THINK TANK

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Ethanol Use Increasing in Delaware

Why ethanol, and why now? On August 8, 2005, President Bush signed the Energy Policy Act of 2005. This act is a broad piece of legislation that addresses everything from underground storage tank compliance (more on that in a future issue!) to renewable energy sources to tax credits for energy-saving technologies.

The Energy Policy Act contained a few key provisions pertaining to ethanol use in motor fuels: it lifted the oxygenate requirement for reformulated gasoline, and it required increased usage of ethanol in gasoline nationwide. The act did not provide a "safe harbor" for MTBE manufacturers against defective product lawsuits. These key factors paved the way for the phase-out of MTBE-blended gasoline and the increased use of ethanol-blended gasoline in our region. Ethanol blends have been sold in the midwestern United States for several years now.

With this in mind, the Tank Management Branch is doing what it can to educate tank owners, operators, contractors, consultants, and consumers about ethanol-related issues. An advisory letter and fact sheet has already been sent to owners and operators. Helpful information is posted on our webpage at: www.dnrec.delaware.gov/awm. In an effort to provide more information to our *Think Tank* readers, this special edition is devoted to a wide range of ethanol-related issues.

Ethanol in Gasoline: The Requirements of the Motor Fuel Tax Administration

by Mike Harrell, Delaware Motor Fuel Tax Administrator

The Environmental Protection Agency announced that, effective May 6th, 2006, federal regulators would no longer specify the oxygen content for clean-burning gasoline in smog-afflicted areas required to use reformulated gasoline, including Delaware. As a result, methyl tertiary butyl ether (MTBE) is no longer required to be added to gasoline. But even before the EPA's announcement, refiners and distributors of gasoline sold in the Northeast Region had decided to drop the controversial additive, which has proven to contaminate soil and drinking water after leaking from underground storage tanks. Instead of dropping an additive altogether, refiners decided to substitute Ethanol in place of MTBE, in a 90% Gasoline/10% Ethanol blend (E10), for various reasons. This change is scheduled to begin regionally as early as April 1st, with the majority of E10 distribution beginning May 1st.

The Delaware Motor Fuel Tax Administration is responsible for regulating the composition and quality of motor fuels sold in Delaware. Motor Fuel Tax is working diligently, in conjunction with the Department of Natural Resources and

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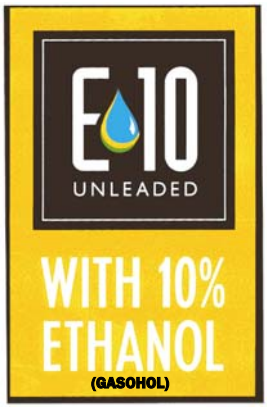
Motor Fuel Tax – Continued from p. 1

Environmental Control, to educate retail gasoline station operators and the motoring public about the fuel composition change. Motor Fuel Tax will provide labels to all Retail Dealers, to insure that these stations are able to meet the labeling requirement of Gasoline Regulation B (3) below. Initially, gas pump labels identifying the E10 product will be provided to all licensed Retail Dealers for each gasoline pump. After the initial distribution, Motor Fuel Tax will provide additional labels at a cost of $1.00 per label.



To aid in the understanding of the responsibilities of the Motor Fuel Tax Administration, as those responsibilities relate to the enforcement of Ethanol composition in gasoline, the following information has been compiled:

- 6 Del. C., ch, 29, §2903 requires that products sold by manufacturers of motor fuel, diesel fuel, heating oil... "shall be in conformity with state standards."

- Retail Sales Regulation 2903.2 (C) states that "Any motor fuel sold at retail...which does not meet or exceed ASTM specifications for that type of fuel...may be ordered corrected or removed from the marketplace."

- 30 Del. C., ch. 51, §5101 (5) states that "a product will be considered 'Gasohol' when it is composed of 1 part anhydrous ethyl alcohol (ethanol) and 9 parts unleaded gasoline."

- Gasoline Regulation B states the following:
  1. "Retailer" shall include a service station, operator, broker, jobber, peddler or any person who offers gasoline for sale in Delaware and who does not possess a valid Delaware Distributor's license.
  2. "Gasoline" as defined in section 5101(4), shall include the mixture of gasoline and ethyl alcohol (ethanol) commonly referred to as "gasohol."
  3. "Gasohol" shall be a blend of nine (9) parts unleaded gasoline and one (1) part ethanol and shall be mixed by a distributor at time of delivery to a purchaser. A retail seller shall clearly label all pumps dispensing gasohol as such.

