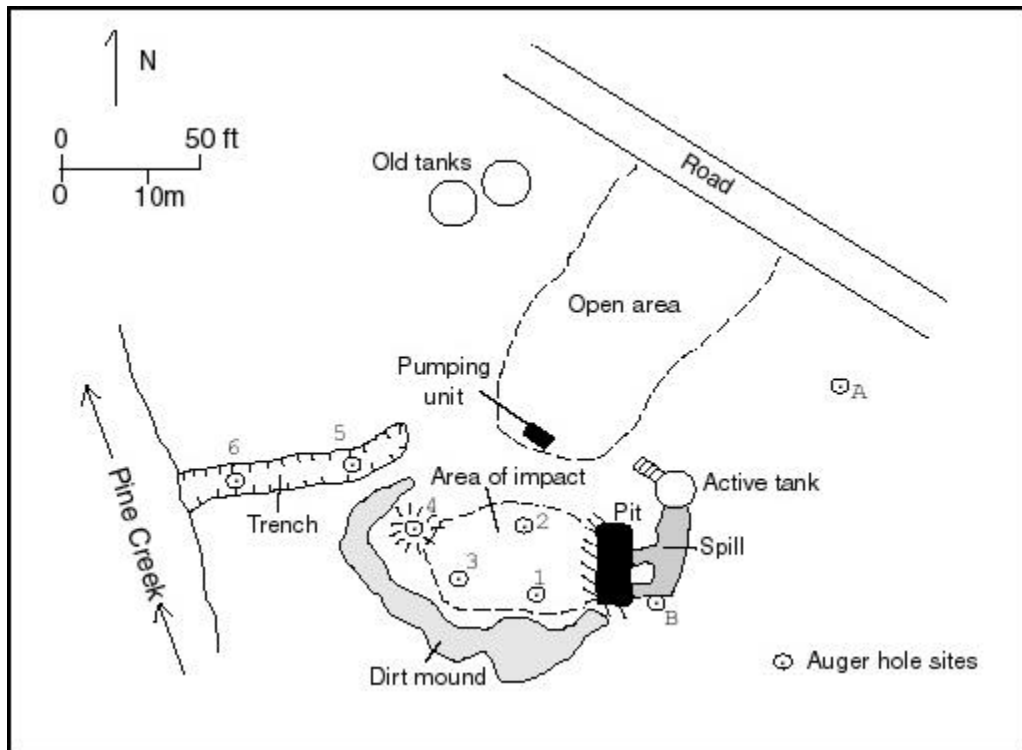


Figure 8A- Sketch map of study site BSF-1 along Pine Creek between Oneida and the east boundary of the park unit. Many features were measured with tape and compass. Site includes evidence of older operations (older large tanks, dirt mound, trench, and pit at site 4) which are heavily overgrown.



Figure 8B- View of active oil tank looking north at site BSF-1 showing spilled oil from tank on soil surface. Pit is just to the left of the view.



Figure 8C- View of oil in pit adjacent to active tank. Oil stains on the small tree mark a higher level of oil in the pit.

The tank and pit are located on the flood plain of Pine Creek. Between the oil-filled pit and Pine Creek is an additional much larger pit, several mounds of soil as much as 6 feet high, and a trench that leads down to the creek's edge (fig. 8A). This area of trenches, pits, and mounds is heavily vegetated. These features may represent older oil and gas production operations at this site. We augered one hole upslope from the tank and the pit (background site, A, fig. 8A; table 1), one hole adjacent to the spilled oil between the tank and the pit (B, fig. 8A; table 1), and 6 holes in the soil between the pit and the stream (1-6, fig. 8A; table 1). The following table shows data for these holes.

Table 1- Soil PID readings for Site BSF-1.

| Hole | Distance downslope from pit (feet) | TD for hole (inches) | Soil sample interval (inches) | Maximum soil PID reading (ppm) | Soil gas sample depth (inches) | Maximum soil-gas PID reading (ppm) |
|------|------------------------------------|----------------------|-------------------------------|--------------------------------|--------------------------------|------------------------------------|
| A | DNA | 33 | 29-33 | 0.3 | 32 | 3.5 |
| B | DNA | 33.5 | 0-11 (oil-stained) | 42.1 | 11 33 | 12.3 12.8 |
| 1 | 20 | 37 | - | - | 27 | 25.1 |
| 2 | 23 | 41 | 34-37.5 | 3.3 | 34 41 | 39.4 29.9 |
| 3 | 49 | 36 | - | - | 36 | 9.8 |
| 4 | 62 | 25 | - | - | 25 | 3.3 |
| 5 | 87 | 34.5 | - | - | 34.5 | 1.4 |
| 6 | 127 | 28 | - | - | 28 | 0.4 |

DNA- does not apply; ppm- parts per million

The authors also made field conductivity and chloride measurements in Pine Creek near the point where the trench leading away from the site encounters the creek. The trench was dry, however the pool of water right at the mouth of the trench showed *Leptothrix Discophora* at the surface and mild iron staining on sediment surfaces suggesting that reduced, iron-bearing ground waters were seeping into the creek at that point. The pool measured 290 microS/cm specific conductance and less than 30 ppm chloride. The main channel (middle) of Pine Creek measured 460 microS/cm and 43 ppm chloride. The main channel (far side) measured 440 microS/cm. Another pool close to the trench pool, but a little farther downstream, measured 260 microS/cm. Treated water from the Oneida sewage treatment plant released into Pine Creek upstream from our sampling points may be responsible for the elevated conductivity and chloride concentrations in the stream (Steve Bakaletz, National Park Service, oral commun., 1999).

Site BSF99-2

This site is located on the crest of a small ridge between Bear Creek and the Clear Fork of the Cumberland River in eastern Scott County (fig. 7). It is in the Honey Creek 7.5'-quadrangle at latitude 36°23'15.28" and longitude 84°39'45.21". The locality includes the site of an old tank battery, now removed, a new tank battery, an active pumping unit, and an area of remediated soil (fig. 9). There is no water production, however the oil has a high gas fraction. No anomalous radioactivity is present. Background radioactivity was about 3 µR/hr.

