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A novel technology for sniffing subsurface contaminants

Une technologie nouvelle pour détecter les contaminants souterrains

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ABSTRACT

This paper describes the integration of a novel Electronic Nose (EN) with a Membrane Interface Probe (MIP) for rapidly screening gasoline contaminated sites. The MIP is an in situ tool that samples volatile organic compounds (VOCs) from the subsurface and transports it through tubing to various detectors on the surface. The electronic nose is an automated odor recognition device that detects and identifies chemical vapors based on the principles of human olfaction. In situ demonstration tests were conducted in collaboration with the United States Environmental Protection Agency (EPA) to evaluate the EN-MIP system in the field. The EN-MIP system was successful in determining the exact depths of gasoline contamination, and was able to estimate their concentration levels.

RÉSUMÉ

Cet article décrit l'intégration d'un nouvel nez électronique « Electronic Nose » (EN) avec une sonde d'interface de membrane (MIP) pour examiner rapidement les emplacements souillés par essence. Le MIP est un dispositif in-situ qui prélève les composantes organiques volatiles (VOCs) sous-sol et qui les transporte via la tuyauterie à de divers détecteurs sur la surface. Le nez électronique est un dispositif automatisé d'identification d'odeur qui détecte et identifie les vapeurs chimiques basées sur les principes de l'olfaction humaine. Des essais in situ de démonstration ont été effectués en collaboration avec l'agence de protection de l'environnement des Etats-Unis (EPA) afin d'évaluer le système d'EN-MIP sur le terrain. Le système d'EN-MIP est réussi à déterminer les profondeurs exactes de la contamination en essence, et à estimer leurs niveaux de concentration.

1 INTRODUCTION

Traditional methods for geoenvironmental site characterization involve drilling, sampling (soil, groundwater, and soil gas), laboratory testing, and analysis using gas chromatography and mass spectroscopy (GC/MS). These methods are often time-consuming, laborious, and expensive. It also requires handling and transportation of hazardous samples to the laboratory. On-site characterization techniques on the other hand reduce the costly and time-consuming laboratory analysis during initial site investigations, limit personnel exposure to contaminated media, and reduce the amount of investigation-derived waste normally generated during conventional drill and sample activities. Therefore, there is a great demand for efficient and economical field measurement techniques for characterizing environmentally affected sites.

In recent years, many new sensors have been integrated with in situ tools for geoenvironmental site characterization. The resistivity cone penetrometer may be used to delineate contaminant plumes by measuring changes in bulk soil resistivity (Campanella and Weemes 1990). The US tri-services integrated Laser Induced Fluorescence (LIF) with cone penetrometer technology (CPT) for the detection of petroleum hydrocarbons (Lieberman et al., 1991). The chemicon is instrumented with temperature, pH, and oxidation-reduction potential (ORP) sensors to acquire data for bio-characterization of contaminated sites (Pluimgraaff et al., 1995). A vision cone penetrometer instrumented with a miniature camera was developed (Raschke and Hryciw 1997) for visual identification of soil, and visual detection of dense non-aqueous phase liquids (DNAPLs). A Raman-cone penetrometer system was developed to detect DNAPLs using remote Raman spectroscopy (Rossabi et al., 2000). The integration of sensors with Direct Push Technologies has been steadily growing since the past decade. This paper describes the integration of a novel Electronic Nose (EN) with a Membrane Interface Probe (MIP) for rapidly screening gasoline contaminated sites.

2 THE ELECTRONIC NOSE - MEMBRANE INTERFACE PROBE (EN-MIP) SYSTEM

The EN-MIP system was developed by integrating a portable electronic nose (Kurup 2000), with an in situ vapor sampling tool known as the MIP (Christy 1996).