- Gasoline Regulation I states the following:
  1. When analyzed by a laboratory, if the ethanol content of a sample of gasohol is significantly more or less than 10%, a "Stop Sale" will be issued to the seller until the situation is corrected.
  2. Assuming a "Stop Sale" is issued for a specification failure of gasohol, adding straight ethanol to the storage tank to raise the ethanol content will not be permitted. The product must be pumped out and reblended at the proper temperature for homogenizing before replacing into storage.
  3. For purposes of the administration of this chapter, the State of Delaware does hereby adopt the specifications of motor fuels as defined by the American Society of Testing and Materials (ASTM).

In addition to the Retail Dealers, this fuel composition change will affect licensed Delaware Motor Fuel Distributors. Specifically, Gasoline (product code 65) and Gasohol (product code 124) must be accurately reported by Distributors, in order to insure proper cross matching of transactions between licensees. This will also allow Motor Fuel Tax to insure that, during the period of transition from Gasoline to Gasohol, Retail Dealers reported as having received Gasohol have properly labeled their pumps. Motor Fuel Tax personnel will provide assistance to licensed Motor Fuel Distributors in the completion of monthly tax returns.

If anyone has questions regarding the use of Ethanol in gasoline, please contact the Motor Fuel Tax Administration at (302) 744-2715.

Marking fill lines for E10

Fill lines for gasoline tanks that will receive E10 fuel should use the standard API color markings of white for regular, blue for mid-grade, and red for premium with a black cross in the center for regular, and a white cross in the center for mid-grade and premium.

In addition, stencil "E10" in the intersection of the cross.

Stress Corrosion Cracking in Steel Ethanol Aboveground Storage Systems

by Erich Schuller

The American Petroleum Institute (API) has recently recognized a condition that can occur in aboveground fuel ethanol storage systems constructed of steel. This condition is called stress corrosion cracking (SCC), and is brittle cracking of steel that results from the combination of three factors:

- The inherent properties of the steel
- The environment to which the steel is exposed
- The stress to which the steel is subjected

SCC in steel can occur at stresses less than normal design levels and significant corrosion is not required to be present for it to occur. If not detected, SCC can result in leaks with the subsequent loss of the entire contents of a tank.

In 2003, the API published Technical Publication 939-D, *Stress Corrosion Cracking of Carbon Steel in Fuel Grade Ethanol: Review and Survey,* which investigated 16 cases of SCC which were reported over the past 15 years. The survey could not definitely identify the exact conditions which lead to SCC but it did list the following contributing factors:

- Storage of denatured fuel grade ethanol (1.96 – 4.76% denaturant by volume)
- High tensile or flexural stresses in the steel
- Welds which were not post-weld heat treated
- Flexing of tank components such as the bottom or the roof

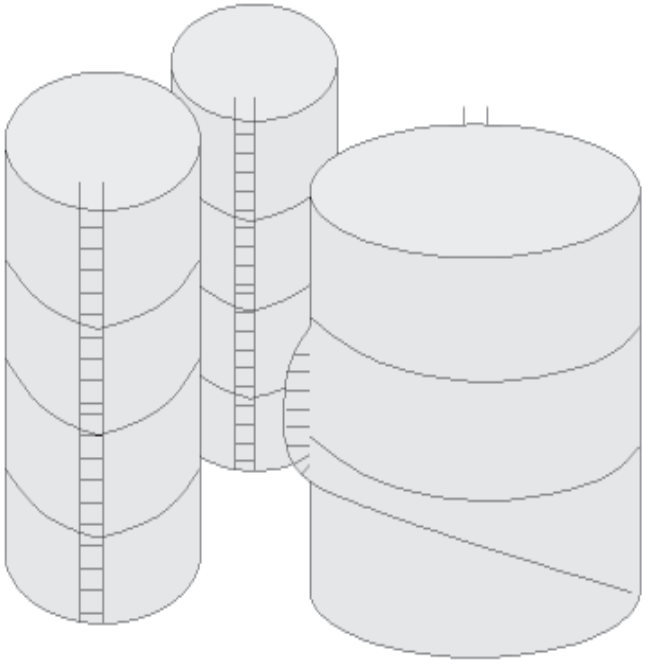
The survey also identified other factors of SCC which appeared in the 16 cases studied:

