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NO_x Emission Control Using Plasma-Assisted Catalysis

by Bernie M. Penetrante, Lawrence Livermore National Laboratory

Governments are becoming more conscious of the need to protect the environment and the need to conserve energy. The increasing consumption of fossil energy resources, for both stationary electrical power and transportation, has led to greater environmental pollution. The world demands better technologies that can increase the efficient use of energy but without the harmful effect of increased pollution.

In the field of catalytic treatment of engine emissions, one application that has been classified as a breakthrough technology is the catalytic reduction of NO_x in oxygen-rich environments using hydrocarbons [1]. This breakthrough will require

dramatic improvements in both catalyst and engine technology, but the benefits will be substantial for energy efficiency and a cleaner environment. Engine and automobile companies are placing greater emphasis on the diesel engine because of its potential for saving fuel resources and reducing CO₂ emissions. The modern direct-injection diesel engine offers demonstrated fuel economy advantages unmatched by any other commercially viable engine. The main drawback of diesel engines is exhaust emissions. A modification of existing oxidation catalyst/engine technology is being used to address the CO, hydrocarbon, and particulates problems. However, no satisfactory solution currently exists for NO_x. Diesel engines operate under net oxidizing conditions, thus rendering conventional three-way catalytic converters ineffective for controlling NO_x emission. NO_x reduction catalysts, using ammonia as a reductant, do exist for oxygen-rich exhausts; however, for transportation applications, the use of on-board hydrocarbon fuels is a more feasible, cost-effective, and environmentally-sound approach.

Selective catalytic reduction

(SCR) by hydrocarbons [2] is one of the leading catalytic aftertreatment technologies for the reduction of NO_x in lean-burn engine exhaust (often referred to as "lean-NO_x"). The objective is to chemically reduce the pollutant molecules of NO_x to benign molecules such as N₂. Aftertreatment schemes have focused a great deal on the reduction of NO because the NO_x in engine exhaust is composed primarily of NO. Recent studies, however, have shown that the oxidation of NO to NO₂ serves an important role in enhancing the efficiency for reduction of NO_x to N₂. It has become apparent that preconverting NO to NO₂ could improve both the efficiency and durability of lean-NO_x catalysts. A non-thermal plasma is an efficient means for selective partial oxidation of NO to NO_x. The use of a non-thermal plasma in combination with a lean-NO_x catalyst opens the opportunity for catalysts that are more efficient and more durable compared to conventional catalysts [3].

The plasma inside a fluorescent lamp is perhaps the most common

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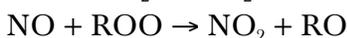
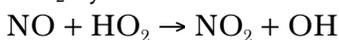
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example of a non-thermal plasma. A non-thermal plasma is an electrically energized gas in which the average kinetic energy of the electrons is much higher than that of the gas molecules. The kinetic energy of the electrons is deposited primarily into the major gas components N_2 , O_2 , H_2O , and CO_2 . The most useful deposition of energy is associated with the production of N, O, and OH radicals through electron-impact dissociation. Oxidation is the dominant process for gas mixtures containing dilute concentrations of NO in mixtures of N_2 , O_2 , and H_2O , particularly when the O_2 concentration is 5% or higher. In the absence of hydrocarbons, the O radicals will oxidize NO to NO_2 ,

and the OH radicals will further oxidize NO_2 to nitric acid. In plasma-assisted catalysis, it is important that the plasma oxidize NO to NO_2 without further producing acids.

Hydrocarbons play an important role in the selective reduction of NO_x to N_2 over the catalyst. The hydrocarbons also play an important role in the selective partial oxidation of NO to NO_2 in the plasma. In the presence of hydrocarbons, the NO is mainly oxidized to NO_2 by



where R is a hydrocarbon radical. The O and OH radicals produced by electron-impact dissociation are consumed mainly by reactions with the hydrocarbons rather than with

NO. Nitric acid formation is minimized because the OH radical reacts preferentially with the hydrocarbon rather than with NO_2 . The hydrocarbons lower the energy cost for the oxidation of NO by converting O and OH to HO_2 ; the OH radical is then reproduced when NO is oxidized by HO_2 . This cyclic process leads to a very efficient use of the plasma-produced radicals and minimizes the electrical energy required by the plasma.

