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Leak detection for long-distance pipelines

Scientists proposed a novel design for monitoring leakage from long-distance pipelines. They developed a mathematical model for predicting airflow distribution for each of the porous tubes that run along the pipeline and make up the detection system. Liang and Tom Kuo (2006) used experimental data from extraction tests to support the model.

System design

The leak detection system consisted of porous and impermeable polyethylene tubes. As shown in Figure 1, the porous tubes, spaced intermittently, were connected in series to the polyethylene tubes and the system was installed above the pipeline in the same trench. The trench was filled with coarse sand. Scientists reported that the new system was “configured to obtain composite samples of the soil gas flowing through the intermittent porous tubes located at various distances from the extraction pump. The mode of operation of the new system was intended to be an intermittent monitoring system (i.e., daily or weekly sampling).” They recommended daily monitoring for best results (Liang and Tom Kuo, 2006).

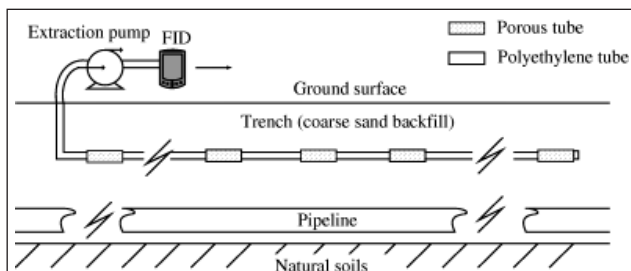


Figure 1: Schematic of new leak detection system.

Backfill permeability was in the order of 10^3 Darcy. Porous tube permeability was in the order of 1 Darcy. The backfill permeability allows for easy vapor extraction and sufficient airflow. The materials used included the following:

- 5-cm-long porous tube, outside diameter 1.8 cm, and inside diameter 1.2 cm
- porous tubes with permeability of 0.9 Darcy
- porous tubes with permeability of 3 Darcy
- 100-cm-long polyethylene tube, outside diameter 1.2 cm and inside diameter 0.9 cm

In the new system, soil-gas flow occurred through the porous tubes and inside the polyethylene tubes. The scientists used Darcy’s law and Hagen-Poiseuille’s law to describe the soil-gas flow behavior through the tubes. They calculated mathematically a simulation of extraction model processes. Liang and Tom Kuo (2006) reported that “model calculations start from the first section near the extraction pump and then proceed section by section toward upstream. Each section consists of one polyethylene tube followed by one porous tube.” The model considered the following:

- inlet pressure
- outlet pressure
- soil gas viscosity
- impermeable tube length
- inside diameter of the impermeable tube
- pressure at the inlet of the extraction pump
- total flow rate at the inlet of the extraction pump
- reference pressure
- total airflow rate
- porous tube permeability
- ambient pressure
- inner and outer radius of the porous tube

- airflow distribution
- extraction pump pressure

The scientists ran extraction tests in which the detection system was sealed on one end and attached to an extraction pump on the other. Two detection systems, a 12-m-long system with 3 Darcy porous tube permeability and a 30-m-long system with 0.9 Darcy porous tube permeability, were used for the experiments. Airflow was measured between porous and polyethylene tubes. The resulting airflow distribution information was used to calculate the percentage of airflow through the last porous tube, which was “critical to determining the effective distance of detection for the new system” (Liang and Tom Kuo, 2006).

The researchers also ran a field leak test using the 30-m detection system. The system was installed at a depth of 1 m below ground surface. The simulated leakage consisted of 3 L of gasoline released near the leak detection system at a depth of 1 m below ground surface. The leak detection test included the extraction pump, with a total flow rate of 7 L/min, and a portable flame ionization detector (FID).

Results

The researchers discovered that the percentage of airflow through each porous tube decreased with an increase in the distance between the porous tube and the extraction pump. For the 12-m system, they measured an air rate decrease from 41.0 L/min to 0.1 L/min from the first porous tube to the 12th porous tube. For the 30-m system, the air rate decreased from 5 L/min to 0.2 L/min from the first to the 30th porous tube. Liang and Tom Kuo (2006) also observed that “the distance of detection for the new system increased as the permeability of porous tubes decreased.” In the 12-m system, airflow percentage through the 12th porous tube was 0.087%, while it was 0.6% in the 30th porous tube of the 30-m system.

The 3-L gasoline leak had a peak concentration of 428 ppm, which “was 1430 times higher than the background concentration at 0.3 ppm. With its increased effective distance of detection, the new method significantly reduced the large amount of soil-gas samples and analyses that are required when conventional soil-gas probes are applied to detect a leakage along a long-distance pipeline.” The leak had a breakthrough time of 19 minutes. Experimental results were supported by results of the mathematical model (Liang and Tom Kuo, 2006).

Liang and Tom Kuo (2006) also employed soil-gas probes for leak detection. These were used to evaluate “the effective detection distance of conventional soil-gas probes compared with the leak detection system.” For the simulated leakage, three probes were installed 1-m deep at 2, 3, and 5 m from the source. The scientists found that total hydrocarbon concentrations decreased between 2 and 5 m from the source. “Thus, applying conventional soil-gas probes to detect a leakage along a long-distance pipeline would require a large number of soil-gas sampling points and analyses because of the small effective detection distance of each soil-gas probe.”

The researchers noted that the leak detection system they designed would be applicable to situations other than long-distance pipelines, such as large-diameter storage tanks and plumes of contaminated ground water. The detection system would also be useful in monitoring natural attenuation and bioremediation of ground water contaminated by petroleum leakage.

Conclusion

Liang and Tom Kuo (2006) concluded, “the effective detection distance of the new system was at least 30 m, while the effective detection radius from the conventional soil-gas probes was only 5 m. Applying the new leak detection system to long-distance

pipelines, a large amount of soil-gas samples and analyses can be saved. A mathematical model to predict the distribution of airflow in the new detection system was developed and verified with the air extraction tests. Darcy’s law and Hagen-Poiseuille’s law were used in the model to describe the flow behavior of soil gas through the porous tubes and inside the polyethylene tubes, respectively. The model is useful in designing the distribution of airflow in a new detection system to monitor fuel leakage from a long-distance pipeline. The approximate location of a detected leakage event could be determined from the measured breakthrough time using the airflow distribution model.”

Reference

Liang, K.F. and M.C. Tom Kuo, “A new leak detection system for long-distance pipelines utilizing soil-gas techniques,” *Ground Water Monitoring & Remediation*, Vol. 26, No. 3, 2006; www.ngwa.org

UTTU thanks Dr. Tom Kuo, mctkuobe@mail.ncku.edu.tw, for his help on this article.