2.1 *The Electronic Nose*

The electronic nose is a novel device that detects and identifies chemical vapors by automated odor recognition (Gardner et al. 1990). It is based on the principles of human olfaction. Figure 1 depicts an electronic nose mimicking the human olfactory system. A portable electronic nose (Fig. 2) consisting of an array of seven metal oxide sensors, a temperature sensor, and a humidity sensor was developed for integration with Direct Push Technologies (Kurup 2000, 2003). The metal oxide sensors were essentially composed of tin dioxide that were doped with different impurities (palladium, platinum etc.) in order to give them slightly different electrical characteristics. Hence, each sensor in the array gave a different electrical response (change in electrical resistance and DC output voltage) for a particular target vapor introduced into the sensing chamber. The combined output response from the sensor array formed a fingerprint or signature that was unique for a particular odor. Different chemicals were presented to the sensor array, to build a database of signatures. This database of labeled signatures was then used to train a pattern recognition system, such as Artificial Neural Networks (ANNs). ANNs are data processing paradigms that work similar to the brain in processing information. Once the network was trained for chemical recognition, the detection mode simply consisted of propagating the sensor data through the trained network to yield automated real-time identification of contaminants.

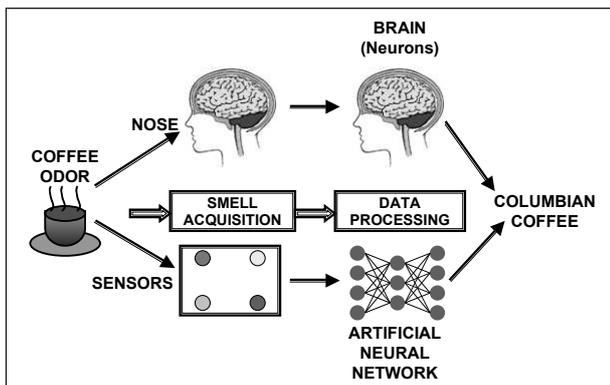


Figure 1. Electronic nose mimicking the human olfactory system



Figure 2. The portable electronic nose system

2.2 The Membrane Interface Probe (MIP)

The portable electronic nose was integrated with the MIP (EN-MIP system) to sniff and detect gasoline contamination in the subsurface (Kurup 2003, Issac 2003). The MIP (Fig. 3) is an in situ tool that samples volatile organic compounds (VOCs) from the subsurface, and transports it through 100 feet of Teflon tubing to various detectors on the surface (Christy 1996). The probe has a semi-permeable thin film membrane, impregnated into a stainless steel screen mounted along the face. The membrane is heated to 120 degree Celsius to accelerate diffusion of VOCs across the membrane. Diffusion occurs because of a concentration gradient between the soil-gas and the clean carrier gas behind the membrane. The carrier gas (ultra zero air containing approximately 19.5-23 % oxygen and balance nitrogen) sweeps the vapors and delivers them to the detectors. The probe is also equipped with a soil conductivity device to measure the electrical conductivity of the soil. The MIP is robust and can be driven into the subsurface using a Geoprobe percussion soil probing equipment. A depth encoder is used for measuring both the probe position, and the rate of advance.

2.3 The Scentograph Portable GC

A portable Gas Chromatograph (GC) was integrated with the MIP to obtain preliminary data for training the EN-MIP system (Deepti 2002, Kurup 2003). The GC-MIP system also provided confirmatory data to validate the EN-MIP results. The Scentograph Plus II GC (Fig. 4) manufactured by SENTEX Systems (Fairfield, New Jersey) was instrumented with dual detectors: Micro Argon Ionization Detector, and a Photo Ionization Detector. It is a complete analytical system with a gas chromatograph column, oven, sample introduction system, gas flow systems, related electronics, and a data acquisition and analysis system.