Figure 1 shows a possible plasma-assisted catalyst processor. There are many ways of producing a non-thermal plasma. The schematic shown in **Figure 1** shows a plasma produced by short pulses of high voltage on a metal wire inside a metallic cylinder. The plasma

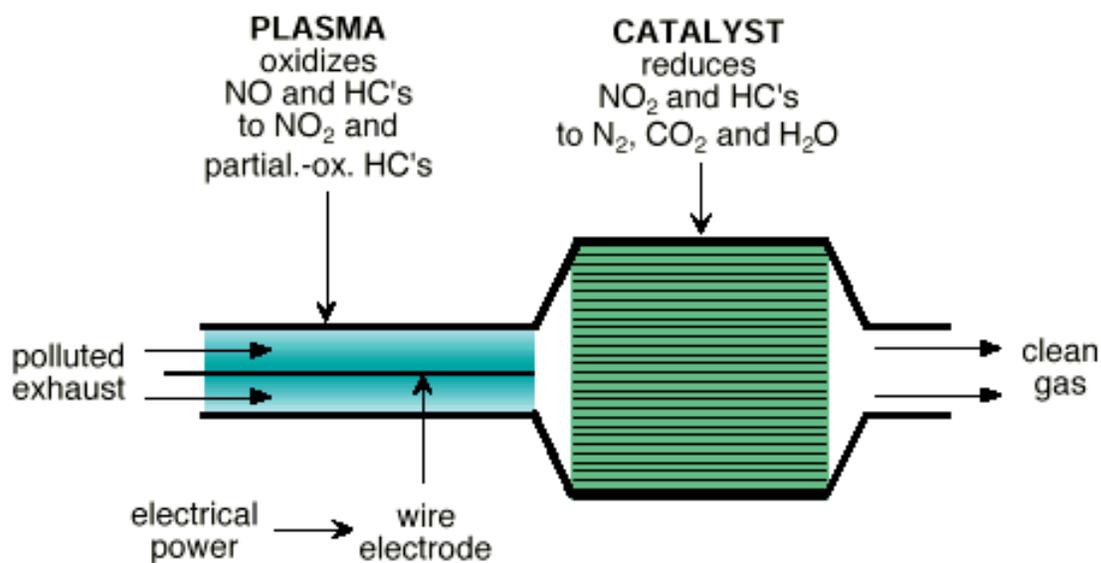


Figure 1 The plasma-assisted catalytic reduction process. Plasma-assisted catalysis can efficiently reduce NO_x without requiring precious metals or low-sulfur fuel. US Patents: 5,711,147; 5,891,409; 5,893,267.