Soil remediation time to clean-up

Researchers developed a method for predicting vapor extraction remediation time, a key tool when selecting the remediation technology appropriate for a remediation project. They focused their efforts on the influence of soil water content (SWC) on remediation time, remediation efficiency and contaminant distribution in each phase of the soil matrix. Contaminant volatility, soil permeability and soil content of natural organic matter and water were considered in the development of the remediation time forecasting method.

Materials and methods

The researchers studied sandy soils contaminated with cyclohexane. They performed a gas chromatographic analysis of cyclohexane and recorded the data. Sandy soil samples were then taken from an uncontaminated beach in the Oporto region of Portugal. The samples were taken at 3-m depth from several different areas of the beach and were stored. The soil was constituted of silica and shell debris and contained “negligible amounts of natural organic matter and clay” (da Conceição Alvim-Ferraz and others I, 2006). Researchers performed the following:

- dried samples at 35°C
- sieved samples for a granulometric fraction of soil with uniform physical and chemical properties
- divided soil into 10 samples, nine of which were considered “real soils”
- dried “real soils” again at 35°C “during different periods in order to remain with different amounts of water content”
- stored “real” samples in stopped vessels
- identified “real” samples as $R_{1.5}$, $R_{2.4}$, $R_{3.2}$, $R_{4.3}$, $R_{5.2}$, $R_{5.8}$, $R_{6.8}$, $R_{7.4}$ and $R_{8.2}$ (subscript indicating the water contents)

The scientists sought to ensure controlled water content and the absence of natural organic matter. Thus, they manipulated the tenth soil sample to yield prepared soils with water contents comparable to “real soils.” They conducted water washings repeatedly until limpid, or clear, water was reached. The sample was then dried at room temperature for 5 days and then at 110°C for 24 hours. The scientists mixed the sand and added varied amounts of deionized water to yield four prepared soils with different water contents. The prepared soil was then stored in stopped vessels with identification indicating water content (P_0 , P_2 , P_4 and P_6) (da Conceição Alvim-Ferraz and others I, 2006).

Contaminant soil distribution

Scientists used specially designed equipment to obtain the equilibrium isotherms for the prepared soils. They first placed the soil into a perspex column, then induced contamination with different amounts of frozen cyclohexane and left the soil to isothermally reach equilibrium. The scientists compacted the soil using the same procedure each time to guarantee the same soil porosity in the column after each introduction. The scientists monitored cyclohexane concentration with gas chromatography. They observed equilibrium for both the prepared and real soils 24 hours later, regardless of water content. The scientists then calculated the following:

- concentration in the aqueous phase
- mass in the solid and non-aqueous phases
- amount of cyclohexane remaining in the soil after remediation
- process efficiency

"The equilibrium isotherms elaborated relate the concentration of cyclohexane in the gas phase to its concentration in the solid and non-aqueous liquid phases (da Conceição Alvim-Ferraz and others I, 2006).

Soil vapor extraction

Da Conceição Alvim-Ferraz and others I (2006) also conducted soil vapor extraction experiments in order to properly simulate remediation of the prepared soils. Soil introduction and contamination were conducted as described previously. "The prepared soils were contaminated with a controlled amount of cyclohexane in order to reproduce the range of contamination of real soils." After equilibrium, scientists used a vacuum pump to create an airflow rate of 2.8 L h^{-1} standard temperature and pressure (STP) through the column containing the soil. They aimed to establish a zone of

advective airflow through the contaminated area. The researchers monitored the cyclohexane concentration in the airflow, collected samples and analyzed them by gas chromatography (da Conceição Alvim-Ferraz and others I, 2006).

The researchers considered remediation completed when cyclohexane concentration in the gas phase was below 1.0 g m^{-3} . They then determined "the time to reach this clean-up goal (considered the remediation time) and the time to reach 90% of remediation. The same procedure was used for both real soils and prepared soils" (da Conceição Alvim-Ferraz and others I, 2006).

Results

The researchers reported that soil characteristics included the following:

- clay content under the detection limit
- negligible natural organic matter content
- relatively high pH values

They concluded that "both the prepared and real sandy soils differ essentially through their water content. The real soils $R_{1.5}$, $R_{2.4}$, $R_{3.2}$, $R_{4.3}$, $R_{5.2}$ and $R_{5.8}$ have water contents belonging to the range covered by the prepared soils, which was not the case for $R_{6.8}$, $R_{7.4}$ and $R_{8.2}$ " (da Conceição Alvim-Ferraz and others I, 2006).

Contaminant distribution

The researchers (da Conceição Alvim-Ferraz and others I, 2006) used two models for adsorption on solids, the Freundlich and the Brunauer, Emmett and Teller (BET), and found that "the BET model showed a good fitting of experimental results for low cyclohexane gas concentrations." The scientists explained that "higher concentrations were justified by capillary condensation of pollutant and/or by the formation of a non-aqueous liquid phase of contaminant. The BET model allowed

the determination of a monolayer capacity of the soil equal to 3.67×10^{-2} , 8.57×10^{-3} , 8.34×10^{-3} and $4.36 \times 10^{-3} \text{ g kg}^{-1}$, respectively, for P_0 , P_2 , P_4 and P_6 ."

Results indicated the following:

- water content decreased the soil sorption capacity
- soil water content increased with low cyclohexane soil concentration
- soil water content induced "a tendency for increasing the percentage of pollutant in the gas phase"
- increased soil water content increased "the percentage of pollutant in the aqueous phase"

They observed that the soil water content affected differently the percentage of pollutant in the solid and non-aqueous liquid phases, depending upon the amount of pollutant present. Lower pollutant concentrations tended to decrease the percentage of pollutant in the solid and non-aqueous liquid phases while higher pollutant concentrations tended to increase the percentage in the solid and non-aqueous liquid phases. "This conclusion confirms the formation of a non-aqueous liquid phase of contaminant predicted by analysis of the fitting of BET model" (da Conceição Alvim-Ferraz and others I, 2006).