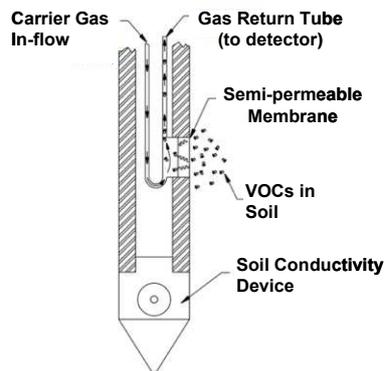


Figure 3. Membrane Interface Probe (Christy 1996)

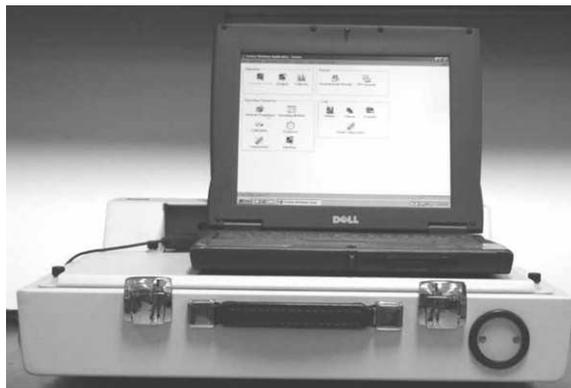


Figure 4. Scentograph Plus II – Gas Chromatograph

A detachable laptop computer controls the operation of the GC and acquires the data. Vapor samples were drawn by an internal pump at a rate less than 40 ml/min. The samples were first adsorbed by a preconcentrator (small glass tube packed with carboxen) and then desorbed into the column by reversing the carrier gas flow while heating the preconcentrator. The GC-MIP system was first calibrated in the laboratory using BTEX spiked aqueous-soil samples. The results determined by the GC-MIP system were confirmed using standard EPA methods for analyzing VOCs in soil, and groundwater.

3 FIELD DEMONSTRATION OF THE EN-MIP SYSTEM

3.1 Test Site Location

The EN-MIP system was demonstrated in the field at the Rhode Island Department of Transportation (RIDOT), highway garage site in Riverside, RI, U.S.A.. The garage had provisions for storing fuel for construction and maintenance equipment, including highway snow shovels and highway-salters, belonging to the RIDOT. A few years ago one of the underground gasoline storage tanks developed a leak and resulted in a spill at the site. The Rhode Island Department of Environmental Management (RIDEM) carried out appropriate monitoring measures and replaced the leaking storage tank. There were several monitoring wells installed within the premises of the garage. Three monitoring well locations (MW5, MW6 and MW7) were chosen for demonstrating the EN-MIP system. The selection of the monitoring wells for the field-sampling plan was carefully made after reviewing the preliminary test reports made available by the RIDEM. Other issues considered were test location accessibility within the site, and the coordination with facility operations.

3.2 Equipment and Machinery

Field equipment and onsite analytical support other than the EN-MIP and GC-MIP systems were provided by the EPA, New England Regional Laboratory. These included the EPA Mobile Laboratory for providing onsite confirmatory analysis, and the Geoprobe Direct Push Machine for advancing the MIP. The Geoprobe Direct Push Machine (Fig. 5) is a percussion hammer that has a stroke of 1.37 m, and capable of generating a push force of 80 kN and a retraction force of 110 kN.



Figure 5. Direct Push Machine

3.3 Results and Discussions

The MIP was advanced using the Geoprobe direct push machine to the desired sampling depths. The probe was halted for fifteen minutes at each depth to sample the vapor samples. The carrier gas led the vapor samples into the electronic nose that was housed inside the EPA mobile laboratory. The collective peak response from the seven metal oxide sensors was recorded as the chemical signature (fingerprint) of the vapor sampled from a particular depth. The MIP was then advanced to the next sampling depth. In situ data acquired by the EN-MIP system near the MW5 test location is shown in Figure 6. The graph shows the response of the seven sensors with time, for the EN-MIP tests conducted at the six different depths. The chemical signatures corresponding to the EN-MIP tests conducted near MW5 are shown in Figure 7. Gasoline contamination was detected at depths of 11.5 feet (medium level contamination), and 13 feet (low level contamination) near MW5. The following activities were carried out at each of the three monitoring well, test locations: GC-MIP testing, EN-MIP testing, soil, vapor, and groundwater sampling and analysis by GC/MS.

