MONITORING OF SOIL AND GROUNDWATER QUALITY

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Summary

Contamination of soil originates from numerous sources such as indiscriminant dumping of materials, bankrupt and abandoned manufacturing plants, insufficient waste storage, treatment and disposal facilities. Methods for characterization and monitoring site contamination have developed substantially throughout the 1990s. The quality of data has increased and costs have decreased, thus enabling a more complete understanding of site conditions. Common methods of detection include monitoring wells, and chemical analysis of soil samples at various soil depths. Samples should then

be analysed by atomic absorption (AA) or inductively coupled plasma – atomic emission spectrometry (ICP-AES) for metals. Analysis by high performance liquid chromatography (HPLC) or gas chromatgraphy (GC) is performed for organic pollutants after extraction with organic solvents. On site analytical methods include colorometric indicator tests, fiber optic chemical sensors, infrared spectroscopy and X-ray fluorescence. Geophysical technologies have recently been adapted for hazardous waste sites and indirect detection of aqueous and nonaqueous phase contaminants such as LNAPLs and DNAPLs. At hazardous waste sites, buried drums and other structures that are sources of contamination can be detected. Electrical conductivity, electromagnetometry and to some extent ground penetrating radar can directly detect contaminants by determining changes in soil conductivities by the chemicals. Others including magnetometry, seismic reflection and refraction, and gamma logging are able to identify subsurface characteristics that provide pathways for contaminant movement. Biomonitoring is used to monitor toxicants in the environment. The biomonitors can be based on biochemical or molecular changes in organisms due to the presence and bioavailability of pollutants in the environment. In general, the monitor must be specific and understandable, be responsive to changes in the environment and ecosystems, simple and inexpensive. In the future, monitoring of species, their diversity, abundance and composition can lead to the development of further methods of biomonitoring.

1. Introduction

Contamination of soil originates from numerous sources. In the late 1970s, improved methods of detection enabled contaminants at parts per billion levels to be identified in the environment. Indiscriminant dumping of materials, bankrupt and abandoned manufacturing plants, insufficient waste storage, treatment and disposal facilities led to discovery of many contaminated sites in the 1970s. In the United States, two hazardous waste laws, RCRA and CERCLA, were enacted to ensure that waste generators were responsible for long term impacts due to their waste handling procedures.

Although regulatory agencies classify wastes according to their sources, for remediation purposes, it is more appropriate to classify them according to the following since it allows similar compounds to be grouped together:

- Whether they are in liquid or solid form
- Whether they are organic or inorganic
- According to the type of chemical (solvent, heavy metal, alkali, acid, etc.)
- According to the most hazardous form (hexavalent chromium as opposed to trivalent chromium).

Major categories would include inorganic aqueous waste (heavy metals, acids/alkalis, cyanide), organic aqueous waste (pesticides), organic liquids (solvents from dry cleaning), oils (lubricating oils, automotive oils, hydraulic oils, fuel oils) , inorganic sludges/solids (lime sludge, chromium dust from metal fabrication, sludges from mercury cells used in chlorine production) and organic sludges/solids (painting operations, tars from dyestuffs intermediates). Other sources of DNAPL are shown in Table 1. Waste generated from manufacturing usually correlate with production. Most waste originates from cleaning of equipment, accident spills and leaks, residue in used containers and outdated materials. Smaller generators of waste include landfills that are improperly managed, automobile service establishments, maintenance shops and photographic film processors. Household wastes that include pesticides, paint products, household cleaners and automotive products can also contribute significantly as sources. Technologies are thus required to remove these wastes that have contaminated the soil.

Industrial manufacturing sources	Disposal sources
Wood preservation	Underground tank storage
Coal gas plants	Drum storage
Pesticide and herbicide manufacturing	Solvent loading and unloading
Electronics manufacturing	Landfill disposal
Dry cleaning	Lagoon or ponds
Transformer oil production	Tool and die operations
Steel industry	Metal cleaning/degreasing
Pipeline compressor stations	Paint stripping

Table 1. Sources of DNAPL contamination

DNAPLs are hydrocarbons that have a density higher than water. Examples include wood preservative wastes, coal tar wastes, chlorinated solvents and pesticides. They are difficult to detect and do not degrade easily. Their components slowly dissolve in the groundwater. Their movement is difficult to predict due to the presence of cracks in bedrock and sand layers. Common methods of detection include monitoring wells, chemical analysis of soil samples at various soil depths, soil borings and cone penetrometry. These methods can create new pathways for DNAPL movement through drilling. Methods for characterization and monitoring site contamination have developed substantially throughout the 1990s. The quality of data has increased and costs have decreased, thus enabling a more complete understanding of site conditions.