Soil vapor extraction

The researchers found that a higher water content in the soil (6% versus 0%) had the following effects on the bioventing remediation process:

- with increased initial soil water content, a higher concentration of cyclohexane contamination (11 mg and 27 mg) remained in the soil after the same passage of time
- soils with higher water content had decreased process efficiency (99% and 97%, respectively, for

0% and 6% of soil water content)

- soil with higher water content required a longer time to reach 90% of pollutant reduction
- soil with higher water content required a longer time to achieve complete remediation (1.8 h and 4.9 h, respectively, for 0% and 6% of water content)

Therefore, the water decreased remediation efficiency and increased remediation time, thus increasing overall remediation costs. The researchers also observed linear fitting with a good correlation coefficient, which allowed them to predict the remediation time for similar soils with water contents different from those used in experiments.

Conclusions

The researchers (da Conceição Alvim-Ferraz and others I, 2006) concluded that, "the presence of water negatively influenced the remediation process, turning it less efficient and more time-consuming, and consequently more expensive." They explained that "increasing of soil water content decreases the soil porosity and permeability, rendering more difficult the movement of the air into the soil. The water also decreases the interfacial area between phases, reducing the mass transfer coefficient between them. Additionally, if the contaminant has significant water solubility, its dissolution decreases the availability of the contaminant for extraction, increasing the amount of contaminant remaining in soil after the remediation and delaying contaminant removal. If the soil water content belonged to the range considered in the experiments with the prepared soils, the remediation time of real soils of similar characteristics could be successfully predicted with relative differences not higher than 10%, through a simple mathematical fitting of experimental results. However, for the soils whose water content was not within the range of the prepared soils, the differences in the remediation time increased with the difference in water contents." These conclusions

apply to contaminant cyclohexane and sand soils with undetectable organic or clay content.

In subsequent research, the researchers investigated the influence of natural organic matter and water contents on soil remediation time. They found that for sandy soils with negligible amounts of clay, artificially contaminated with cyclohexane before vapor extraction, when a negligible amount of water was present in soil, an increase in natural organic matter resulted in the following:

- increased cyclohexane concentrations remaining in the soil after remediation
- decreased cyclohexane that remains in the gas phase
- decreased process efficiency (99% and 90%)
- increased remediation time (1.8 h and 13 h), respectively, for 0% and 7.5% SWC

The researchers explained that "the increase of the monolayer capacity...leads to a higher sorption of cyclohexane into the solid phase. Consequently, cyclohexane is less available for extraction, increasing the amount of contaminant that remains in the soil after remediation and delaying contaminant removal" (da Conceição Alvim-Ferraz and others II, 2006).

When the sandy soils contained a negligible amount of organic matter and increased soil water content, the researchers found the following:

- increased cyclohexane concentrations remaining in the soil after remediation
- increased cyclohexane remaining in the aqueous phase after remediation, due to water dissolution
- decreased process efficiency (99% and 97%)
- increased remediation time (1.8 h and 4.9 h), respectively, for 0% and 6% SWC

They explained that increased soil water content

decreased the soil porosity and permeability, making air movement into the soil difficult. "The water also decreases the interfacial area between phases, reducing the mass transfer coefficient between them. Besides that, if the contaminant has significant water solubility, its dissolution decreases the availability of the contaminant for extraction, increasing the amount of contaminant that remains into the soil matrix after the remediation, and delaying contaminant removal." Thus, they concluded that the water and natural organic matter of soils negatively influence remediation process in terms of time, efficiency and, consequently, expense (da Conceição Alvim-Ferraz and others II, 2006).

Reference

- da Conceição Alvim-Ferraz, M., Albergaria, J.T. and C. Delerue-Matos, "Soil remediation time to achieve clean-up goals I: Influence of soil water content," *Chemosphere*, Vol. 62, No. 5, 2006; www.sciencedirect.com
- da Conceição Alvim-Ferraz, M., Albergaria, J.T. and C. Delerue-Matos, "Soil remediation time to achieve clean-up goals II: Influence of natural organic matter and water contents," *Chemosphere*, Vol. 64, No. 5, 2006; www.sciencedirect.com
- UTTU thanks Dr. Maria da Conceição Alvim-Ferraz, aferraz@fe.up.pt, for her help on this article.**



Determining naturally occurring MTBE biodegradation

Researchers performed a five-year investigation of degradation at a site contaminated with methyl *tert*-butyl ether (MTBE), paying particular attention to the production, accumulation and degradation of metabolites and by-products.

Materials and methods

Site

The MTBE plume was located at an old industrial site in Leuna, Germany, where large-scale MTBE production occurred from the early 1980s until 1996, when the refinery was closed. Spills during filling processes and leaking underground storage tanks have left the area with a subsurface contaminated with free-phase mineral oil, including benzene, toluene, ethylbenzene and zylene isomers (BTEX) and MTBE, which are dissolving into the ground water. In addition, the site is contaminated with ammonia, which was produced upstream of the former refinery.

The Leuna site was characterized by the following:

- heterogeneous aquifer
- fine to coarse gravel and sand
- main aquifer 2-4 m thick
- groundwater table 3-4 m below the surface
- northwest to southeast groundwater flow

Drinking water production wells and the Saale river were located downstream of the contamination. MTBE had been detected in small concentrations in the wells, which were 1500 m away. A large-diameter remediation well was installed to prevent further contamination.

Martienssen and others (2006) determined the hydraulic conductivity, ground water flow velocity, and ground water temperature. These were,

- 4×10^{-4} m/s in middle to coarse sand and gravel
- 6×10^{-2} m/s in coarse gravel
- 9×10^{-5} m/s in medium- to fine-grained sand
- between 0.3 m/day and 1.0 m/day
- between 7°C and 14°C (mean 11°C)

More than 200 monitoring wells were available to characterize MTBE spreading and degradation.

The researchers chose 105 of these, arranged in 10 transects, for their investigation. Among these were 15 multi-level wells. The 105 wells were located both in contaminated and uncontaminated areas. Researchers collected ground water samples and water-level measurements from March 2002 to June 2005. "Older measurements from the beginning of 2001 were also evaluated" (Martienssen and others, 2006).

Researchers prepared five individual samples from each well on site. Samples were taken for Fe(II) and heavy metal analysis, sulfide determination, and organic and inorganic analysis. The researchers used bench scale experiments to "verify the field results, and to determine the biodegradation kinetic parameters. For that purpose, an aquifer model (160-cm long, 30-cm wide and 40-cm high), including eight sampling ports and seven oxygen sensors, was filled with original aquifer material from the field site. To establish homogenous laminar flow through the model, 15 influent and effluent ports were installed to supply the model aquifer continuously with original groundwater from the field site. The groundwater was amended with pure oxygen or hydrogen peroxide immediately prior to entering the model. The groundwater flow rate was 4.6 cm/d" (Martienssen and others, 2006).