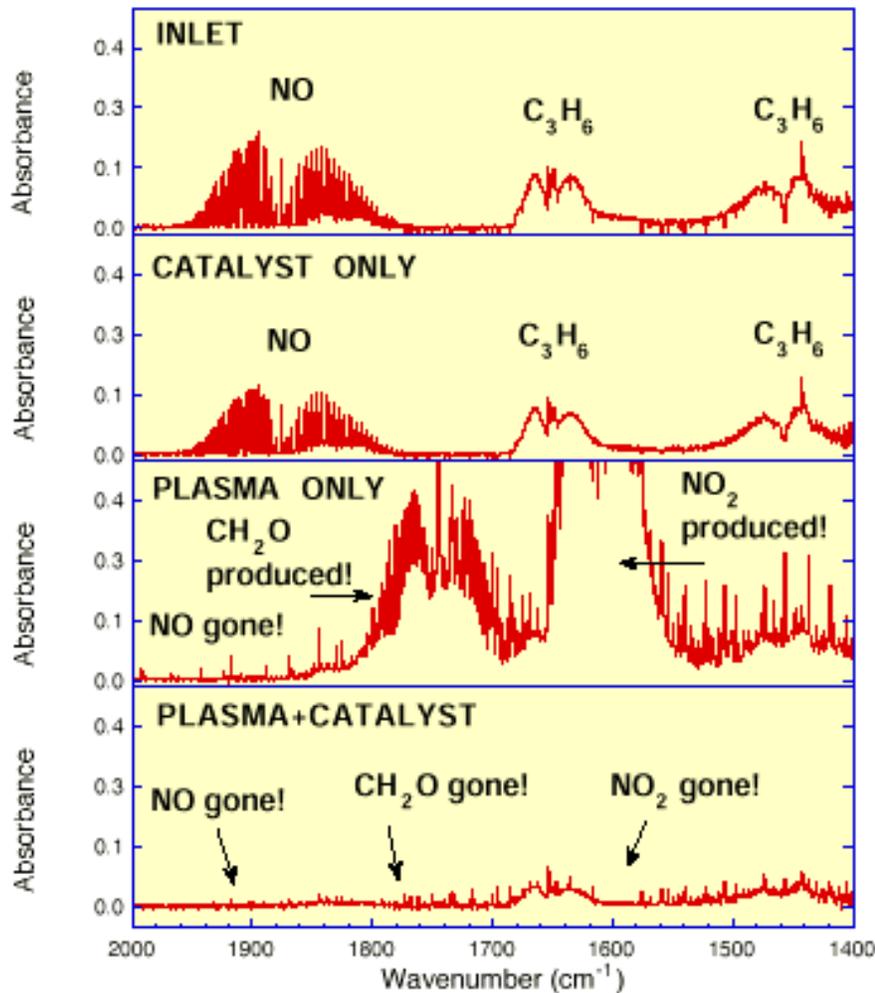


Figure 2 Fourier Transform Infrared (FTIR) spectroscopy data showing the effect of catalyst, plasma, and plasma-plus-catalyst combination on the NO_x and hydrocarbons. The plasma-plus-catalyst combination efficiently removes NO_x and hydrocarbons under conditions where the plasma or the catalyst alone is ineffective.

serves to oxidize the NO and hydrocarbons to NO_2 and partially-oxidized hydrocarbon (HC) products, respectively. The plasma-conversion products are then reduced over the catalyst to N_2 , CO_2 , and H_2O .

Figure 2 shows Fourier Transform Infrared (FTIR) spectra illustrating the effect of catalyst, plasma, and plasma-plus-catalyst combination on the NO_x and hydrocarbons. In this example, propene is used as the hydrocarbon reductant. When the electrical

power to the plasma reactor is turned off and the gas mixture is passed through the catalyst, the efficiencies for both the NO_x reduction and the hydrocarbon oxidation are very low, as shown in the second box ("Catalyst Only"). When the electrical power to the plasma reactor is turned on, the NO is oxidized to NO_2 and the propene is partially oxidized to formaldehyde, as shown in the third box ("Plasma Only"). When the NO_2 -containing gas stream from the plasma is then passed through the

same catalyst, both the NO_x and the hydrocarbons are eliminated, as shown in the bottom box ("Plasma + Catalyst"). The plasma-plus-catalyst combination efficiently removes NO_x and hydrocarbons under conditions in which the plasma or the catalyst alone is ineffective.

There is a heated debate between engine and oil companies over the

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need to reduce sulfur in the fuel so that catalyst technologies can efficiently reduce tailpipe emissions of NO_x . State-of-the-art lean- NO_x catalysts require precious metals (e.g., platinum) to convert NO_x to N_2 with high efficiency, particularly at the relatively low temperatures (300° C and below) of diesel engine exhaust. In addition to oxidizing NO to NO_2 , the precious metal is very effective in oxidizing SO_2 to SO_3 . The SO_3 forms sulfate on the catalyst sites, leading to degradation of the NO_x reduction. The SO_3 also leads to the production of sulfuric acid, which adds to particulate emission. Furthermore, the precious metal is also very active in the oxidation of the hydrocarbons; this results in a decrease in the availability of the hydrocarbon as a reductant for NO_x .

Plasma-assisted catalysis can efficiently reduce NO_x without requiring precious metals or low-sulfur fuel. The plasma oxidizes NO to NO_2 , but does not oxidize SO_2 to SO_3 . This makes the plasma-assisted process more tolerant to the sulfur content of fuel compared to conventional lean- NO_x technologies. Furthermore, in a plasma, the hydrocarbons are converted to partially oxygenated hydrocarbons, but not completely oxidized to CO_x and H_2O . For some catalysts, the partially oxygenated hydrocarbons could be more effective compared to the original hydrocarbons in reducing NO_x to N_2 . The plasma can efficiently oxidize NO to NO_2 over a wide range of temperature

without depleting the amount of hydrocarbon available for reduction of NO_x to N_2 .

Efficient reduction of NO_x has been demonstrated with plasma-assisted catalysis when propene is used as the reductant. Notwithstanding reasonably favorable economic projections for such a system (compared to the best available technology that uses ammonia and precious metal catalysts), the use of propene would require an extra logistical trail. Eliminating this extra logistical requirement would greatly reduce the operational cost for the emission control system. In practice, it would be desirable to use the same fuel (i.e., diesel) for both the engine and the emission control device. We are continuing development and scale-up of the plasma-assisted catalyst technology, with the intent of optimizing the use of diesel fuel as the NO_x reductant. We are also investigating several types of catalysts that could provide the optimum combination with the plasma.