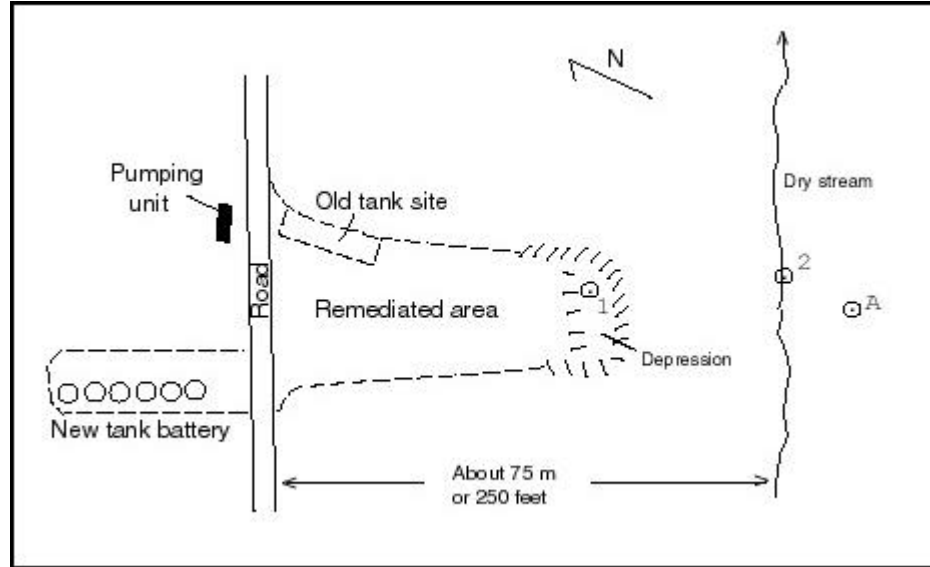


Figure 9- Sketch map of Site BSF99-2 showing local features, remediated area, and 3 localities where holes were augered (1,2,A).

About six years prior to our visit, lightning struck one of the tanks in the old tank battery. The gas in the headspace of the tank exploded and about 200 barrels of oil were released (fig. 9). This oil moved south downslope into the small stream, then into Bear Creek, and subsequently into Clear Fork (Steve Bakaletz, National Park Service, oral commun., 1999). The affected area immediately below the old tank battery was remediated by tilling the soil to a depth of 4-5 inches, fertilizing, then planting with winter wheat and winter rye (Steve Bakaletz, National Park Service, oral commun., 1999). Three holes were augered at this site: one in the low end of the remediated area in a small depression created by a low berm (1, fig. 9; table 2); a second in the floor of a small dry wash several tens of feet below the remediated area (2, fig. 9; table 2); and a third on the opposite hillslope (background site, A, fig. 9; table 2). At the site of hole 1 there were sedges growing suggesting that the site is damp at least part of the year. Soil in the upper 9 inches of the hole contained semisolid fragments of residual hydrocarbon, but no noticeable hydrocarbon odor. Below 12 inches a strong hydrocarbon odor was present. In hole 2 the soil was damp throughout but no hydrocarbon odor was noticed. Small pools of water were noted downstream from hole 2. On the hillslope above and below hole A sandstone ledges were observed and the soil was sandy.

Table 2- Soil PID readings for Site BSF-2.

| Hole | TD for hole (inches) | Soil sample interval (inches) | Maximum soil PID reading (ppm) | Soil gas sample depth (inches) | Maximum soil PID reading (ppm) |
|------|----------------------|-------------------------------|--------------------------------|--------------------------------|--------------------------------|
| 1 | 32 | 0-9 21-28 | 0.3 52.8 | 8.5 | 0.6 |
| | | | | 21 | 20.9 |
| | | | | 28 | 26.4 |
| | | | | 32 | 32.2 |
| 2 | 20 | - | - | 20 | 4.1 |
| A | 32 | - | - | 23 | 1.1 |
| | | | | 32 | 0.7 |

Site BSF99-3

This site is located along a small, unnamed stream on the west side of the New River just south of the town of Winona (fig. 7; fig. 10A). It is in the Norma 7.5'-quadrangle at latitude $36^{\circ}21'59.75''$ and longitude $84^{\circ}27'22.49''$. The site includes a pumping unit, two oil tanks, a separator tank mounted on top of one of the oil tanks, a pit filled with oil and water(?), and a smaller brine pit partly filled with water

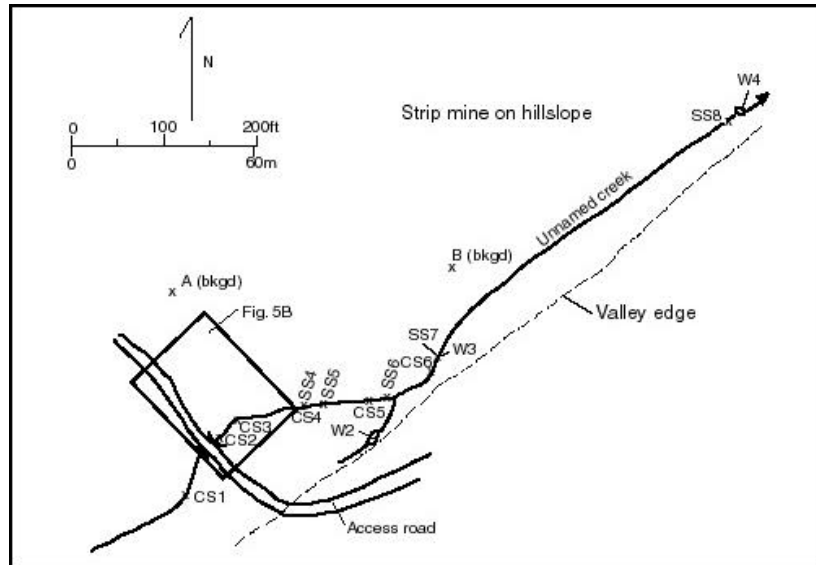


Figure 10A- Sketch map of Site BSF99-3 showing stream conductivity sample sites (CS1-6), soil sample sites (A, B, SS4-SS8), and water sample sites (W2-W4). Some sites are identical. Map is derived from topographic sheet for the site and tape and compass and pace and compass measurements of the site. Soil sample sites A and B are approximately located. Mapped valley edge marks the edge of the flood plain to the southeast. The edge of the flood plain to the northwest was not mapped.

(fig. 10B). The larger oil-filled pit is about 25 by 40 feet (fig. 10C). The pits sit on a hillslope about 10 feet above the level of the flood plain of the small stream. The soil on the hillslope below the two pits, and the soil on the flood plain between the toe of the slope and the stream is barren of vegetation (figs. 10B and 10D). The barren zone also extends across the flood plain beyond the stream channel, however immediately adjacent to the stream channel wetland plants are abundant. Several dead tree stumps lie at the toe of the slope. Oil has overtopped the larger pit and flowed downslope onto the flood plain of the stream. An oily sheen was present in a small pool adjacent to the active stream channel near the toe of the oil-stained soil.