- SCC has not been reported **after** ethanol has been blended with gasoline
- SCC does not appear to be a problem for tanks and piping at the ethanol manufacturing plant
- SCC has not been reported in the first stage of the distribution system (barges, tanker cars, tank trucks, pipelines)
- SCC has appeared at or after the first major holding point in the distribution system (terminals and gasoline blending facilities)
- SCC has not been reported on the East Coast but this could possibly be attributed to the limited use of ethanol as a gasoline additive on the East Coast at the time of the survey

What can you do to prevent SCC in your steel ethanol storage system and prevent any leaks? The TMB recommends the following:

- Clean and inspect the tank system prior to the storage of ethanol.
- Apply an ethanol-compatible coating on the interior of tank after it has been cleaned.
- Keep water and contaminants out of the tank system.
- Monitor the ethanol to ensure it meets ASTM Standard D4806 which is the quality specification for fuel ethanol.
- Conduct periodic inspections and testing of your storage tank system as recommended by industry standards or as required by Delaware's *Regulations Governing Aboveground Storage Tanks* .
- Operate, maintain, test, and use the tank system's leak detection equipment.

If you have any questions, please call the Tank Management Branch.



Ethanol in the Environment

By Patricia Ellis

The requirement for the use of oxygenates in reformulated gasoline was eliminated by the Energy Policy Act of 2005. But this same legislation required increased use of ethanol in gasoline nationwide, increasing from 4 billion gallons per year in 2006, to 7.5 billion gallons per year in 2012. Therefore, while ethanol is not required to be used in gasoline to meet the air standard requirements of RFG, the nation's use must nearly double in the next 6 years. The quota is on a refinery or blender basis and, if the blender or refiner chooses not to use ethanol, they must buy or trade credits from another entity. The bill did not ban the use of MTBE in gasoline, but most refiners appear to be phasing out the use of MTBE because the legislation did not provide protection from defective product lawsuits.

Area refineries are now in the process of changing over from adding MTBE to their gasoline to adding ethanol. So, with ethanol coming any day now to a gasoline station near you, it's time to become knowledgeable about how gasoline with ethanol behaves differently in the environment than gasoline with MTBE.

There are several similarities in the behavior of MTBE and ethanol in water. MTBE is highly soluble in water compared to the other components of gasoline. In a pure solution, nearly 5% MTBE can dissolve in water. Ethanol is infinitely soluble in water. Both MTBE and ethanol have a very low tendency to adsorb to mineral surfaces or volatilize from an aqueous phase. The primary difference between MTBE and ethanol is that ethanol is highly biodegradable. The tert-methyl and ether groups on the MTBE molecule make it difficult to degrade in the subsurface, whereas ethanol is readily degraded under both aerobic and anaerobic conditions and likely will be effectively attenuated under natural conditions.

Cosolvency Issues

Although ethanol is unlikely to be a significant groundwater pollutant, there is some concern regarding the effects of ethanol on concentrations of other gasoline constituents. Two issues are of most concern. One concern is the potential cosolvency effect that ethanol in water can have with other components of gasoline. Although compounds in gasoline are relatively immiscible in water, ethanol is completely miscible in both water and gasoline at all concentrations. If a sufficiently large amount of ethanol is present in a localized subsurface environment, gasoline and water will become completely miscible with each other and will merge into a single phase. The place where this would be most likely to occur would be where neat ethanol (95-100 percent ethanol, not yet blended with gasoline) might be spilled onto an area previously contaminated by a gasoline spill, such as at a terminal where ethanol is blended into gasoline. Ethanol concentrations of less than 10% by volume in the aqueous phase in groundwater near the site of an RFG spill would be expected to be much lower than the 80% by volume concentration in the aqueous phase that is required to create a single phase.