Researchers investigated ground water samples for the following, using a flow-through cell:

- temperature
- oxygen content
- oxidation-reduction (redox) potential
- electrical conductivity
- pH

They did not detect significant differences between field and laboratory results.

Martienssen and others (2006) measured the following within five to 24 hours after sampling:

- phosphate
- nitrite
- iron
- ammonia
- nitrate
- sulfide
- MTBE
- *tert*-butyl alcohol (TBA)
- *tert*-butyl formate (TBF)
- 2-methyl-2-hydroxy-1-propanol
- isopropyl alcohol, acetone
- hydroxyacetone
- ethyl *tert*-butyl ether (ETBE)
- *tert*-amyl methyl ether (TAME)
- *n*-propane
- *iso*-propane
- *cis*-pentene
- *trans*-pentene
- *diiso*-propyl ether

The researchers conducted headspace analysis for the samples and used gas chromatography/mass spectrometry for further analysis. They determined acid intermediates with high performance liquid chromatography (HPLC). "Samples were also screened for anaerobic degradation products such as acetate, succinate, pyruvate, propionate and citrate" (Martienssen and others, 2006).

Iron and other heavy metals content were determined by atomic absorption spectroscopy while cations and anions were analyzed by ion chromatography.

Results

Martienssen and others (2006) observed that the contaminated area was "characterized by free light

non-aqueous phase liquids (LNAPL) up to 40 cm in height located at the top of the ground water table." Alkanes, BTEX, and MTBE were the primary contaminants dissolved into the ground water. BTEX concentration was 150 mg/L, and MTBE concentration was 130 mg/L. Concentrations of mineral oil hydrocarbons, 30 mg/L, were "relatively low and limited to a small area around the NAPL phase." Ammonia was also observed to be a ground water pollutant with maximum concentrations of 110 mg/L (Martienssen and others, 2006).

The scientists determined that ground water outside of the highly contaminated area was microaerobic to moderately anaerobic. "Within the source area, redox potentials less than -100 mV indicated strictly anaerobic conditions, and sulfate-reducing processes were detected. In this area, sulfate has been more or less completely reduced over time and methanogenic conditions predominated. As a result, enriched sulfide, up to 7 mg/L, and methane concentrations were measured" (Martienssen and others, 2006).

They found the following ions:

- HCO_3^-
- Cl^-
- Ca^{2+}
- Mg^{2+}
- Na^+
- K^+
- PO_4^{3-}

Sulfate was the primary electron acceptor. Overall phosphate concentrations were relatively low in uncontaminated areas.

The scientists found high concentrations of BTEX within a limited area around the source. Benzene had traveled the farthest from the source, decreasing in

concentration from 50 mg/L to < 1 mg/L, about 300 m. MTBE, however, was transported about 1700 m from the source in a plume several hundred meters wide. Analysis of ground water samples within and around the MTBE plume revealed that MTBE concentrations decreased during groundwater transport. However, "significant amounts of TBF and TBA were formed along the ground water flow path, before being later degraded. Thus, the ratio of TBA to MTBE increased from 0.37% near the source to 3.6% in samples containing maximum TBA concentrations, about 750 m downstream of the source." They observed TBF biodegradation to correlate with the formation of formate, suggesting that TBF and TBA were produced during MTBE degradation. In both the field and lab experiments, TBA was linked to oxygen concentration. "At high oxygen concentrations, TBA accumulated and was degraded again, when the oxygen concentration decreased." Methacrylate was not detected (Martienssen and others, 2006).

The researchers found that sulfate reduction occurred only within the NAPL free phase at the source area, corresponding to the mineral oil and BTEX degradation. The concentration of Fe(II) was also lower near the sulfate zone, resulting in high concentrations of precipitated FeS. However, outside the source area, within the MTBE plume, conditions were observed to be microaerobic rather than anaerobic. Fe(II) was not found within the MTBE plume outside the BTEX plume, "likely due to Fe(II) oxidation and precipitation." Sulfate concentrations, redox potentials, and TBA accumulation significantly increased immediately once the BTEX compounds had been degraded. The TBA accumulation indicated accelerated MTBE degradation (Martienssen and others, 2006).

Conclusions

The researchers noted that the aquifer's processes, since it was unconfined near the ground surface, could be significantly influenced by oxygen. Rainfall, related ground water fluctuations, and air bubbles created and trapped by these fluctuations all contributed to soil oxygen levels. Researchers did not find "significant correlations between decreasing MTBE concentrations and either nitrate, Fe(II) or sulfate. Moreover, redox potentials above 300 mV and significant oxygen concentrations in the groundwater samples indicated microaerobic processes" (Martienssen and others, 2006).

Martienssen and others (2006) reported that "MTBE is significantly degraded under natural conditions at the investigation site in Leuna. This conclusion is based on the formation of, and variation in, several intermediates along the groundwater flow path. The main intermediates were TBF and TBA. The carcinogenic intermediate methacrylate was not detected."

MTBE degradation was aerobic. TBA production and fate "were the result of different kinetic parameters for substrates and oxygen. Thus, TBA production within the MTBE plume can be used as a significant marker for aerobic MTBE biodegradation. Oxygen is supplied by recharging precipitation, combined with groundwater table fluctuations and diffusion/dispersion from the unsaturated zone. Since the oxygen supply is limited, natural attenuation of MTBE requires large reaction zones" (Martienssen and others, 2006).

They concluded, "natural attenuation (NA) may be an option for the remediation of MTBE-contaminated sites. However, reliance on NA processes for MTBE remediation requires much larger reaction zones than for other pollutants. The main limiting factor for MTBE degradation seems to be a sufficient oxygen supply" (Martienssen and others, 2006).

Reference

Martienssen, M., Fabritius, H., Kukla, S., Balcke, G.U., Hasselwander, E. and M. Schirmer, "Determination of naturally occurring MTBE biodegradation by analyzing metabolites and biodegradation by-products," *Journal of Contaminant Hydrology*, Vol. 87, No. 1-2, 2006; www.sciencedirect.com



Bioaccumulation of polycyclic aromatic hydrocarbons in plant shoot tissues

Scientists examined the bioaccumulation of polycyclic aromatic hydrocarbons (PAH) by halophytic plants. They focused their efforts on *Salicornia fragilis*, an edible coastal plant, by exposing the plant to soil contaminated with varying degrees of heavy fuel oils and analyzing plant tissues for PAH content versus sediment pollution and exposure duration.