A feed-forward ANN, trained by back-propagation, was used in this research because of its simplicity and robustness. The network consisted of seven input-layer neurons (for inputs from the seven sensors), and six hidden-layer neurons (Fig. 8). There were four output-layer neurons to predict the four different gasoline contamination levels (High, Medium, Low, and No). The BTEX concentrations in soil measured by the GC-MIP system were used to designate the four different contamination levels: No (< 6 mg/kg), Low (6-30 mg/kg), Medium (30-150 mg/kg), and High (> 150 mg/kg). The electronic nose was trained using 10 vapor sample signatures obtained from MW5, MW6, and MW7, representing all four contamination levels. It was then tested with all 21 signatures obtained from the EN-MIP tests conducted near MW5, MW6, and MW7 (consisting of 10 training signatures and 11 new signatures that were not used for training). The trained ANN model correctly predicted the concentration levels for all the 21 signatures obtained by the EN-MIP system (Table 1). Results from the GC-MIP tests, and

the GC/MS analysis on soil and groundwater samples were used for confirmation of the concentration levels predicted by the EN-MIP system.

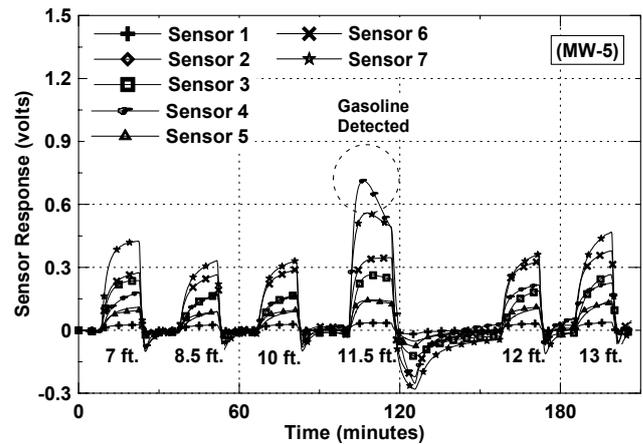


Figure 6. EN-MIP response from various depths at the MW 5 location

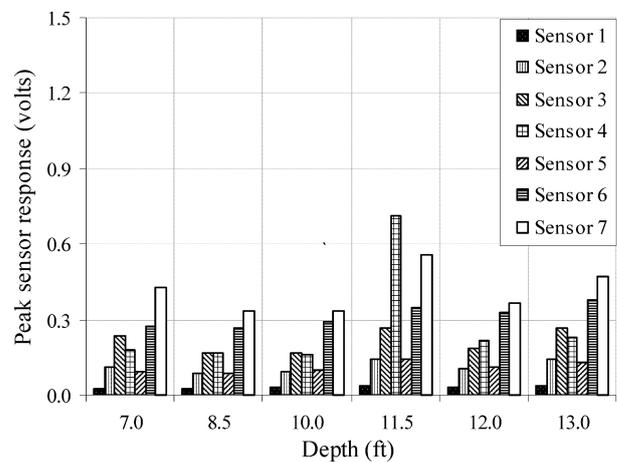


Figure 7. Odor fingerprints from EN-MIP tests at MW5

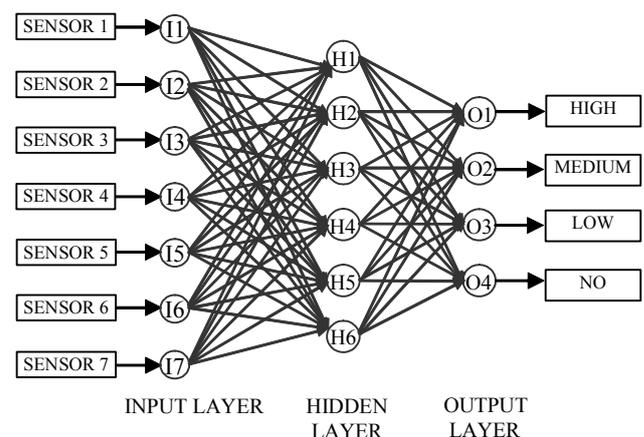


Figure 8. Architecture of the ANN model

Table 1 presents a summary of the test results obtained from the field demonstration program. It can be seen that the MW6 location was the most contaminated one, with the EN-MIP system measuring 'High' level contamination at a depth of 4 feet,