1.1 Sampling and monitoring

Soil samples are obtained as disturbed or undisturbed samples. Disturbed samples are obtained mainly by split barrel samplers. These types of samplers are used to obtain samples for chemical analyses. Soil gas surveys can also be performed to indirectly determine the level of VOCs in the groundwater since highly volatile components will volatilize from the groundwater into the voids in the soil. This is a less expensive method than installation of monitoring wells for groundwater. Samples can be taken within 152 cm of the water table for clay soils and 30.5 cm for sandy soils and then analysed by GC.

To obtain groundwater samples for subsequent analysis, monitoring wells are used (Figure 1). Conductivity and pH can also be monitored in situ by the monitoring well. The well should be placed out of the contaminated area to avoid causing the contaminants to migrate due to the drilling. There are numerous protocols that exist for sampling and monitoring of groundwater. After installation of the monitoring wells and sampling of the groundwater, samples can then be analysed by numerous techniques such as GC-MS.

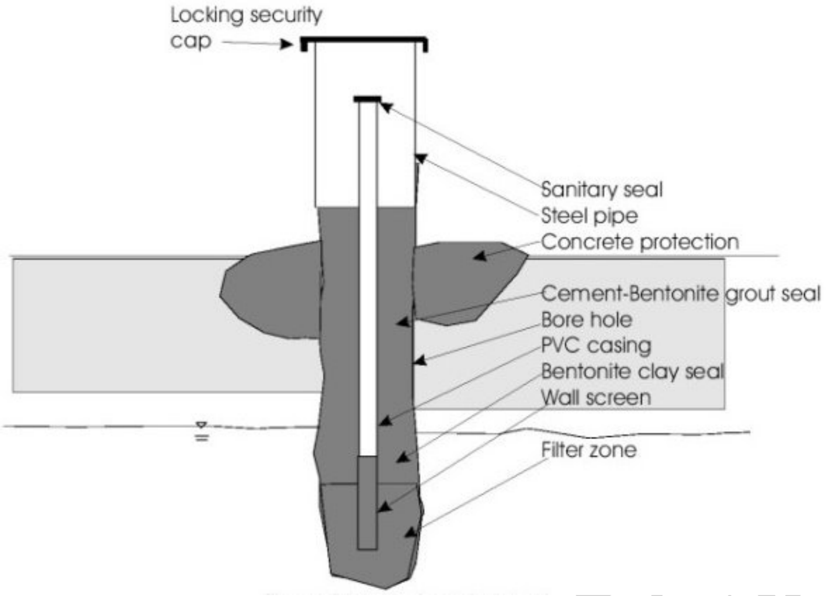

Figure 1. Schematic of a monitoring well

Since soil is a sink for many pollutants and a filter for groundwater due to its sorptive capacity, soil monitoring is essential. However, the composition of the soil does not need to be monitored frequently since concentrations will not change as frequently as in water. The main problem with soil is its heterogeneity, causing variations in the background composition. Thus, numerous samples are required.

If analysis for atmospherically deposited contaminants is required, samples must be taken in the 5 cm of the topsoils. If the soil is to be monitored to determine the effect of the use of sewage sludges, fertilizers and manures, samples of depths up to 15 cm will be taken.

Domestic gardens should also be monitored due to their use for vegetable growth and a potential play area for children. Surface areas will be exposed to atmospheric pollutants. Other sources of contaminants include burial of metallic scrap, ash from coal fires, used engine oil, paint scrapings from windows, and other household and garden chemicals. Samples should be from 0 to 15 cm and even from 15 to 30 cm at random sites.

Lots and abandoned lands are analysed to determine if contamination is present and at what level, particularly if the land is to be resold or redeveloped. Numerous housing areas have been built on not previously investigated hazardous waste sites such as Love Canal, NY. Samples should be taken down to several meters at several locations following a grid.