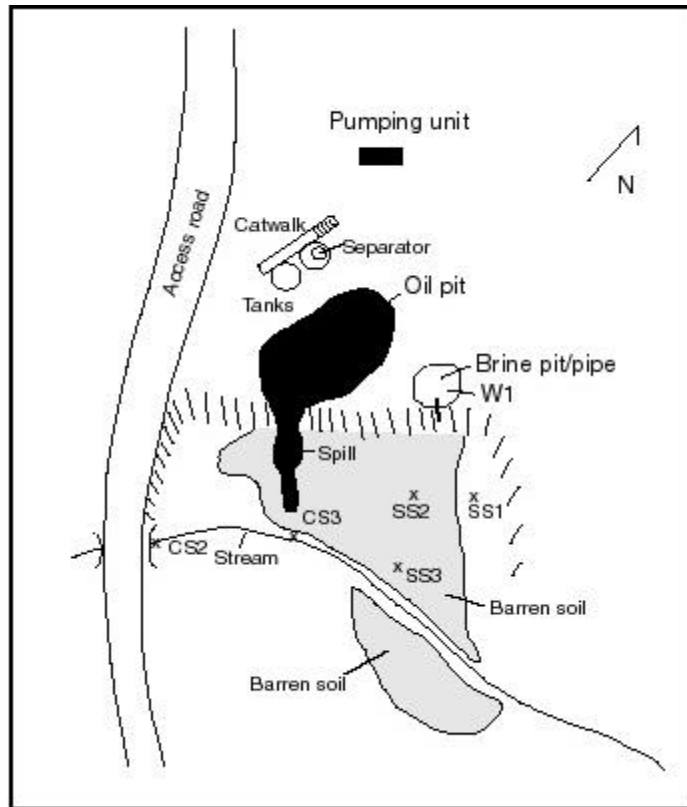


Figure 10B- Closeup sketch map of pit and tank area adjacent to stream (see figure 10A for location) showing stream conductivity sites (CS2-3), soil sample sites (SS1-SS3), and brine pit water sample site (W1). Most features are approximately located. The width of the area in the figure is approximately 100 feet (30m). Areas of barren (salt-scarred) soil are shaded. The site was abandoned at the time of our visit (November 1999).

The brine pit (fig. 10E) has a thick layer of *L. discophora* growing on the surface. *L. discophora* is a bacterium that grows on water surfaces where reduced iron is present in the water column. It forms a thin film on the water surface that superficially resembles an oil sheen except that the surface film breaks up into plates when disturbed and the film does not show the variable rainbow colors characteristic of thin oil films.

Background radioactivity for the site is 10 μ R/hr, apparently due to the underlying shale bedrock. No anomalous radioactivity was noted on the oil tanks or the separator. Mud surrounding the water in the brine pit read as much as 35 μ R/hr. Water from the overflow pipe for the brine pit has eroded a small hole in the hillslope. Sediment in the bottom of this hole was 120 μ R/hr. Soil on the flood plain below this hole measured 15-30 μ R/hr.



Figure 10C- Oil-filled pit at Site BSF99-3 (see figure 10B for location). Oil spilled from far edge of pit downslope onto the flood plain of the small stream.



Figure 10D- Salt-scarred soils and dead trees just downslope from the brine and oil pits at Site BSF99-3. Note strip of wetland vegetation growing along stream margin and barren soil area beyond. Lip of oil-filled pit is at lower left edge of photo. A small area of oil-stained soil extends from the lip of the pit onto the flood plain of the stream. Some oil has reached the stream and a sheen is present.



Figure 10E- Brine pit at Site BSF99-3 (see figure 10B for location). The oil-filled pit is to the right of the view. A small diameter pipe exits this pit from the opposite edge and passes through the wall of the pit. The water surface is unusually reflective because of the *Leptothrix discophora* colonies on the surface. Note persons at left edge of pond for scale.

Water conductivity measurements were made in the brine pit and in the stream at locations that extend upvalley from the site several tens of feet to locations several hundred feet downvalley from the site (figs. 10A and 10B). Field geochemistry measurements for water at this location are reported in Table 3.

Table 3- Specific conductance and dissolved chloride concentration in water samples from site BSF99-3.

| Sample | Distance from reference (feet) | Specific Cond. ($\mu\text{s}/\text{cm}$) | Cl (ppm) | Remarks |
|-----------------|--------------------------------|--|----------|---|
| Distilled water | DNA | 2.9 | - | Purchased at local store |
| Brine pit | DNA | 890 | 130 | Stagnant. W1 from this site |
| CS1 | +100 | 170 | - | Barely flowing |
| CS2 | +30 | 95 | - | Flowing, culvert outlet |
| CS3 | 0 | 90 | - | Flowing, oil sheen |
| CS4 | -70 | 90 | - | Flowing |
| CS5 | -140 | 95 | - | Flowing |
| Above SS6 | -180 | 90 | | Flowing |
| Side pool | DNA | 500 | 147 | Frogs in water. W2 from this site |
| CS6 | -210 | 120 | | Flowing |
| At SS7 | -245 | 405 | 50 | Flowing, ground water seeps with Iron. W3 from this site. |
| Below SS9 | -650 | 1500 | 219 | Pool fed by seeps. W4 from this site |

DNA- does not apply. $\mu\text{s}/\text{cm}$ - microSiemens/centimeter. ppm- parts per million

Soil samples were collected at two background sites (A and B, fig. 10A; table 4), in the salt-scarred area on the flood plain adjacent to the pits (SS1-3, fig. 10B), and in the stream valley below the site for several hundred feet (SS4-8, fig. 10A). Soil leachate data for the samples are given in Table 4. Distances noted are distances from the outlet pipe at the brine pit. Some stream water samples were collected adjacent to the soil sample sites (see tables 3 and 5).

Selected soil leachates and water samples from this site were subsequently analyzed in the laboratory for comparison to field data (table 5). Those samples measured with the chloride strips in the field were remeasured in the lab if the field data were within the range of the strips (<30 to >655 mg/l). All samples were measured for chloride and sulfate by ion chromatography (I.C.).

Table 4- Soil leachate data for site BSF99-3.

| Locality | Distance from brine outlet (feet) | Leachate field cond. ($\mu\text{s}/\text{cm}$) | Leachate chloride (ppm) | Cl/Cond | Remarks |
|----------|-----------------------------------|--|-------------------------|---------|--|
| A bkgnd | DNA | 56 | Assumed <30 | | Above site |
| B bkgnd | DNA | 195 | Measured <30 | | On flood plain downstream from SS7 |
| SS1 | 14 | 2800 | Measured >655 | | Reed and sedges |
| SS2 | 14 | 890 | 254 | 0.29 | Scarred soil |
| SS3 | 31 | 7400 | Assumed >655 | | Scarred soil adj. to stream |
| SS4 | 66 | 4600 | Assumed >655 | | Scarred soil adj. to stream |
| SS5 | 86 | 8400 | Assumed >655 | | Scarred soil adj. to stream |
| SS6 | 185 | 120 | Assumed <30 | | Entrenched stream, soil isolated from flow |
| SS7 | 260 | 5950 | Measured >655 | | Seep zone, reduced iron in sample |
| SS8 | 660 | 74 | Assumed <30 | | No surface flow, below land surface, just upstream from saline pool in Table 3 |