Material and methods

Meudec and others (2006) conducted their research using *Salicornia fragilis*, commonly named glasswort, an annual, leafless, flowering plant with articulated and succulent stems. The scientists collected *Salicornia fragilis* plants and surrounding sediments from a natural salt marsh in Finistère, France.

The plant samples included 7-cm-long shoots, which, with their associated segments, were replanted in a greenhouse and acclimated for two weeks. Scientists took samples of sediments surrounding the plants. The samples were washed, drained and homogenized before being artificially polluted with heavy fuel oil (No. 6 type). The fuel was composed of the following:

- 20% saturated hydrocarbons ($n_{c9-n_{c25}}$)
- 52% aromatics

- 27% polar compounds (resins and asphaltenes)

The scientists mixed 2, 20 or 200 g of fuel oil with 1000 g of sediments to get 0.2%, 2% and 20% oiled sediments (w/w). Sediment-filled pots were set in containers filled with a 5-cm-high liquid layer of a nutritive solution, renewed weekly. The solution was composed of commercial manure. Salinity was artificially fixed at 15 g L⁻¹.

Fuel exposure

Scientists exposed 20 plants to each of the three oiled sediment conditions (0.2%, 2% and 20% oiled sediments). Following one week of exposure, 2-cm-long shoot segments were cut for analysis, and roots were removed from the substratum. The sampled plant sections were cleaned carefully. The researchers noted, "the complete removal of viscous and sticking residues of heavy oil from roots proved to be very difficult, namely impossible despite washings. Although they were carefully cleaned, the roots remained black and limed. Thus, PAHs were quantified only in a single sample of roots, contrary to shoot parts" (Meudec and others, 2006).

The researchers also planted 120 plants in 0.2%-oiled sediment to assess the bioaccumulation of PAHs versus time. During the six-week study period, 20 plants were sampled each week.

Meudec and others (2006) grew control plants in oil-free sediments within the same greenhouse as contaminated plants and soils. The sediment PAHs were assayed at the beginning and end of treatments every week.

PAH analysis

PAH assays were conducted by gas chromatography-mass spectrometry (GC-MS). Frozen aliquots of the shoot mixture were

- weighed

- crushed
- homogenized in ethanol
- extracted from plant matrix with KOH
- shaken at 140 rpm for 1 h at room temperature
- incubated for 16 h at 60°C
- isolated with hexane
- washed
- separated from substances more polar than PAHs
- concentrated under vacuum
- resuspended in dichloromethane

The researchers also ran blanks of deuterated PAH standards and the PAH controls with every set of extractions to yield the recovery rate. They quantified the PAHs with GC-MS and conducted data acquisition and integration with chromatography software. "Identification of the PAHs in samples was based on the retention times and ion m/z ratios of the 16 PAH standards in the control. They were quantified as referred to deuterated pyrene (Pyd₁₀) and benzo(α)pyrene (BaPd₁₂) as internal standards" (Meudec and others, 2006).

Results

The researchers did not find detectable amounts of PAHs in the aerial parts of *Salicornia* plants grown in unpolluted sediments.

PAH concentrations in plant shoots

Meudec and others (2006) reported significant variation among PAH concentrations among the different degrees of sediment pollution. The greatest PAHs were found in plants grown in the most polluted sediment. Total PAHs for roots of 0.2% sediments were 33.5 mg kg⁻¹ dry weight (DW). This value was about 10 times the level in shoots. The researchers determined that "the uptake of individual PAH by plants depended

on its concentration in polluted sediments. The higher the concentration of a given PAH was in sediments, the higher it was in the shoots." This was not the case with high-weight PAHs, indenopyrene, dibenzoanthracene or benzoperylene, which "remained below the detection limit of 20 $\mu\text{g kg}^{-1}$ DW in shoots of plants grown on 0.2%-oiled substratum despite their significant levels in this sediment."

The researchers found phenanthrene, pyrene and chrysene to be the primary PAHs bioaccumulated in the plants. Their amounts increased with the level of sediment pollution. Plants grown in 20%-oiled sediment were observed to contain, respectively, 13380, 8430 and 2255 $\mu\text{g kg}^{-1}$ DW of phenanthrene, pyrene and chrysene, while the plants grown on the 0.2% oiled substratum contained 655, 1320 and 335 $\mu\text{g kg}^{-1}$ DW, respectively. These three PAHs were also the most concentrated in polluted sediments, with phenanthrene, pyrene and chrysene ranked in descending order. "By contrast, under the other conditions, PAH concentrations showed differences between tissues and sediments: pyrene was clearly predominant in tissues conversely to sediments where phenanthrene, pyrene and chrysene looked similarly distributed" (Meudec and others, 2006).

The scientists classified the PAHs in three groups, low, medium and high, in terms of weight. They reported that low- and medium-weight PAHs were the major contributors to total PAHs in plants, 7.6–10.1% under 0.2% and 20% oil-pollution conditions. High-pollution sediments, they found, significantly increased the contribution of low-weight PAHs and decreased that of the medium-weight PAHs.

PAH time to bioaccumulation

Meudec and others (2006) quantified PAH contents on 0.2% polluted soils as individual and total amounts during the monitoring period. In the first week of

monitoring, they observed total PAHs to be significant, 3.5 mg kg^{-1} DW, but the peak PAH total came in the fourth week, 10.4 mg kg^{-1} DW. Except for acenaphthylene and acenaphthene, PAHs remained available for uptake by the plants during that time.

Bioaccumulation increased for naphthalene, fluorene, phenanthrene, anthracene and benzo(a)pyrene until a sudden fall after the fourth week. Fluoranthene and pyrene bioaccumulation continued for an additional week. Benzo(a)anthracene and chrysene rates increased during the first week but then dropped. The scientists reported that "this pattern was also followed by benzo(b)- and benzo(k)fluoranthene, but at lower concentrations, which made them below the detection limit at week two. The three high-weight PAHs remained undetectable in tissues throughout the six-week monitoring despite their significant presence in sediments" (Meudec and others, 2006).

PAH tissue distribution versus time revealed naphthalene, phenanthrene, fluoranthene and pyrene to be predominant. Scientists observed that 13 out of 16 PAHs contributed to the total PAH concentration after one week. The contributions of acenaphthylene, acenaphthene, fluorene, benzo(b)- and benzo(k)pyrene to total PAHs decreased with time. At the end of the six-week monitoring period, total PAH concentration was mainly due to naphthalene, phenanthrene, anthracene, fluoranthene, pyrene and chrysene.