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[1] "Breakthrough Catalytic Technologies: The Future," Chapter 12 in R.M. Heck and R.J. Farrauto, **Catalytic Air Pollution Control: Commercial Technology** (Van Nostrand Reinhold, New York, 1995) ISBN 0-442-01782-0.

[2] "Selective Catalytic Reduction of NO_x with N-Free Reductants", M. Shelef, *Chem. Rev.* **95**, 209 (1995).

[3] "Plasma-Assisted Catalytic Reduction of NO_x ," B.M. Penetrante, R.M. Brusasco, B.T. Merritt, W.J. Pitz, G.E. Vogtlin,

M.C. Kung, H.H. Kung, C.Z. Wan and K.E. Voss, SAE Paper Number 982508, in **Plasma Exhaust Aftertreatment** (SAE/SP-98/1395, ISBN 0-7680-0309-1), Edited by J. Hoard and H. Servati (Society of Automotive Engineers, Warrendale, 1998) pp. 57-66.



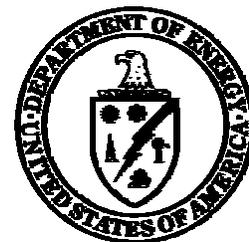
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Sleuthing MTBE with Statistical Data

by Gloria Wilt, Lawrence Livermore National Laboratory

Methyl tertiary-butyl ether, more commonly known as MTBE, is a chemical Janus. It benefits air quality by making gasoline burn cleaner, thus reducing automobile emissions. But it can also find its way into groundwater supplies and give drinking water an unpleasant taste and odor. At present, more than 20 public drinking-water wells in California have ceased water production because of MTBE pollution. Worse yet, the health effects of MTBE are uncertain—the U.S. Environmental Protection Agency currently classifies MTBE as a possible human carcinogen.

Since 1992, MTBE has been the compound of choice for U.S. oil refineries required by the federal Clean Air Act to add an oxygenate to gasoline to help reduce air pollution. However, some MTBE has appeared in drinking water

wells throughout the U.S. This discovery has sparked a national controversy between the need to reduce air pollution (especially in heavily populated areas) and the necessity to safeguard precious water resources from contamination. In an effort to resolve this controversy, the U.S. Environmental Protection Agency (EPA) formed a 14-member panel of MTBE experts from government, the oil industry, academia, regulatory agencies, and environmental groups to explore the environmental and public health effects of MTBE and make policy recommendations by July 1999.

Anne Happel, an environmental scientist at Lawrence Livermore, is a member of this EPA blue-ribbon panel. She leads a multidisciplinary team in the Environmental Restoration Division studying MTBE

contamination of groundwater from leaking underground fuel tanks (LUFTs) throughout California (see **Figure 3**). The team's goal is to help water quality regulators, public health specialists, and MTBE users understand more about how MTBE enters and behaves in groundwater so they can better manage its use, prevent harm to humans, and protect limited groundwater resources. The team has estimated how often MTBE escapes into groundwater through gasoline release and traced the behavior of MTBE in groundwater. The team is currently designing a data management system to target LUFTs most in need of remediation because of the risk they present to drinking water sources (**Figure 4**). The database will allow those responsible for water quality to better manage the cleanup of leaking tank