Samples should then be analysed by AA or ICP-AES for metals after drying, screening for through 2 mm and homogenization. Digestion is then performed with a concentrated acid such as nitric acid, nitric acid/hydrochloric acid, or nitric/perchloric acids. Analysis by HPLC or GC for organic pollutants after extraction with organic solvents.

2. Chemical analyses

2.1 Colorimetric indicator tests

Colorimetric tests are based on chemical reactions that produce a color to indicate the presence of contaminants. These tests can be used for a variety of applications including health and safety monitoring to extensive site characterization. They are quick, portable, easy to use, of low cost, and useful for a wide variety of contaminants. Some tests indicate only the presence of contaminants, whereas other can provide semiquantitative indications of contaminant concentrations. More sophisticated tests require more experienced operators. Several tests have been approved by the EPA including EPA method 8510 for RDX in the soil, method 8515 for TNT in soil by colorimetric screening, method 9078 for screening of PCB in soil and method 9079 for screening of PCB in transformer oil.

Indicator tubes are for the analysis of air and gases. Air is drawn through the tube containing a reagent sensitive to the contaminant. If the contaminant is present, the tube's reagent layer will change color. They can be used to indicate contaminants in soil gas at hazardous waste sites such as at the top of a monitoring well or at any other location to detect gases from soils. They are qualitative or semi-quantitative and are used at temperatures from 0 to 40^{o}C and relative humidities of 10 to 90%. Equipment includes the tubes and a hand pump to deliver specific quantities of air to the tubes. Indicator kits are used for up to 300 industrial gases, solvents and other vapors of organic or inorganic nature. Detection limits are in the ppm range for most tubes although some can reach the hundreds of ppb range. No calibration is required for this method as long as the appropriate air volume is drawn into the tube.

Reagent kits are designed for analysis of water. Thus kits for solids such as soil contain solvents to extract the contaminants from the soils for subsequent analysis. The equipment required for each kit can vary widely from a color wheel or chart to an electronic spectrophotometer to detect color change. Most kits include containers, reagents and calibration standards. Reagent kits can be used for individual or general classes of compounds. Some contaminants detected by the kits include PCBs, polyaromatic hydrocarbons (PAHs), various oils and fuels, benzene, toluene, ethylbenzene and xylenes (BTEX), trihalomethanes, and explosives such as trinitrotoluene (TNT), RDX and HMX.

Understanding what components can interfere with the results of the kits is very important. For example, relative humidity can interfere with the results of indicator tubes. Manufacturers will list such interferences. For the reagent kits, detection limits are dependent on the type and contaminants and the media from which the contaminant is found. For example for the Hanby tests, the analytical range for various petroleum fuels are in the 1 to 1000 mg/kg range for soil and 0.1 to 20 mg/L in water. The Envirol Quick test works for 1.5 to 90 ppm for PCP in soil and water, 3 to 100 ppm for TNT in soil and 1 to 3,000 ppm for PAHs in soil.

The major advantage of the indicator kits is that they are easy to use with a minimal amount of training. The tubes and kits are available for many classes and types of contaminants. Most kits are portable and can run with batteries, if necessary. Results are much quicker than by laboratory analysis and usually less expensive.

2.2 Fiber optic chemical sensors

Chemical sensors involve the use of a transducer to determine the presence of particular chemicals. Fiber optic chemical sensors, in particular, transmit light by wavelength or intensity to indicate the chemical in the environment near the sensor. Sensors can be extrinsic or intrinsic. For example, a laser induced fluorescence cone penetrometer is extrinsic since it uses the laser induced fluorescence for transport to a detector. Others have a chemically selective layer on a portion of the optical fiber for direct detection of the chemical. The change in the chemical layer causes a change in the light characteristics of optical fiber.

There are two parts to the optical fiber, the core with a refractive index of 1.6 for glass and the cladding with a different index such as 1.5. Plastic fibers have a core of polymethacrylate with a refractive index of 1.5. For the coating-based sensor, a portion of the cladding is replaced by a coating that can adsorb the organic contaminant reversibly. This adsorption causes the refractive index of the coating to change so that less light is produced by the light emitting diode (LED). The amount of light lost is directly proportional to the chemical concentration.