Medium-weight PAHs were found to contribute most to total PAH concentration, regardless of exposure time. "The variations of respective contributions observed over the two last weeks may result from differences in the behaviors of individual PAH within the plant. In sediments, no time change was noticed" (Meudec and others, 2006).

Discussion and conclusions

The researchers determined that "Due to their fast and persistent adsorption onto particles, PAHs are strongly accumulated in sediments. The slight changes in PAHs concentrations and distributions over the six-week monitoring described here suggest a lack of significant oil degradation in sediments under our experimental conditions. Degradation of fuel oils by evaporation, photo-oxidation or microorganism biodegradation is slowed down by the anaerobic properties of salt-marsh substratum liable to enhance the long-term fate of pollutants. Therefore, the reduction of total PAHs concentrations after four weeks of *Salicornia* culture on 0.2%-oiled substratum would result more from the inherent properties of this species rather than from oil weathering. Indeed, except for acenaphthylene and acenaphthene, all PAHs were at sufficient concentrations in sediments to allow significant uptake by plants versus time. The time reduction of PAH contents and eventually their disappearance could result from biotransformation or salting-out" (Meudec and others, 2006).

Meudec and others (2006) concluded, "To our knowledge, this study provides the first quantification of fuel oil PAHs bioaccumulated by a halophytic plant from a polluted soil. It evidenced the fast and intense bioaccumulation of PAHs from oil-polluted sediments in the shoots of a halophytic plant, *S. fragilis*. This bioaccumulation depended on exposure duration and pollution degree. Accordingly, the phytotoxicity of PAHs needs to be thoroughly investigated to allow a better assessment of ecological impacts by oil spill on terrestrial vegetation and salt marshes. Ongoing investigations within our lab are focused on establishing correlations between the PAHs concentrations in *S. fragilis* and their developmental and physiological consequences."

Reference

Meudec, A., Dussauze, J., Deslandes, E. and N. Poupart, "Evidence for bioaccumulation of PAHs within internal shoot tissues by a halophytic plant artificially exposed to petroleum-polluted sediments," *Chemosphere*, Vol. 65, No. 3, 2006; www.sciencedirect.com

UTTU thanks Dr. Anna Meudec, anna.meudec@univ-brest.fr, for her help on this article.



Monitoring subsurface microbial ecology in a contaminated aquifer

Researchers investigated Bio-Sep® bead biotrap as a method for monitoring subsurface microbial ecology of a gasoline-contaminated aquifer. During a 15-month pilot study prior to the investigation, a sulfate amendment had been injected and investigated for efficacy of enhancing attenuation of benzene, toluene, ethylbenzene and xylenes (BTEX). The researchers compared bead biofilms to planktonic samples from ground water monitoring wells.

Materials and methods

Study site

The study took place at a shallow, unconfined, fractured-rock aquifer in Bellingham, Washington. A ruptured gasoline pipeline contaminated the aquifer in 1999. The pipeline released 870 m³ of gasoline between Whatcom Creek and Hannah Creek. Sublette and others (2006) reported that "a significant amount infiltrated into soil near the source area and migrated into underlying sedimentary rock fractures extending toward Whatcom Creek."

The area was characterized by the following:

- near-surface geology of sandstone, siltstone, shale and coal
- 4.5 m fill and/or silty fine sand to silty clay glacial sediment above bedrock
- thin veneer of forest duff or topsoil directly on bedrock in some locations
- steeply graded sedimentary bedding planes that dip toward the east
- bedding planes with north-south orientation

The gasoline migrated through the "utility backfill surrounding the large-diameter water supply piping and the near-vertical bedding planes and fractures in sedimentary bedrock" (Sublette and others, 2006).

Following the event, workers excavated more than 7500 m³ of impacted soil from the site. A horizontal/vertical well couplet and traditional recovery wells were installed. The site also underwent air sparging and soil vapor extraction. Five months following excavation, no significant amounts of free-product gasoline were present or recovered. In 2002 vapor extraction was terminated. Air sparging continued, primarily in the source zone. "Collectively (free product + vapor), 3.8 m³ of gasoline had been removed from the aquifer by mid-2003" (Sublette and others, 2006).

Site BTEX concentrations, scientists reported, "were monitored monthly downgradient of the source zone by a network of monitoring wells from 1999 to the present. Even after much of the free product was removed, dissolved-phase concentrations of BTEX in the central untreated area of the plume attenuated only very slowly. Sulfate was depleted in the plume (< 1 mg/L) relative to upgradient (5 to 12 mg/L), suggesting the presence of sulfate-reducing bacteria (SRB) and active sulfate reduction." Thus, a sulfate injection pilot test was run. A 61-m-long, 1.2-m-deep infiltration gallery was installed in April 2003. The infiltration gallery crosscut

north-south running bedrock fractures (Sublette and others, 2006).

Researchers used Bio-Sep® biotrap consisting of the following:

- 120 Bio-Sep® beads
- 11.4-cm polyfluoroalkoxy (PFA) tubing, perforated
- glass wool and nylon plugs

The biotrap were assembled prior to transport to the field site.

Sulfate injection

Sulfate injection began in June 2003. Injection consisted of 3.8 m³ of 500 mg/L sulfate as Na₂SO₄. For three months, injections were repeated approximately every other day. Injection frequency was reduced to eight per month, from 15, in October, and sulfate concentration was decreased. Sublette and others (2006) reported, "The volume of each injection remained at 3.8 m³, but the sulfate concentration was increased to 368 mg/L in mid-April and then to 500 mg/L in mid-August of 2004. The water used to initially prepare the sulfate solution for injection was saturated with air."

Sampling and analysis

The researchers collected ground water samples before and after sulfate injection once a month. The samples were analyzed for gasoline-range hydrocarbons and sulfate. Ground water samples were also collected from monitoring wells pre- and post-sulfate injection and analyzed for phospholipid fatty acids (PLFA).

In May 2003, the researchers installed biotrap into five of the monitoring wells "in order to establish preamendment conditions." The biotrap were attached to a nylon line 30 cm below the water level. They were retrieved in June and analyzed for PLFA. Fresh biotrap were installed over the next 15 months during the sulfate injection. PLFA analysis consisted of lipid extraction into

neutral lipids, glycolipids, and polar lipids, separation into fatty acid methyl esters (FAME), and analysis by gas chromatography/mass spectrometry. Screening for the catabolic gene (benzylsuccinate synthase-bssA) "associated with the first step of anaerobic toluene and xylene degradation" allowed researchers to "quantify the number of bacteria that are genetically capable of anaerobic toluene or xylene degradation in a given sample." (Sublette and others, 2006).