Bkgnd- background

Table 5- Laboratory data for water and soil leachate samples from Site BSF99-3

| Sample | Spec. cond. (uS/cm) field data | Cl-strip (mg/l) field data | Cl-strip (mg/l) filtered, lab | Cl (mg/l) I.C. lab | SO4* (mg/l) I.C.- lab | Cl/Spec. cond. | Cl/SO4 |
|---------------------------|-----------------------------------|-------------------------------|----------------------------------|-----------------------|--------------------------|----------------|--------|
| 1:1 soil leachates | | | | | | | |
| SS1 | 2800 | >655 | - | 935 | 650 | 0.33 | 1.44 |
| SS2 | 890 | 254 | 254 | 260 | 140 | 0.29 | 1.86 |
| B (bkgd) | 195 | <30 | - | 15.2 | 54 | 0.08 | 0.28 |
| A (bkgd) | 56 | <30 | - | 2.5 | 22 | 0.04 | .011 |
| | | | | | | | |
| Surface waters | | | | | | | |
| W1-Brine pit | 890 | 130 | 130 | 115 | 260 | 0.13 | 0.44 |
| W2-Side pool near SS6 | 500 | 147 | 147 | 140 | 134 | 0.28 | 1.05 |
| W3- At SS7 | 405 | 50 | 43 | 37 | 48 | 0.09 | 0.77 |
| W4- Below SS9 | 1500 | 219 | 227 | 229 | 161 | 0.15 | 1.42 |
| | | | | | | | |
| Blind rep. of W2 | | | | 141 | 132 | | |
| 100 ppm Cl standard | | | | 98 | n.d. | | |

*Sulfate data is less accurate because dilutions were optimized to measure chloride.
Estimated errors are +/- 5% for IC for most samples

Site BSF99-4

This site is in a small valley at the head of Potter Branch at the south end of Hurricane Ridge in western Scott County (fig. 7). It is in the Honey Creek 7.5'-quadrangle at latitude 36°25'13.52" and longitude 84°40'19.83". This gas production site shows no radioactivity above background (about 3 µR/hr) on equipment or soils. There is no water production at this site and no evidence of natural gas or natural gas condensate releases.

Site BSF99-5

This site is along Hurricane Ridge in the upper part of the drainage of the North Fork of Honey Creek (fig. 7). It is in the Honey Creek 7.5'-quadrangle at latitude 36°25'55.67" and longitude 84°40'21.20". Site consists of a tank battery with nearby pumping unit (fig. 11). No water production is associated with this oil production. The bermed tank battery has 4 oil storage tanks. The floor of the bermed area is covered with a thin layer of gravel. Each of 4 tanks has a

valve near the base on the side away from the road. The soil and the berm adjacent to these valves have been oil-stained in a pattern that suggests that oil has sprayed from the valves when opened. Oil-stained soil extends from the valves at the base of each tank to a distance of as much as 9 feet. We augered two holes in and near the oil-stained soil associated with the third tank (inset, fig. 11). This oil-stained soil patch included an inner zone of pooled oil at the surface.

Hole 1 was augered about 18 inches from the edge of the stained soil. Hole 2 was augered at the toe of the oil-saturated soil pool (inset, fig. 11). PID data are reported in Table 6.

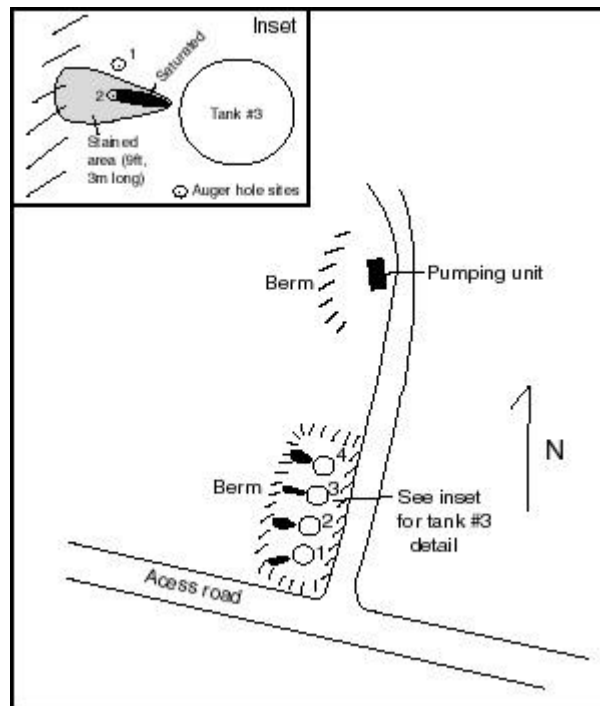


Figure 11- Sketch map of Site BSF99-5 showing tank battery and adjacent pumping unit. Width of the area in the figure is about 200 feet, however, features are not to scale. Inset- Closeup sketch of Tank #3 and adjacent soil area with stained and oil-saturated soils and auger hole locations. Features not to scale.

Table 6- Soil PID readings for Site BSF99-5.

| Hole | TD for hole (inches) | Soil sample interval (inches) | Maximum soil PID reading (ppm) | Soil gas sample depth (inches) | Maximum soil gas reading (ppm) |
|------|--|-------------------------------|--------------------------------|--------------------------------|--------------------------------|
| 1 | 30 (5-6 inches of gravel at top) | - | - | 30 | 0.2 |
| 2 | 16 (3 in. gravel at top, partly oil coated) | - | - | 11 16 | 4.1 5.0 |

- not sampled.

Site BSF99-6

This site is along a ridge just north of the Clear Fork in the upper part of the drainage of Joe Branch (fig. 7). It is in the Honey Creek 7.5' quadrangle at latitude $36^{\circ}22'51.73''$ and longitude $84^{\circ}42'57.47''$. This is an oil-gas production site that includes a pumping unit, an oil storage tank, and two small separator units (fig. 12). The background radioactivity is about $4 \mu\text{R/hr}$. No anomalous radioactivity was measured on soils or on any gas flow lines or other equipment.