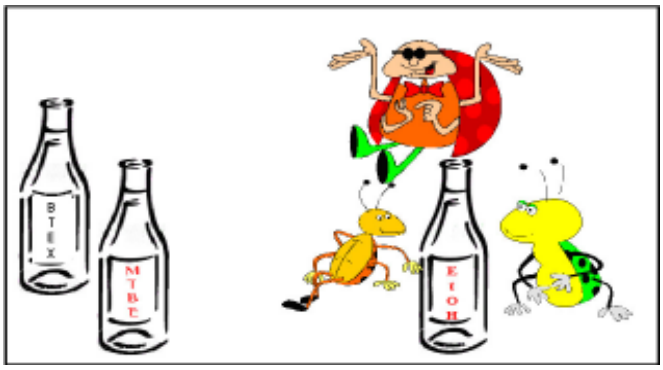
Aqueous phase concentrations of ethanol that leach from gasoline containing ethanol could be high enough to increase the groundwater concentrations of individual chemicals equilibrated with the gasoline. The monoaromatic hydrocarbons are of the most concern, including benzene. Ethanol also affects equilibrium partitioning relationships by the "cosolvent effect," which is observed as a reduction of the aqueous-phase polarity when high concentrations of polar organic compounds are present. Experimental studies have shown an approximately logarithmic increase in benzene, toluene, ethylbenzene, and xylene concentrations with increasing ethanol concentrations. At aqueous concentrations of ethanol up to 15%, BTEX concentrations generally increase by 20-60%. A spill of gasoline initially containing 10% ethanol, once diluted by mixing in the aquifer, would not be likely to show much effect from co-solvency. A spill of neat ethanol at a bulk terminal onto an area of existing petroleum contamination in the ground, however, could result in very high ethanol concentrations in a localized area and as much as an order of magnitude increase in BTEX concentrations.

Biodegradation Issues

Ethanol will be biodegraded at a faster rate than other components of gasoline in both aerobic and anaerobic environments. High concentrations (>100,000 mg/L) of ethanol are not biodegradable because high concentrations are toxic to most microorganisms. Such high concentrations would not be expected from a spill of an ethanol-blended gasoline, but could occur near a spill of neat ethanol. Ethanol plumes should be readily degraded by indigenous microorganisms. Aquifers with low microbial concentrations, cold temperatures, or depletion of electron acceptors will result in plumes that are

longer-lived or longer in length than those where conditions are better for biodegradation. It is expected that ethanol will biodegrade much faster than other gasoline components.

Because of its high oxygen demand, ethanol is likely to be degraded primarily under anaerobic conditions. None of the products of anaerobic degradation of ethanol are toxic, but some of the metabolites, such as butyrate or methane, or changes to inorganic chemicals caused by changing redox potential, may have unaesthetic impacts. Methane analysis should be considered in groundwater sam-



pling programs for monitoring wells in the vicinity of a denatured ethanol release.

Biodegradation is often the most important mechanism for attenuation of gasoline contamination. Quantification of biodegradation rates is necessary to predict net transport of contaminants from a spill and to evaluate the potential for risk to groundwater resources. BTEX degradation is however, integrally linked to the biodegradation of ethanol. Ethanol is likely to be degraded by the indigenous microorganisms that would otherwise feed on BTEX. Degradation of high concentrations of ethanol would exert a greater biochemical oxygen demand than other soluble components of gasoline. Degradation of ethanol is likely to accelerate the depletion of dissolved oxygen and decrease the extent of BTEX degradation. This is particularly important for the fate of benzene, which is the most toxic of the BTEX compounds. Depending of the chemistry of the aquifer and the rate of natural replenishment of electron acceptors, ethanol could also deplete the electron acceptors and nutrients needed for fully degrading ethanol and BTEX.

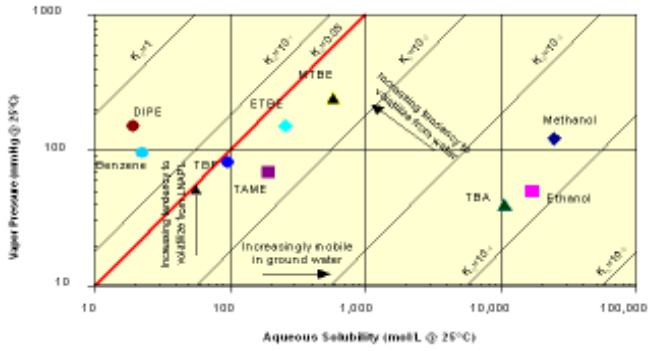
Increased Plume Length

If the presence of ethanol increases BTEX solubilities, BTEX plume length is also likely to increase. Modeling studies have shown that benzene plumes from an ethanol-blended gasoline spill will be from 20 to 150% longer as compared with non-oxygenated gasoline spills. Variability in predicted plume lengths depends of the modeling assumptions and the nature of the aquifer and transport properties investigated. Ethanol constitutes a significant demand on oxygen (and other electron acceptors); the presence of ethanol can deplete electron acceptors, retarding BTEX degradation.