Researchers extracted bead samples and then performed real-time polymerase chain reaction (PCR) on each, using oligonucleotides designed to target the DNA region of interest.

Results and discussion

Preinjection geochemistry

The scientists observed "some decrease in concentrations of toluene and xylenes," but benzene and ethylbenzene concentrations were relatively stable. Dissolved oxygen (DO) concentrations were typically 0 to 1 mg/L and sulfate concentrations were typically below 1 mg/L (Sublette and others, 2006).

Postinjection geochemistry

Reductions in BTEX components, both pre- and post-injection, were "modeled as first-order reactions, and apparent first-order rate constants were obtained for the plume wells with the highest BTEX concentrations. First-order rate constants were consistent with those observed from previously reported field studies" (Sublette and others, 2006).

The researchers observed significant increases in the apparent first-order rate constants in three wells for toluene and xylenes, "in two wells for benzene and gasoline-range total petroleum hydrocarbons (TPH-G), and in one well for ethylbenzene in the 15 months following initiation of sulfate injection." They found that toluene concentration decreased significantly during

and after injections, compared to BTEX overall (Sublette and others, 2006).

Following injection, Sublette and others (2006) initially observed sulfate accumulation in the aquifer. Sulfate concentrations then decreased, but as total BTEX concentrations were reduced, sulfate concentrations again rose. Similarly, they found dissolved oxygen to increase in concentration with injection, but later to decrease. Sulfate and oxygen levels after 200 days were similar to preinjection levels. Mean sulfate and DO concentrations before and after this date were significantly different.

Subsurface microbial ecology

Scientists determined that a significant difference in relative proportions of cyclopropyl fatty acids pre- and post-200 days existed. "Cyclopropyl fatty acids are commonly found in anaerobic bacteria and are major components of *Desulfobacter* species." A linear correlation exists among cyclopropyl fatty acids concentrations and redox potential and concentrations of DO and sulfate in ground water." This indicated increased anaerobic bacteria populations (Sublette and others, 2006).

The scientists also observed the following:

- increased branched monosaturated (BrMonos) fatty acids
- increased mid-branched saturated (MidBrSats) fatty acids
- increased sulfate-reducing bacteria (SRB) activity
- no significant changes of monoenoics or terminally branched saturates (TerBrSats)
- decreased pmol PLFA
- increased bssA gene concentrations in biotrap beads, particularly for two of the monitoring wells

Sublette and others (2006) reported that the results, collectively, indicated "that sulfate injection resulted in

a shift in the subsurface microbial community structure to increased anaerobic character and increased proportions of SRB. This shift to a predominance of anaerobic growth was accompanied by a subsequent reduction in growth rates as readily degradable electron acceptors were depleted."

Biotrap vs. ground water sampling

The scientists made comparisons between PLFA results from biotrap samples and those from ground water samples "in order to determine whether ground water sampling of plume wells could have led to the same conclusions regarding shifts in microbial community structure as the biotrap samples." They discovered that the two sets of results pre-200 days were significantly different except in proportion of TerBrSats. After 200 days, though, results for ground water and biotrap samples were comparable. Ground water samples pre- and post-200 days were not found to be significantly different and therefore "did not indicate any significant changes in subsurface microbial ecology during sulfate injection, whereas biotrap sampling did and was consistent with geochemistry." Scientists explained that this difference was likely due to biotrap's requirement for growth, while ground water samples detect organisms whether they are growing or not. They said, "Biotrap samples are more indicative of the microbial activity actually being expressed in the aquifer. Further, a ground water sample is a grab sample indicative of only a moment in time, whereas a biotrap sample is integrative of subsurface conditions during the entire period of incubation in the aquifer" (Sublette and others, 2006).

Conclusion

Sublette and others (2006) concluded that BTEX biodegradation and gasoline-range hydrocarbons were enhanced by sulfate injection. Bio-Sep® biotrap samples were useful because they "indicated changes in subsurface microbial ecology, which were consistent with observed

changes in geochemistry such as sulfate concentrations, dissolved oxygen concentrations, and rates of BTEX biodegradation." Biomarker analysis of ground water samples did not detect these changes.

Reference

Sublette, K., Peacock, A., White, D., Davis, G., Ogles, D., Cook, D., Kolhatkar, R., Beckmann, D. and X. Yang, "Monitoring subsurface microbial ecology in a sulfate-amended gasoline-contaminated aquifer," *Ground Water Monitoring & Remediation*, Vol. 26, No. 2, 2006; www.ngwa.org

UTTU thanks Dr. Kerry Sublette, kerry-sublette@utulsa.edu, for help on this article.



Research notes

Decision-making under uncertainty in case of soil remediation

Scholz, R.W. and U. Schnabel, *Journal of Environmental Management*, Vol. 80, No. 2, 2006; www.sciencedirect.com

Scholz and Schnabel (2006) presented a decision-making method for choosing among remediation alternatives where "assessment of contamination is uncertain, the costs of remediation are high, and the impacts on the environment are multiple." The authors primarily focused on soil washing, phytoremediation, and no remediation as options for site treatment. Their decision-making criteria included the following:

- remediation cost
- human health and agricultural impact
- economic gain

They employed probability density functions as representations of contamination for all site coordinates and examined "the probability of different types of correct decisions such as a hit or a true rejection and erroneous decisions such as a false alarm or miss."

The authors applied the decision model to a case study on heavy metal-contaminated soil.

They evaluated soil-testing costs with utility scores. The utility function allowed consequences of actions to be assessed. "As utility functions often include a personal perspective, they can be seen as a compromise between accurate scientific knowledge and subjective information" (Scholz and Schnabel, 2006).

Scholz and Schnabel (2006) integrated cadmium (Cd) estimation uncertainty, a class of possible errors, and a multi-criteria utility analysis to yield a proper decision on soil remediation alternatives. They defined non-redundant dimensions and comparable criteria for the decision. The researchers demonstrated the method with the Cd case example and utility function. Based upon the case study results, the researchers advised taking geostatistical uncertainties into account. They also suggested that principles beyond the expected utility principle be applied for the most useful results.