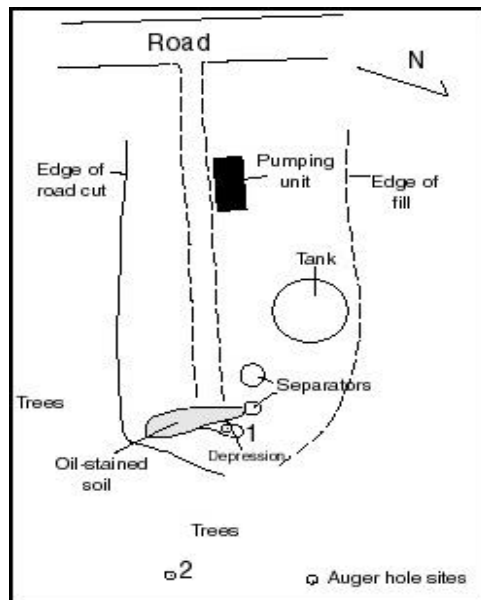


Figure 12- Sketch map of Site BSF99-6 showing tank and adjacent small separator units. Area of stained soil indicated by shading. Height of the area in the figure is about 100 feet.

A valve at the base of the smallest separator is a source for sprayed oil that stains adjacent soil in a zone 12-13 feet long and up to 3 feet wide. Saline water is also sprayed out with the oil. Near the downslope end of this oil- and brine-sprayed area is a small depression that at times has had standing water in it. We augered a hole in the middle of this depression (1, fig. 12; table 7). We also augered a hole at a background site in the wooded area about 40 feet east of this site (2, fig. 12; table 7). All soil samples taken from depths less than 20 inches. Soil leaches were performed at this site, no PID measurements were made.

Table 7- Soil leachate data for Site BSF99-6.

| Hole | Field cond. (microS/cm) | Chloride (ppm) | Remarks |
|------|----------------------------|-------------------|---------|
| 1 | 57 | Assumed <30 | |
| 2 | 41 | Assumed <30 | |

Nearby compressor station on the other side of the road includes compressor, multiple flow lines, and an old tank (downslope). No radioactivity readings on soil or equipment are above the local background of about 2.5 μ R/hr.

Site BSF99-7

This site is located on the crest of a small ridge between Bear Creek and the Clear Fork of the Cumberland River in eastern Scott County about 1200 feet eastnortheast of Site BSF99-2 (fig. 7). It is in the Honey Creek 7.5'-quadrangle at latitude 36°23'21.78" and longitude 84°39'31.35". The site consists of an open, reclaimed area about 175 by 150 feet, formerly the location of a sludge pit about 100 feet in diameter and several feet deep (fig. 13). Reclamation work, done in 1993 and 1994, included spreading of the sludge mixed with soil, lime (for pH adjustment), and Triple 12 fertilizer across the land surface and then tilling the surface. The site was planted in clover, winter wheat, and winter rye. Initial TPH analyses for composite soil samples at the site were in the 500-700 ppm range

(Steve Bakaletz, National Park Service, oral commun., 1999). Low, bermed areas occur at the north and south edges of the field where the slope drops off into stream valleys. No radioactivity readings are above the local background of about 3.5 $\mu\text{R/hr}$. No produced water was stored in the pit.

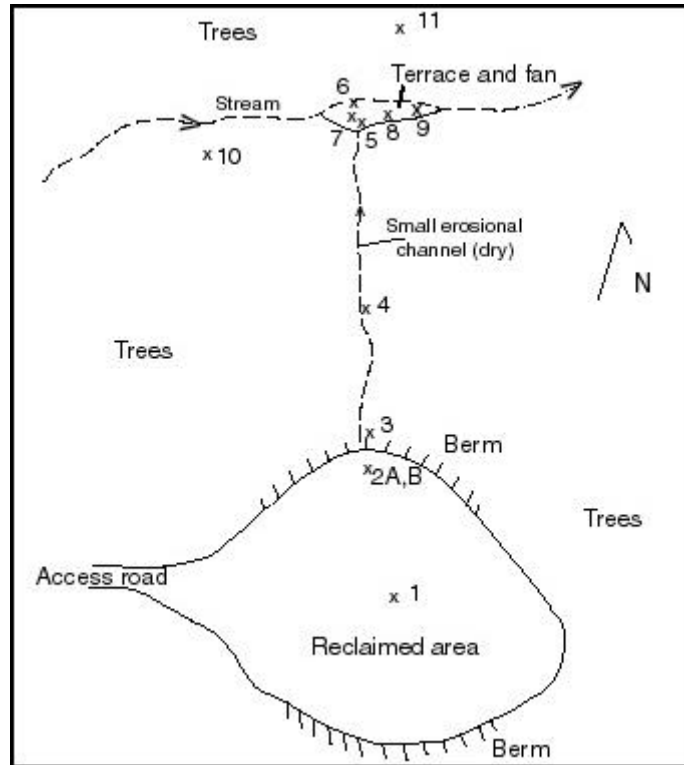


Figure 13- Sketch map of Site BSF99-7 showing reclaimed area, stream drainage to the north, and auger hole locations. A small erosional channel extends from the low, bermed north edge of the reclaimed area northward to the head of a small alluvial fan. This feature is believed to have been formed by sediment runoff from the site. Reclaimed area about 175 feet east to west and 150 feet north to south (pace and compass). Distance from center of reclaimed area to stream about 300 feet (measured from topographic map).

We augered a hole close to the center of the open area (1, fig. 13), two holes close together just upslope from the berm in the low spot along the northern edge of the reclaimed area (2A,B, fig. 13), one hole on the hillslope below the northern edge of the reclaimed area (3, fig. 13), one hole on the hillslope below the reclaimed area (4, fig. 13), five holes on a

small fan and stream terrace below the toe of the slope just above the valley floor (5-9, fig. 13), one hole on the north-facing slope but upvalley from the alluvial fan (10, fig. 13), and one hole in a background site on the south-facing slope (11, fig. 13). In picking hole sites downslope from the reclaimed area, we followed a natural drainage channel established by runoff from the site through a break in the berm (fig. 13). The small alluvial fan merges with a narrow terrace along the stream. The PID results for these holes are recorded in Table 8.

Table 8- Soil PID readings for Site BSF99-7.

| Hole | Location description | TD for hole (inches) | Soil gas sample depth (inches) | Max. soil gas PID reading (ppm) | Remarks |
|------|--|----------------------|--------------------------------|---------------------------------|---|
| 1 | Middle of reclaimed area | 34 | 32 | 0.2 | Refused at TD by bedrock. |
| 2A | Low, bermed area at north edge of reclaimed area | 12 | 11 | 0.1 | Hit WT at 12 inches. |
| 2B | 15 feet upslope from 2A | 16.5 | 16.5 | 0.2 | Refused at TD by bedrock |
| 3 | Just below berm at edge of reclaimed area | 18 | 18 | 0.2 | Refused at TD by bedrock |
| 4 | About halfway down slope to stream | 14 | 14 | 0.4 | Background at 0.2 ppm |
| 5 | At head of small alluvial fan | 16 | 16 | 9.8 | Refused at TD by bedrock |
| 6 | Toe of fan at toe of slope | 9 | 9 | 0.9 | Refused at TD by gravel/bedrock |
| 7 | Near head of fan- 4 ft from #5 | 16 | 16 | 0.2 | Refused at TD by bedrock. |
| 8 | Downvalley on fan/terrace | 23.5 | 23.5 | 13.9 | Hole TD just above WT. |
| 9 | Downvalley from #8 | 16 | 15 | 4.7 | TD just below WT. |
| 10 | On hillslope upvalley from reclaimed site | 21 | 21 | 1.8 | Away from area possibly affected by hc movement |
| 11 | On opposite slope from reclaimed site | 13 | 13 | 1.3 | Away from area possibly affected by hc movement |