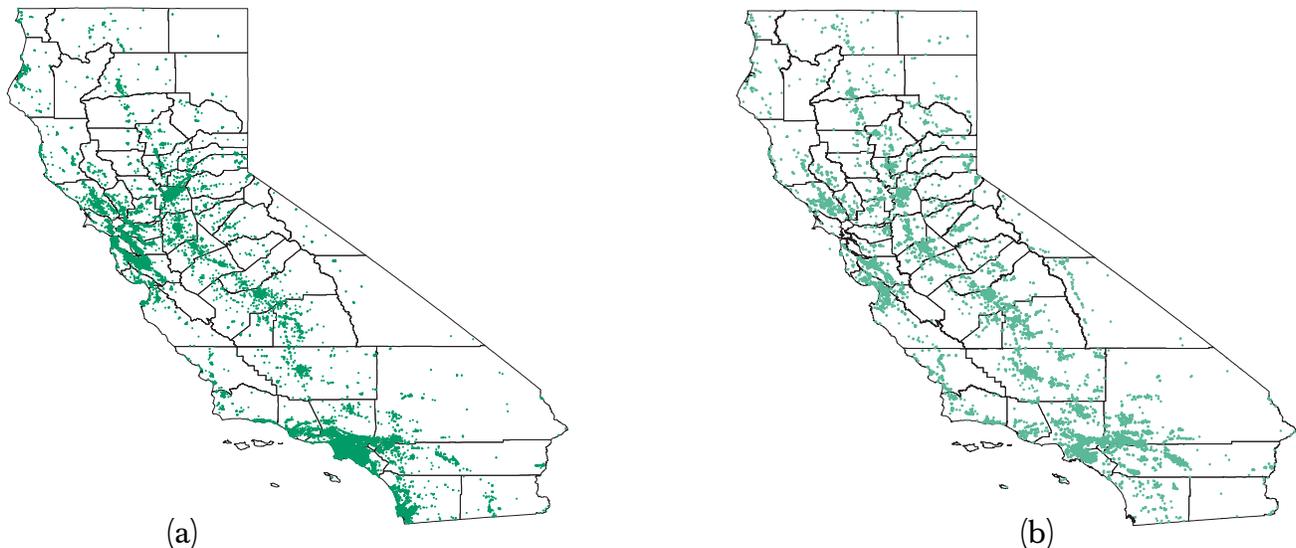


Figure 3 A side-by-side comparison of (a) the locations of leaking underground fuel tanks (LUFTs) in California and (b) the locations of public drinking water wells strongly suggests a high instance of proximity, and highlights concern that MTBE in gasoline from LUFTs will find its way into deeper drinking-water aquifers.

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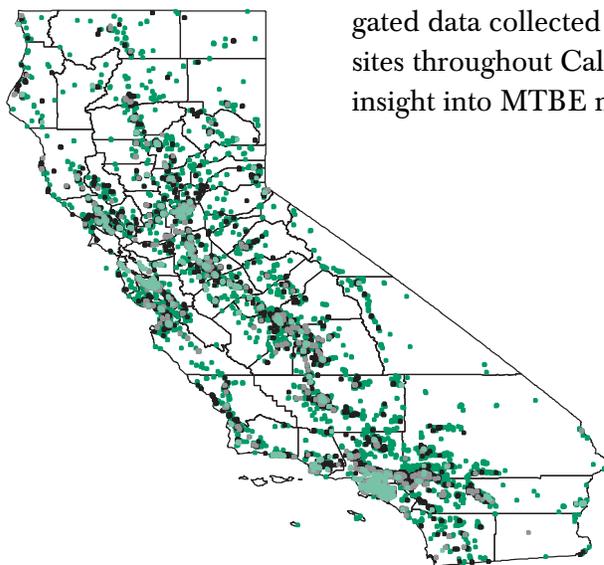
sites and strategically protect drinking water from MTBE.

The study results to date have provided the project sponsors—the California State Water Resources Control Board, the U.S. Department of Energy, and the Western States Petroleum Association—with fundamental information for effective management of California’s groundwater resources. They will also be used to help make legislative decisions and set policy regarding MTBE’s use as a gasoline additive in California and nationwide.

ANALYZING FIELD DATA

Scientists know that MTBE behaves differently in groundwater than other petroleum products such as benzene. Unlike petroleum hydrocarbons, it is highly water soluble, not easily adsorbed to soil, and resists biodegradation. Thus, with widespread use, MTBE has the potential to occur in high concentrations in groundwater, travel far from leak sources, and accumulate to become a hazard on a regional scale.

To investigate these potentialities, the Livermore project team designed a study of MTBE subsurface plumes based on statistical analysis of historical data from California LUFT sites. Researchers investigated data collected at leaking tank sites throughout California to gain insight into MTBE movement from



Public drinking water wells
 ● More than 10 LUFT sites within 1 km
 ● 4–9 LUFT sites within 1 km
 ● 1–3 LUFT sites within 1 km
 ● No LUFT sites within 1 km

Figure 4 The Livermore team determined the number of LUFT sites within 1,000 meters of public drinking water wells. Analysis such as this, together with other data shared through a geographical information system on the Internet, will assist regulators, industry, and other stakeholders in targeting the wells at greatest risk of MTBE contamination and managing LUFT cleanup accordingly.

actual gasoline releases. They examined the frequency of MTBE contamination of groundwater at LUFT sites and public water wells throughout California, and analyzed the behavior (mobility and attenuation) of MTBE plumes as compared to benzene plumes at LUFT sites.