The researchers noted that soil remediation decisions "should be based on the relative importance of each utility for different stakeholders." Weighting could be performed in order to aid the selection of the best remediation alternative. Weighting would be particularly useful, they noted, if "the difference between the utility scores of the best and the worst alternative are considered to be of different importance or value for different dimensions" (Scholz and Schnabel, 2006).

The decision-making method, Scholz and Schnabel (2006) reported, is appropriate for many situations despite the strong assumptions made. If uncertainties are linked and types of errors and correct decisions,

such as miss, false alarm, hit, and correct rejection, are given a nominal value, the impacts of applying different remediation alternatives may be predicted. They concluded that their method "increases decision makers' knowledge, provides insight into the comparison of different remediation options, and presents a formal, consistent, and transparent approach for making management decisions for contaminated land management."

Applications of comprehensive two-dimensional gas chromatography to the characterization of petrochemical and related samples

von Mühlen, C., Zini, C.A., Caramão, E.B. and P.J. Marriott, *Journal of Chromatography A*, Vol. 1105, No. 1-2, 2006; www.sciencedirect.com

Scientists examined the uses of comprehensive two-dimensional gas chromatography (GC×GC) for analysis of petrochemical and related samples. Compared to one-dimensional gas chromatography (1D-GC), the resolution, component selectivity, signal-to-noise ratio, and as a result the sensitivity, have been reported to be significantly enhanced in GC×GC. "A unique outcome of GC×GC is well-structured chromatograms according to chemical class definition within the two-dimensional (2D) separation space, which provides new capabilities for sample characterization in ways hitherto impossible in GC analysis. All these characteristics render this technique extremely useful for the analysis of complex matrices or other samples where 1D-GC is incapable of providing a reasonable or acceptable separation, as for example, in enantiomeric separations" (von Mühlen and others, 2006).

They reported that GC×GC has been applied to petrochemical matrices in the past because

“chromatographic characterization of all compounds in crude oils is practically impossible in a single separation step even with spectroscopic (e.g. MS) detection, resulting usually only in identification of a limited number of different group-type compounds.” Group-type analysis with GC×GC has evidently been helpful to researchers in the past because it yields ordered structures in two-dimensional contour plots that “allow unequivocal chemical compound classification and identification through a visual inspection of the contour plots.” (von Mühlen and others, 2006)

The scientists examined the applications in which GC×GC may be used for the analysis of petrochemicals including gasoline, jet fuels, light gas oil, diesel fuel, crude oil, non-aromatic solvents, kerosene, wash oils, biomarkers and environmental pollutants in soil, sediments, water and air. Analyses were conducted with GC×GC on these chemicals during past research, which the authors discussed (von Mühlen and others, 2006).

von Mühlen and others (2006) concluded that GC×GC is a useful technique for extracting information about petroleum and related matrices because it allows the ordered retention of structurally related compounds to be shown in a contour plot, “which allows the immediate recognition of chemical classes present in a complex sample, as in a fingerprint.” In addition, it has high resolution and sensitivity for compound identification. They determined that sample preparation steps may be reduced and sample identity information increased when GC×GC was used in conjunction with time-of-flight mass spectrometry (TOFMS).

“All these characteristics have also led to a more detailed and efficient monitoring of different stages of petroleum processing, giving information about sub-products, reaction mechanisms, and allowing the improvement of the processing stages and their

monitoring. Although petrochemical applications of GC×GC are not yet established as industry-accepted analytical methods, in some areas they have already been used as routine analytical procedures, such as in the analysis of SVOC in fine particulate matter and for in situ VOC monitoring. In this case, the acquisition of a great amount of reliable information was only possible because of the use of GC×GC” (von Mühlen and others, 2006).

Simulated gravitational response to hydraulic testing of unconfined aquifers

Damiata, B.N. and T.C. Lee, *Journal of Hydrology*, Vol. 318, No. 1-4, 2006; www.sciencedirect.com

Scientists developed a general expression to calculate the gravitational response of shallow unconfined aquifers to hydraulic testing, based on the gravitational attraction of the drawdown cone, which is considered a solid of revolution. Their derivation assumed that “the unconfined aquifer is relatively incompressible and that the gravitational response is due to the instantaneous and complete drainage of the pore spaces above the water table as it lowers” (Damiata and Lee, 2006).

The scientists numerically simulated the gravitational response caused by pumping groundwater from a homogeneous, laterally isotropic, unconfined aquifer. The model “assumed isotropic hydraulic conductivity in both the radial and vertical directions. The purpose of the modeling was to help assess the feasibility of using the gravity method to augment hydraulic testing and not an exhaustive examination of all possible field conditions that may be encountered” (Damiata and Lee, 2006)

The scientists chose representative values for hydraulic properties of an aquifer of silty to clean sand. These included the following reference set of test conditions:

- 25 m depth to static water level
- 50 m initial saturated thickness
- 10^{-4} m/s hydraulic conductivity
- 0.001 storativity
- 0.25 specific yield

Damiata and Lee (2006) focused their analysis primarily on “the drawdown at a radial distance of 1 m from the pumping well, the gravitational response at this same distance, and the ‘detection’ distance which is here defined as the radial distance to the point where the absolute value of the gravitational response decreases to 1 μ Gal.” They ran simulations of the gravitational response due to both total and incremental drawdown.

The scientists concluded, “The relationship between drawdown and gravitational response is complex because the former is independent of depth while the latter is a volumetric response with an inverse-depth-squared dependency. Thus, the signals generated during hydraulic testing depend not only on the parameters of the test and properties of the aquifer but also on the depth to the static water level” (Damiata and Lee, 2006).

Damiata and Lee (2006) determined the following;

- hydraulic testing of a shallow unconfined aquifer with representative properties should produce a gravitational response on the order of tens of μ Gals
- high-resolution gravity surveying may be “a relatively convenient and cost-effective means to augment hydraulic testing by spatially monitoring the development of the drawdown cone that otherwise would require an extensive system of monitoring wells or piezometers”
- gravitational response increased with increasing specific yield

- unconfined aquifers comprised of fine- to medium-grained sands with minor amounts of silt should produce the largest signals and are the most promising candidates for monitoring

They noted that "there is considerable debate in the literature as to whether the groundwater released above the moving water table is instantaneous or time dependent." For non-instantaneous conditions, the model will overestimate the gravitational response at early pumping times but the difference should decrease with increasing time (Damiata and Lee, 2006).

UTTU thanks Dr. Brian Damiata, damiata@ucla.edu, for his help on this article.