WT- water table; TD- total depth

DISCUSSION AND CONCLUSIONS

Use of PID

Reconnaissance field measurements conducted by the authors at sites in and near the Big South Fork National River and Recreation Area suggest that a PID can be used to indicate elevated concentrations of VOC in soil gas and to trace movement of hydrocarbons related to spills and pit leakage at production sites. At Site BSF99-1 (fig. 7), the data indicate that hydrocarbons may have moved in the subsurface several tens of feet westward from an oil-filled pit. At Site BSF99-2 (fig. 7) the data suggest that hydrocarbons escaped the immediate vicinity of the site and that traces remain in the nearby stream drainage. At BSF99-7 (fig. 7), the data suggest that hydrocarbons likely escaped the oil waste storage pit and moved downslope into a stream drainage to the north.

PID data may also be used to assess the completeness of remediation at reclaimed sites. At Site BSF99-2, hydrocarbons remain in the soil profile in damp soils in a depressional area at the low end of the reclaimed site. The persistent dampness, as suggested by wetland plants, may prevent the oxygenation of the soils, slowing bacterial remediation of the hydrocarbons. At Site BSF99-7, which is sandier and better drained, no hydrocarbon traces remain at sampled sites within the reclaimed area.

The data suggest that downhole measurements of soil gas using a thin Teflon tube to extend the reach of the PID input port are more consistent in detecting hydrocarbons than soil samples brought to the surface and placed in baggies. Sorption of hydrocarbons on the walls of the tube must be checked by running background measurements on ambient air. However the baggy technique can provide significant additional information in many settings. At Site BSF99-6, hydrocarbons were confined to a surface layer. Since an open-hole measurement of hydrocarbons may be influenced by contamination from the surface layer, establishing the depth of penetration of free-phase hydrocarbons may require soil sampling at progressively greater depths and using the baggy technique.

Evaluation of individual site PID data

Site BSF99-1

At Site BSF99-1, the data (fig. 8A, table 1) demonstrate that hydrocarbons have moved downslope from the pit site towards Pine Creek. Soil gas VOC measurements above background extend as much as 49 feet from the edge of the pit (Hole 3- 9.8 ppm) and possibly as much as 62 feet (Hole 4- 3.3 ppm). The value

for Hole 4 (3.3 ppm) is indistinguishable from the upslope background sample A (3.5 ppm), however PID values for Holes 5 and 6 continue to drop below the site A background value suggesting that Hole A may not represent background for this lower, more sandy and gravelly part of the stream terrace. The extent and shape of the hydrocarbon contamination plume could be estimated by augering additional holes on a close-spaced grid and carefully contouring resulting PID values. Possible limits to the area of impact are suggested in figure 8A.

Site BSF99-2

At Site BSF99-2, the PID data (fig. 9, table 2) suggest that hydrocarbon remediation has not been complete at the lower end of the reclaimed area, however that finding could have been determined qualitatively by augering holes and smelling the samples for hydrocarbon odor. The PID value for the hole in the wash bottom (Hole 2- 4.1 ppm) suggests that hydrocarbons may still be present in the subsurface in the shallow alluvium along this drainage. Further checking along this drainage in places where hydrocarbons may have accumulated may be warranted.

Site BSF99-5

At Site BSF99-5 (fig. 11), volatile hydrocarbons in soil gas are not above background at depths of several inches at a distance of 18 inches from the margin of the stained soil surface. This suggests that neither hydrocarbons nor VOCs have moved laterally from the margins of the pooled oil. PID readings at depths of 11 and 16 inches at the edge of the pooled oil show above background readings. The downhole readings may be influenced by VOCs given off by oil in the surface moving downward during sampling. We would recommend, in hindsight, that a bagged soil sample be taken and measured under these circumstances to see if free or sorbed hydrocarbons are present in the soil at depth.

Site BSF99-7

PID readings at Site BSF99-7 (fig. 13) indicate that hydrocarbons at the reclaimed site have been effectively remediated to background levels within the soil profile, however our aerial coverage of the site was limited. There are no apparent traces of hydrocarbons above background in the soil profile at site 1 in the middle of the reclaimed area, at the low end of the reclaimed area where the water table is near the surface (sites 2A and 2B), nor on the downhill slope to the north of the reclaimed site (sites 3 and 4).

Volatile hydrocarbons at above background levels were detected in the small alluvial fan and associated stream terrace at the base of the slope below the north edge of the reclaimed area (Sites 5,8, and 9). Hydrocarbons from the site moved downslope and accumulated in the shallow sediment along the

stream margins. The nature of this movement is unknown, but it could have occurred as surface flow of oil, surface water carrying dissolved hydrocarbons, or shallow ground water carrying dissolved hydrocarbons. Additional measurements downstream from this locality seem warranted.

Soil gas PID readings in auger holes on the fan and terrace gave highest readings at depths just above the level of standing water in the lower part of the hole. This suggests that sensitivity to VOCs is increased if downhole measurements can be made immediately above saturated ground. Humidity can lead to spurious high readings under these conditions if care is not taken to keep condensing moisture out of the ionization chamber. The PID did not measure above-background hydrocarbons in Hole 2A (fig.13) where sampling was done about 1 inch above the shallow water table.

Use of field conductivity meters and chloride strips

In areas of known or suspected impact by saline produced water, elevated values of specific conductance (ion concentration) in waters or soil extracts may be sufficient to document contamination. Additional measurements of dissolved chloride provide confirmation that waters or soil extracts have a high ratio of chloride/conductance (Cl/Cond) compared to local background samples. High ratios of Cl/Cond are characteristic of dissolved salts in produced water. Chloride measurements can be particularly diagnostic if suspected contaminated samples have only marginally elevated conductance, or it is necessary to distinguish produced water impacts in areas where background conductance values are high, but background ratios of Cl/Cond are low.