Ethanol and Remediation

The same chemical properties that determine how ethanol behaves in the environment govern which remedial technologies will be effective. The low Henry's Law coefficient for the alcohols, including ethanol, shows that air stripping would not be an effective technology for removal from water. In addition, ethanol does not volatilize readily from LNAPL. The poor adsorption of the alcohols indicates that carbon treatment is not effective. The ease with which ethanol biodegrades in either aerobic or anaerobic environments is a redeeming feature, and BioGAC should be an effective remedial technology.

With our current level of knowledge, it appears that impacts to our groundwater resources associated with the use of ethanol will be less significant and more manageable than those associated with MTBE.



Plot of Vapor Pressure, Solubility and Volatility as expressed in Henry's Law

From "Overview of Groundwater Remediation Technologies for MTBE and TBA," Interstate Technology Regulatory Council, February 2005. http://www.itrcweb.org/documents/mtbe-1.pdf

UST System Compatibility and Ethanol Blends

by Peter Rollo

As Delaware prepares for the delivery of the first load of gasoline blended with 10% ethanol (E10), it is important to consider how to safely store this new product. The technology for storing and dispensing ethanol is essentially the same as that used for gasoline. However, what may have been compatible with gasoline is no longer fully compatible with ethanol blends.

Compatibility

Ethanol blends do not have the same compatibility characteristics of conventional fuel when it comes to storage and dispensing. Soft metals such as zinc, brass or aluminum, which are commonly found in conventional fuel storage and dispensing systems, are not fully compatible with ethanol blends.

Some nonmetallic materials may also degrade when in contact with ethanol such as natural rubber, polyurethane, alcohol-based adhesives (frequently used in older fiberglass piping), certain elastomers and polymers used in flex pipe, bushings, gaskets, meters, filters, and materials made of cork. In order to store and dispense ethanol blends safely, UST systems must be made ethanol compatible.

Remember:

The most important item is to clean your existing tank. No water in the tank is acceptable.

Tank linings with epoxy or polyester resins from the late 1970s and early 1980s may fail when in contact with ethanol. Tank leak detection equipment such as Automatic Tank Gauges using capacitance technology may not work properly and magnetostrictive probe floats may have compatibility/operability issues with ethanol blends due to changes in the specific gravity of the product.

Product dispenser meters may need to be recalibrated after conversion to ethanol and special filters with 10 micron or smaller pores need to used on product dispensers as well.

Phase separation is a concern because ethanol is completely miscible in water. Ethanol also blends well with gasoline. When water infiltrates a tank (i.e. through sump covers and loose fittings at the top of the tank), the ethanol in the ethanol-gasoline blend will absorb the water. If enough water is present, it will overwhelm the ethanol's capacity to remain blended with the gasoline. The ethanol will be drawn from the gasoline into the water at the bottom of the tank, separating from the gasoline and causing sub-standard low-octane gasoline. At this point, the fuel is no longer an ethanol blend, but a greater concentration of ethanol or gasoline. This could be a problem for a vehicle's fuel lines. In addition, once phase separation occurs, the affected tank(s) must be completely emptied by a disposal company before a delivery of new product can occur.

Ethanol can accelerate corrosion in steel tanks by loosening deposits on the internal surfaces of the tanks and piping. If a corrosion cell (a small pocket of corrosion activity) exists, ethanol will accelerate the corrosion process and create a hole in the tank. Ethanol is not compatible with soft metals such as zinc, brass, lead or aluminum, which are commonly found in conventional fuel storage and dispensing systems. Ethanol tends to cause leaching from such soft metals, which can contaminate a vehicle's fuel system, resulting in poor performance.

Ethanol Conversion Process

1. The following equipment/components/materials should be compatible with the ethanol blend you intend to store and dispense:

- Drop tube shutoff valve
- Tank (Is the warranty in effect? Is it certified or UL listed for the product stored?)
- Submersible pump, O-rings and gaskets
- Line leak detectors
- Leak detection equipment (i.e. ATG probes, floats, sump sensors)
- Spill containment devices and sumps (Is it certified or UL listed for the product stored?)