Numerous chemicals such as BTEX, chlorinated VOCs, TCE, PCE, and carbon tetrachloride in soil gas have been determined by fiber optic chemical sensors. In situ measurements can be performed in monitoring wells for groundwater analysis. Most sensors determine total VOCs. In some cases semivolatile VOCs can be determined. Various light sources and detectors can be used. Light sources are usually LED or dye lasers while detectors are photomultiplier tubes, photodiodes or photon counters. Usually the detection limit is about 1 ppm of VOCs in water. Calibration standards are used for calibration.

Overall, these types of sensors can be used for in situ monitoring. They are small in size, easy to use, portable and the results can be transmitted long distances from the deep wells that are monitored. Thus monitoring can be done at hazardous sites. However, this method can only provide a total VOC concentration, not individual VOCs. Temperature sensors should also be added since the sensor is dependent on the temperature. The probes also need to be regenerated over time. Costs depend on the design and accessories of the instrument.

2.3 Gas chromatography

Gas chromatography (GC) involves the separation of complex mixtures of thermally-stable contaminants by transportation by an inert gas through a column containing a stationary phase. The inert gas is called the mobile phase and does not react with the chemicals to be analysed. The mobile phase is helium, nitrogen or hydrogen. The stationary phase interacts with the contaminants to enable their separation. This stationary is silica material coated or covalently bonded with an organic liquid. Components with a high affinity for the stationary phase move much slower than those with little affinity. The components can then be determined qualitatively and quantitatively after they pass by the mobile phase through a detector. A chromatogram is plotted.

Method	Detector
Phenols Method 8041	FID or ECD
Phthalate Method 8061A	ECD
Amines Method	NPD
Chlorinated pesticides Method 8081A	ECD
PCBs Method 8082	ECD
PAHs Method 8100	FID
Chlorinated hydrocarbons Method 8121	ECD
Volatile organic chemical s Method 8240	FID
Organophosphorus compounds Method 8141A	NPD or FPD
Chlorinated herbicides Method 8151A	ECD
MTBE Method 8260	MS
Halogenated VOC Method 8260B	MS
SVOCs/base neutral acids (BNA) Method 8270C	
Dioxin Method 8280	
	MS

Table 2. EPA SW 846 methods for gas chromatography

Water, soil, soil gas and air can be analysed by GC. This method is frequently used for environmental applications such as testing and monitoring of contaminant sources, evaluation of hazardous waste sites for determining personal safety, monitoring during remediation, site characterization and during emergency response procedures.

Various types of detectors can be used. The principal one is photoionization detection (PID) for analysis of VOCs and BTEX. Flame Ionization detectors (FID) and electron capture detectors (ECD) are applicable for analysis of chlorinated pesticides. GC-mass spectrometric analysis is also possible for detection since quadrupole mass spectrometers are now portable. The EPA has verified various SW846 methods for use with GC and various detectors. These are shown in Table 2.

The photoionization dectector (PID) emits ultraviolet light at a wavelength of 121 nm from a lamp of 10.2 eV. This detector can be used for the detection of VOCs , BTEX and petroleum compounds. BTEX can be detected in the low ppb to upper ppt range. Since it is a non-destructive detector, it can be used prior to other detectors. The disadvantages of this detector are that it is sensitive to water and that it must be recalibrated more frequently than FID.

The flame ionization detector has a stainless steel jet enabling the carrier gas from the column to mix with hydrogen for subsequent burning. The molecules ionize and are attracted to a metal collector electrode beside the flame. An electrometer amplifier amplifies the current to the millivolt range. This detector is a destructive detector. All hydrocarbons such as VOCs (aromatic and chlorinated), SVOCs, petroleum compounds, and PCBs can be detected with this detector in the low ppb to high ppt range. Standard procedures have been devised for GRO-TPH, volatile organics and ethylene glycol.