The historical data used present some inherent limitations. Happel says that data from actual leaking tank sites are filled with real-world complexity, uncertainty, and variability. For example, a leaking tank site may have had multiple past releases, each formulated with different quantities of MTBE; the ages of the releases are also unknown; and estimates of their volume are uncertain.

When natural variability is added into the analyses—for example, MTBE transport can vary in different geologies, or it can fluctuate because of the elevation and gradient of the groundwater surface—it is easy to see that data from these sparsely monitored individual sites are less than ideal for precise, quantitative contaminant transport research, which relies on data from large, heavily monitored sites. The project team overcame some of these limitations by treating data from a large number of sites as a statistical population. Similar to an epidemiological survey, this approach allowed them to deduce general trends in the behavior of MTBE and other petroleum hydrocarbons.

The first data analyzed were from 236 LUFT sites located in 24 counties where groundwater had been monitored for MTBE prior to the beginning of 1996, earlier than

legally required. The Livermore team began by assessing how well standard Environmental Protection Agency analytical methods (EPA 8020 and EPA 8260) performed for detection and quantification of MTBE in groundwater samples in the presence of dissolved gasoline. This evaluation enabled the team to quantify the margin of error in the historical data collected using the EPA methods so that the data could be interpreted, presented, and used with appropriate caveats and qualification.

The project team found that the groundwater of 78% of these 236 sites contained detectable levels of MTBE. Given that at least 13,278 of the 32,409 regulated LUFT sites are known to have contaminated groundwater, the project team inferred that more than 10,000 LUFTs may have released MTBE into groundwater. These conclusions are consistent with recent work in which data were collected from over 4,000 sites throughout California.

THE CONCLUSIONS THEY REACHED

Whereas the inferred 10,000 sources of MTBE contamination were the focus of journalistic reporting on MTBE problems, that number was an estimate of the extent of contamination and only one of the findings from the overall investigation. The project team also measured MTBE plume lengths and compared them with the lengths of benzene plumes—benzene is currently the petroleum compound of greatest regulatory concern—to

determine the overall plume migration of the two compounds. Finally, team members analyzed the behavior of MTBE groundwater plumes over time. They were fortunate to obtain MTBE data for 29 sites in San Diego County collected since the beginning of 1992 by an oil company that had analyzed for MTBE while sampling for other hydrocarbons.

The team's work confirmed and quantified what other informal, piecemeal studies had hypothesized, namely, that MTBE is a frequent and widespread contaminant in shallow groundwater throughout California, that MTBE plumes are more mobile than hydrocarbon plumes, and that MTBE may attenuate primarily through dispersion because it resists biodegradation. Put together, these conclusions point to a compound that may progressively accumulate until it contaminates groundwater resources on a regional scale. The team's findings substantiate the need for MTBE regulation and help provide the initial regulatory boundaries.

MORE INSIGHTS TO COME

Given the widespread distribution of MTBE in groundwater at leaking tank sites throughout California, the State Water Board is asking Lawrence Livermore to develop a statewide geographical information system to manage the threat of MTBE contamination to public water supplies. This system will allow regulators for the first time to "triage" sites by targeting manpower and resources for

analysis, characterization, and remediation of leaking tank sites closest to drinking water supplies. The Livermore team has designed a system that will provide detailed information on leaking tank sites and public water supplies to multiple regulatory agencies. Furthermore, access over the Internet will overcome current limitations for obtaining and sharing data among multiple regulatory agencies, industry, and other stakeholders. Happel explains that the goal is to give all interested parties oversight management of leaking tank sites by providing them with access to LUFT data and on-line tools to analyze the data. "We believe that this system has the potential to dramatically transform the way regulators and industry make cleanup decisions and establish priorities for managing cleanup."

The team also will be performing more studies of MTBE biodegradation. All the while, it will be leveraging information and technologies from other projects in Livermore's Environmental Restoration Division to further its MTBE work. The team's insights will be valuable contributions to revising MTBE regulations.

For further information contact Anne Happel (925) 422-1425 (email: happel1@llnl.gov).

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Ground Water Production Council Annual Meeting, Newport, Rhode Island. Water Pollution Control commission in cooperation with State and Federal agencies and industry. Contact Ben Grunewald at 405/516-4972, Fax 405/516-4973, or Paul Jehn at 509/775-3247.

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