and 'Medium' level contamination at depths of 5 and 6 feet. MW5 had 'Medium' level contamination at 11.5 feet, and 'Low' level contamination at 13 feet. The MW7 location was found to be the least contaminated with 'Low' level contamination measured at a depth of 6 feet. The EN-MIP predictions were qualitatively confirmed by the GC-MIP measurements, and the GC/MS analysis of the soil samples (Table 1).

Table 1: EN-MIP Field Demonstration Results

M W	Depth (ft)	GC/MS analysis	GC-MIP	EN-MIP	
		BTEX in Soil mg/kg	BTEX in Soil mg/kg	Expected Conc. Level	Predicted Conc. Level
M W 5	7.0	*	4.78	No	No
	8.5	*	1.89	No	No
	10.0	*	5.94	No	No
	11.5	5.98	106.45	Medium	Medium
	13.0	*	29.83	Low	Low
M W 6	4.0	25.30	227.08	High	High
	5.0	0.88	41.79	Medium	Medium
	6.0	0.12	32.33	Medium	Medium
	8.0	1.46	3.03	No	No
	10.0	1.81	3.59	No	No
	12.0	*	5.12	No	No
M W 7	6.0	2.59	7.75	Low	Low
	8.0	0.22	3.26	No	No
	10.0	1.48	1.00	No	No
	12.0	*	1.01	No	No
	14.0	*	0.66	No	No

Note: * indicates below reporting levels (0.025-0.031 mg/kg) for BTEX

From the results summarized in Table 1, it can be seen that there is a significant difference in the BTEX concentrations measured by the GC-MIP system, and those determined by the GC-MS analysis on the soil samples collected from the site. This difference could be attributed to the following factors:

- The heterogeneity in the distribution of the subsurface contamination and the difference in the sampling locations. The MIP sampled vapor samples from the soil adjacent to the heated membrane, whereas the physical soil samples for confirmatory analysis were obtained by an open-ended soil sampler adjacent to the MIP test location.
- The difference in the "soil matrix" used for the laboratory calibration of the GC-MIP and that encountered in the field. Uniformly graded Ottawa sand was used for the laboratory calibration of the GC-MIP, whereas the soil at the test site was poorly-graded medium to fine sand.
- The inherent difference between the in situ GC-MIP vapor sampling and analysis method, and the conventional method that involves soil sampling from discrete depths, followed by laboratory testing and analysis. The conventional method is prone to losses due to the volatilization of VOCs during sampling, storage, transport and laboratory testing.

From these limited test data it appears that in situ methods such as the GC-MIP and the EN-MIP systems may be able to better characterize subsurface VOC contaminants compared to the traditional approach of drilling, sampling, and laboratory testing. Additional field studies are needed to verify the applicability of these novel technologies in a variety of geological regimes.

4 CONCLUSIONS

A novel site characterization technology was developed by integrating a portable Electronic Nose with a Membrane Interface Probe (EN-MIP). The technology was successfully demonstrated at a gasoline contaminated site in Rhode Island, U.S.A. The EN-MIP system was successful in identifying the exact

depths of gasoline contamination, and was able to correctly determine their concentration levels. Onsite analysis of vapor samples performed by the EPA in their mobile laboratory provided confirmation in the field. Predictions by the EN-MIP system were further validated by GC-MIP test results, and by conventional GC/MS laboratory analysis performed on soil and groundwater samples obtained from the test site. The results from the laboratory as well as the field testing have shown that the EN-MIP system is a reliable tool for rapid screening of gasoline contaminated sites. Additional field studies are needed to verify the validity of the technology in a variety of geological regimes. Research is currently in progress to increase the sensitivity and detection speed of the EN-MIP system.

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