- Piping material (Is it certified or UL listed for the product stored?)
- Pipe sealant/adhesives
- Flex connectors, grommets
- Product filters
- Dispenser and hanging hardware
- Vapor recovery equipment (Is it certified or UL listed for the product stored?)

2. No amount of water in the tank is acceptable due to phase separation problems. All fittings and connections at the top of the tank must be tight (no vapors leaving and no water entering) and all sump and spill containment covers must prevent water from entering. Any water intrusion problems must be corrected.

3. The tank(s) dedicated to the ethanol blend should be cleaned before adding product. After any water infiltration problems have been corrected, you should clean the UST system to remove all sludge from the bottom of the tank and lines. Any sludge or particulates left in the UST system will be suspended in the ethanol and cause problems with filter and vehicle fuel lines if not removed during the cleaning process.

4. A 10-micron, inline ethanol compatible filter is recommended for ethanol dispensing equipment. This filter will trap most of the impurities that might be in the storage tank and prevent them from being transferred into the vehicle during refueling. There are filters specifically designed for stripping water from fuel . There will be increased moisture in the fuel and these filters will help remove it before the fuel enters the vehicle's fuel tank. As a result of water retention, the fuel filters can clog and reduce or discontinue fuel flow altogether, creating the need for frequent replacement. Fill pipe, access covers and dispensers must be properly identified.

5. Before the dispensing facility commences operations with an ethanol blend, the facility owner should check with the Department of Transportation, Motor Fuel Tax Administration at 302-744-2715 for any specific requirements they may have.

6. Follow normal delivery procedures for the first delivery of ethanol. The Renewable Fuels Association recommends filling the tank to 80% capacity and to keep the tank as full as possible for 7 to 10 days.

7. As soon as the product stabilizes, it is recommended that you conduct a system precision test (0.1 gph) to be sure your system is tight and the leak detection equipment is operating properly. Promptly report any failures.

8. As per the Renewable Fuels Association, you must test for water each day for the first 48 hours after a delivery. Additional water testing shall also be conducted every day thereafter. Checking for water regularly is an ongoing maintenance item with ethanol storage.

9. Spills and releases should be handled as they would with gasoline. Spills greater than 25 gallons or those of any size that cannot be cleaned up within 24 hours must be reported to 1-800-662-8802 (302-739-9401 out-of-state).

10. The Fire Marshal has determined that ethanol is to be treated like gasoline so they have no special requirements.

References

1. Health, Environmental and Economic Impacts of Adding Ethanol to Gasoline in the Northeast States, Volume 3, Water Resources and Associated Health Impacts, July 2001, New England Interstate Water Pollution Control Commission.

2. Fuel Ethanol: Industry Guidelines, Specifications and Procedures, Renewable Fuels Association, RFA Publication #960501, Revised December 2003.

3. Storing and Handling Ethanol and Gasoline-Ethanol Blends at Distribution Terminals and Service Stations, API Recommended Practice 1626, Reaffirmed June 2000.

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Announcements and Upcoming Events

DNREC's Tank Management Branch will be soliciting Requests for Qualifications (RFQ) for consultants to become eligible to participate in its new Pay for Performance remediation program. To become eligible, consultants should obtain a copy of the RFQ during the advertising period, scheduled for June 5th through June 15th, and send qualification packages to the Department by the dates advertised in the RFQ. Bid requests will subsequently be submitted to one or many qualified consultants for individual sites in accordance with the contract. Please refer to the Delaware News Journal, the Delaware State News and Review, and the following websites during the advertising period:

http://www.dnrec.delaware.gov/default.htm
http://www.dnrec.delaware.gov/AWM
http://www.state.de.us/dss/

The 2006 Brownfields Conference "Sustainable Progress through Partnership" will be held at the Chase Center on the Riverfront (formerly Bank One Center) Thursday, April 27, 2006. This is an ideal opportunity to hear about DNREC's new Brownfields Development Program. State and local officials will talk about the impact of Brownfields to our communities, and the advantages of Brownfields redevelopment. **Marianne L. Horinko**, former acting EPA Administrator and champion of Brownfields Revitalization and the One-Cleanup Program, will be the keynote speaker at the conference. In addition, concurrent sessions will be available in the afternoon on the financial and technical aspects of developing Brownfields. More information and a registration form are available online at: http://www.dnrec.delaware.gov/awm/BrownfieldsConf.htm.

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