A generalized plot of dissolved chloride concentration versus specific conductance illustrates how these two parameters can be used to identify waters and soils impacted by chloride-rich produced water (fig. 14). Waters and soil extracts from background areas plot near the origin and scatter about a best fit line that has a slope (X) defined by the Cl/Cond ratio of local soluble salts. Evaporative concentration of natural salts or further buildup of dissolved salts related to natural water/rock, water/soil interactions should produce an array of points that scatter about an upward extension of the line of slope X (Hem, 1995). In contrast, chloride-rich produced waters or highly saline soil extracts from areas affected by produced water spills plot far removed from the origin and scatter about a more steeply sloping line (Y) that reflects a much higher Cl/Cond ratio of soluble salts. Initial dilution of chloride-rich waters or soil salts with chloride-poor natural water and

salts produces an array of points scattered along a downward extension of the line of slope Y. As chloride-dominated water and salts become even more diluted, the resulting mixtures plot along linear mixing lines that connect chloride-rich and chloride-poor end members. A zone of mixing encompasses all possible mixing lines that could be drawn (fig. 14). Mixed waters or soil extracts that have high Cl/Cond ratios compared to background samples should plot in the zone of mixing, generally well above the extrapolated trend line defined by natural background samples.

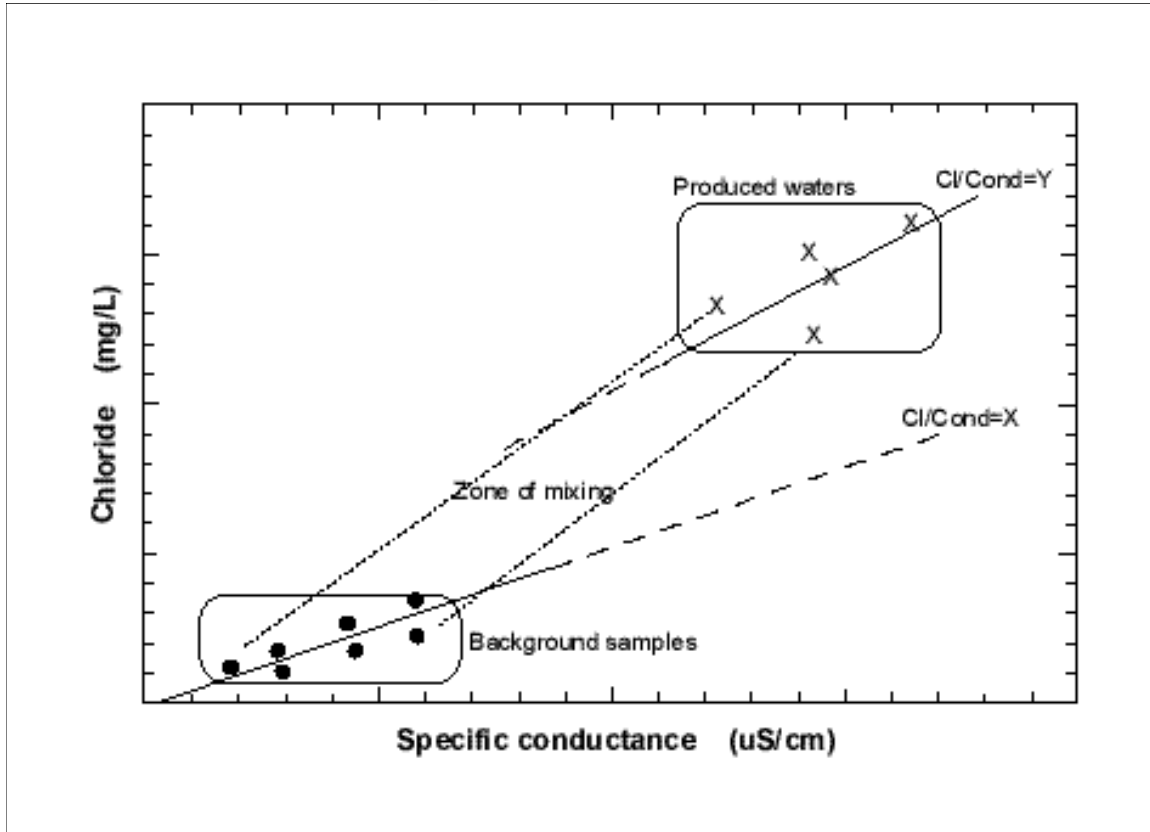


Figure 14- Generalized plot of specific conductance versus chloride concentrations showing where background, produced water, and mixed soil and water samples may plot at a site under investigation. Best fit lines for produced water and background samples are shown.

A similar plot that includes data for water and soil leachates from site BSF99-3 (table 3, figs. 10A, 10B) is shown in figure 15. A trend line for background samples is drawn through points representing extracts of background soils (A and B) located away from the production site and the stream valley. The water sample W3 falls on this trend line. Samples of stream water that were monitored for conductance only (CS1-CS6, table 3) have conductances that are uniformly low (90-170 $\mu\text{S}/\text{cm}$) and

that fall between the conductance values for A and B. The lack of elevated conductance values in the section of stream near the production site indicates that at the time of sampling the site was not a source of salinity to surface water. Water sample W1, collected from the brine pit, plots very close to the extrapolated trend line for natural samples. This surprising result indicates that, at the time of sampling, the pit water contained naturally derived salts that were concentrated by evaporation or water/soil interaction. Water samples W2 and W4 collected at sites of ground water seeps plot slightly above the proposed trend line for natural samples. In the absence of background samples of shallow ground water, marginally elevated chloride concentrations in W2 and W4 could be interpreted as falling within the range of scatter of evolved natural ground water compositions.

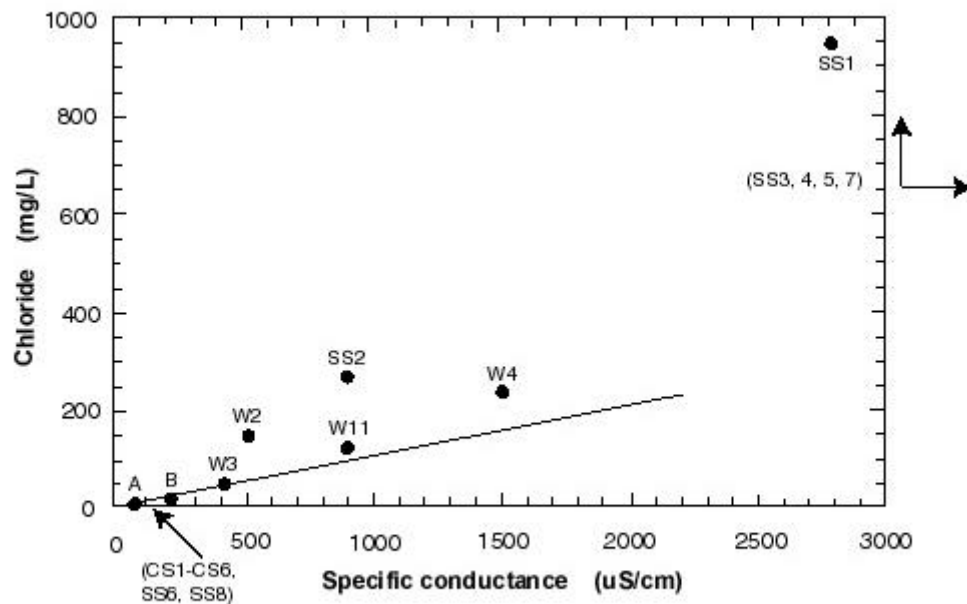


Figure 15- Plot of conductance versus chloride for soil extracts and water samples for Site BSF99-3. Best fit line for background samples is shown.