The electron capture detector (ECD) uses radioactive nickel 63 in a sealed stainless steel cylinder. Beta electrons are emitted that collide with the carrier gas molecules. Halogenated molecules in the cell take up free electrons. The electronic pulse of the detector determines the amount of electrons remaining in the cell. This detector is non-destructive and thus can be used with other detectors. PCBS, chlorinated pesticides and dioxins can all be detected in the low ppb to ppt range. In general, the higher the degree of halogenation, the greater the sensitivity for that compound. Radioactivity licenses for usage may be required. The electrolytic conductivity detector (ELCD) involves the combustion of organic compounds in a quartz tube furnace after mixing with hydrogen gas with a nickel catalyst at 1000^{o}C. Hydrochloric acid (HCl) is produced from the halogen containing compounds and this, in turn, ionizes to change the conductivity. This type of detector is destructive and applicable for halogenated VOCs, PCBs, chlorinated pesticides and dioxins. Its linear range (low ppb to ppt) is greater than the ECD but more maintenance is required.

The thermal conductivity detector (TCD) is based on the Wheatstone bridge configuration. The filaments become hot as electrical current passes through them. A carrier gas that has passed through the column removes excess heat and allows the filaments to equilibrate. As compounds from the column, the thermal conductivity of the gas over the filaments change. This increases the heat of the filaments and alters the whetstone bridge balance. The TCD is a destructive detector and is used to detect nitrogen, oxygen, methane and other such gases in the ppm range. Nitrogen must not be used as the carrier gas since it is detected by the TCD. The nitrogen-phosphorus detector (NPD) uses a low flow rate of hydrogen gas (1 to 3 ml/min). As compounds exit the column, nitrogen and phosphorus produce electrons as they hit a thermionic bead above the jet orifice. The electron then goes towards a collector electro and electrometer amplifier in a manner similar to the FID. This detector is destructive and sensitive to water. Nitrogen and phosphorus compounds are detected in the ppb range.

The mass spectrometer (MS) detector is highly versatile and is used for the detection of a dioxins, organic acids, VOCs, and base/neutrals. Detection limits for quadrupole mass spectrometers are in the ppb range while for magnetic section are in the ppt to ppq range for compounds such as dioxin. It will be discussed later on.

Calibration of gas chromatographs is by injection of a standard at a known concentration. The retention time and the height or area of the peak on the chromatogram are determined. All conditions such as the type of column, temperatures and gas flow rates must be identical for the standard and the sample to be analysed. Coelution of compounds can occur so a completely positive identification is not possible. Coupling with a mass spectrometer can increase compound identification.

Overall, gas chromatography can be performed for the analysis of a large range of compounds from water, air, soil extracts, soil gas and headspace above soil or water samples. Portable gas chromatographs are available for field analysis. Many samples can be processed within a short time period. A higher degree of expertise is required to operate the equipment and interpret the data. Prices vary from less than $10,000 for simple GC to bench-scale models with mass spectrometer detectors for over $100,000. Instrument rental is an alternative.

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Biographical Sketch

Dr. Catherine Mulligan has worked for the past 15 years in the field of biotechnology in research, industrial and academic environments. After six (6) years in the production of biosurfactants by fermentation at McGill University and the Biotechnology Research Institute, she joined the SNC

Research Corporation in 1989, a subsidiary of SNC-Lavalin Group where she has conducted various projects in the development of environmental processes, bioconversions, fermentation, process evaluation, and technico-economic studies. She was involved in the development of the anaerobic treatment of various types of industrial wastewater and air, in addition to the bioleaching of mining residues. She has recently joined Concordia University, Department of Building Civil and Environmental Engineering, as a professor where her research interests include biosurfactant-washing of contaminated soils, treatment of metal-contaminated soils and wastes, bioremediation, the biological treatment of wastewater and the biological treatment of air. She has taught courses in Site Remediation, Environmental Engineering, Fate and Transport of Contaminants in the Environment and Geoenvironmental Engineering. She earned B.Eng. and M.Eng. degrees in Chemical Engineering and a Ph.D. in Civil Engineering at McGill University, Montreal, Canada. She is a member of Order of Engineers of Québec, Canadian Society of Chemical Engineering, American Institute of Chemical Engineering, Air and Waste Management Association, Association for the Environmental Health of Soils, Canadian Society of Civil Engineering, American Chemical Society and the Canadian Geotechnical Society. She has authored over 30 articles and presented at numerous conferences.