Clearer evidence of contamination by a chloride-rich salt assemblage is provided by some of the soil extracts. As expected, obviously saline soils on the flood plain adjacent to the production site (SS1, SS2) have elevated ratios of Cl/Cond. (table 3, fig. 15). Other soil extracts at the site (SS3) or along the stream bank from 30 to 260 feet downstream of the site

(SS4, SS5, SS7) have highly elevated conductances that range from 4600-8400 $\mu\text{S}/\text{cm}$ and chloride concentrations that exceed the upper range of the chloride strips (655 mg/L). Predicted chloride concentrations in these samples exceed 1000 mg/L based on a laboratory determination of 940 mg/L chloride in relatively "fresh" soil extract SS1 (2800 $\mu\text{S}/\text{cm}$). These high conductance samples plot off figure 15 and have chloride concentrations that place them well above the extrapolated trend line for natural samples. Contamination of stream bank sediments with chloride-rich salts is spotty because SS6 and SS8 have specific conductances of only 120 and 74 $\mu\text{S}/\text{cm}$. Sediments marginal to the stream channel probably contain chloride-rich salts supplied when wetter conditions permitted surface runoff or ground water recharge from the area of the production site. Dryer conditions allow salts to be retained in some patches of stream margin sediments and promote near surface concentration of salts through evaporation. The dry period that preceded sampling undoubtedly facilitated the detection of salts in surface soils. In wetter environments the detection of introduced salts may need to concentrate on deeper levels in the soil profile or sampling of shallow ground water.

Use of microRmeter

In and near the Big South Fork National River and Recreation Area, oil and gas production sites and reclaimed sites examined by the authors show no radioactivity above background where there is no water production. Background radiation at sites ranged from about 2.5-3 $\mu\text{R}/\text{hr}$ on sandy soils underlain by sandstone bedrock to 10 $\mu\text{R}/\text{hr}$ on clayey soils underlain by shale bedrock.

One site investigated by us, Site BSF99-3, has significant water production (about 4 barrels of water per barrel of oil; Jeff Laxton, Tennessee Department of Environment and Conservation, Division of Geology, oral commun., 1999). Radioactivity was not detected in the separator and storage tanks in the tank battery nor in the flow lines leading away from the separator as is often the case at sites studied by us (Otton and others, 1997 a,b,c). Instead, elevated radioactivity (35-120 $\mu\text{R}/\text{hr}$) was only found surrounding the brine pit and below the outflow pipe from the brine pit. We speculate that local produced water has insufficient dissolved barium to form barite (barium sulfate) precipitates in the production equipment. It is these precipitates that typically incorporate dissolved radium present in produced waters. As produced water enters the brine pit, barite begins to precipitate because barium is

supplied from the soils hosting the brine pit. Coprecipitation of radium with relatively dense barite ($\delta = 4.50$ g/cc) is supported by the observation that the highest radiation readings (120 μ R/hr) occur in a small depression formed immediately beneath the end of the outflow pipe from the brine pit. Based on the elevated radioactivity of the margins of the brine pit, we also predict elevated radioactivity in the bottom sediments of the brine pit.

The μ R levels seen in soils at Site BSF99-3 suggest that the standard for radium in soils proposed by some states (5 pCi/g; Gray, 2000) may be exceeded. Radioactivity levels at other sites in and near Big South Fork could be higher if there are sites where water is produced and scale is forming in equipment. Gas-processing equipment was not found to be radioactive suggesting that radon-222 is not a significant component of the natural gas at sites examined by us or that, if radon is present, its decay product, lead-210, is not plating out on equipment surfaces.

Conclusions

The methods described in this study provide rapid, real-time measurements that can be used to assess the dispersion of contaminants from oil and gas E&P sites and to prioritize sites for further, more detailed evaluation or remediation. The equipment is cheap to rent or buy. It is easily portable and field rugged. Reconnaissance measurements can be made at several sites in one day. However, sampling is limited to the surface and shallow subsurface accessible with a soil auger.

The findings at site BSF99-1 and site BSF99-7 suggest that if oil is pooled in pits or behind retaining structures of various types for any length of time, it can seep into the soil and move with the ground water. If the soil and its substrate are sufficiently permeable (alluvial sand and gravel as at BSF99-1, sandy soils developed on sandstone bedrock as at BSF99-7), then oil can move significant distances, tens to a few hundreds of feet.

Remediation for hydrocarbons at two sites (BSF99-2 and BSF99-7) seems to have been successful. Some hydrocarbon remains in poorly drained, poorly oxygenated soils at the low end of Site BSF99-2. Hydrocarbon traces appear to extend downslope beyond the limits of remediation at Sites BSF99-2 and BSF99-7. At Site BSF99-2, crude oil reportedly flowed a considerable distance down stream from the site and traces of this crude oil may still be present along the affected stream reach. At Site BSF99-7 the data indicate that crude oil or soluble crude oil fractions may have moved downslope, possibly

in the shallow ground water, during the life of the oil waste pit. The stream drainage south of the reclaimed area should be checked.

Interbedded sands and shales are common at the surface in many areas of oil and gas production in the U.S., thus we believe that this study suggests reasonably broad applicability of the techniques. There are however, many areas where the soil characteristics, rainfall, and other parameters are different. These areas should be evaluated.

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Appendix 1- Field equipment/supplies used during this study*

RAE-2000 Photoionization Detector
RAE Systems
1339 Moffett Park Drive
Sunnyvale, CA 94089

Ludlum Model 192 MicroR meter
Ludlum Measurements, Inc.
501 Oak Street / P.O. Box 810
Sweetwater, TX 79556

Portable conductivity meter
Markson Science
P.O. Box 35375
Newark, NJ 07019-53575

Chloride test strips
Quantab titrators Cat. #27449-00
30-600 ppm range, also available in 300-6000 ppm range
HACH Company
P.O. Box 608
Loveland, CO 80539-0608

Soil auger
2 ¼" diameter general purpose soil auger- threaded, stainless
steel bit, cross handle, and 3 foot extension rods
AMS Supplies
105 Harrison
American Falls, ID 83221

* Mention of equipment used during this study is for information only and does not imply endorsement by the U.S. Geological Survey. Instruments and equipment sold by other manufacturers may achieve the same results.