CSWAB

Citizens for Safe Water Around Badger
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Jeff Ackerman, Remediation Program
Wisconsin Department of Natural Resources
3911 Fish Hatchery Road
Madison, WI 53711

SENT BY ELECTRONIC MAIL

August 4, 2011

Dear Mr. Ackerman,

We are writing to ask the WDNR to consider updating soil testing and cleanup requirements at Badger Army Ammunition Plant (Badger) to include all six isomers of the carcinogenic explosive dinitrotoluene (DNT) and the biotransformation/degradation products of DNT. In addition to other considerations, this recommendation is intended to assure consistency with Wisconsin's recently-adopted groundwater enforcement standards for DNT and anticipated health advisory levels and/or interim groundwater standards.[i]

Further, on April 28, 2011 the WDNR received the Army's Alternative Feasibility Study which proposes natural attenuation as the final remedy for three groundwater contaminant plumes emanating from Badger that contain all six isomers of DNT and other carcinogenic compounds. The WDNR's response requests that the Army include a fuller illustration and valuation of contaminant mass distribution and other analyses to show that this remedy has a reasonable probability of restoring groundwater to the extent practicable.

Current Protocol. The explosive DNT exists as a mixture of two or more of its six isomers (forms). The 2,4- and 2,6- DNT isomers are the most predominant and have been used in military munitions and dye manufacture. Technical grade DNT is a mixture composed of approximately 76% 2,4-DNT, 19% 2,6-DNT, and 5% other DNT isomers (2,3-DNT, 3,4-DNT 3,5-DNT and 2,5-DNT). In the environment, however, these isomers may be found independently and in significantly different ratios.

Citizens for Safe Water Around Badger (CSWAB) first petitioned for regulation of DNT in 2006 when it became evident that adequate cleanup of Badger Army Ammunition Plant and other contaminated military sites would only be achieved with enforceable standards. On January 1, 2011 the State of Wisconsin adopted groundwater standards for all six isomers of DNT. The new health-based standard, measured as the summed total concentration of all DNT isomers, is 0.05 micrograms per liter (ug/l).

A search of the WDNR Groundwater Retrieval Network and Groundwater and Environmental Monitoring System databases in 2007 showed that:

- The 2,3-DNT isomer was detected in 103 wells (3 private water supply and 100 monitoring/ groundwater extraction) at concentrations as high as 2,200 micrograms per liter (ug/l).
- The 3,4-DNT isomer has been detected in 37 wells (1 private water supply and 36 monitoring) at concentrations as high as 419 ug/l.

- The 3,5-DNT isomer has been detected in 20 wells (1 private water supply and 19 monitoring) at concentrations as high as 23.9 ug/l.
- The 2,5-DNT isomer has been detected in 19 wells (1 private water supply and 18 monitoring) at concentrations as high as 1.5 ug/l.

Pursuant to the 2005 Addendum to the Infield Conditions Approval which governs cleanup at Badger, the Army has been required to test groundwater and drinking water wells for all six isomers of DNT. According to the Army, the source of this contamination is surface and subsurface soils at Badger but, unlike groundwater, the Army has not been required to test soils, land-applied sludges or sediments for 2,3-DNT, 3,4-DNT, 3,5-DNT and 2,5-DNT.

Test methods. For more than a decade, the Department of Defense has had the capacity to test soils and sediments for all forms of DNT. A 1999 study by the U.S. Army Corps of Engineers tested three types of soils[ii] – sand, silt, and clay – for all six isomers of DNT.[iii] In 2001, the U.S. Army Corps of Engineers tested soil samples[iv] from military training ranges at two Army installations (Fort Lewis, Washington and Fort Richardson, Alaska) and detected 2,5-DNT, 3,4-DNT, and 3,5-DNT.[v]

At the April 27, 2009 public meeting of the Badger Restoration Advisory Board, Army officials affirmed that while the facility has the ability to develop and implement a soil testing method for all six isomers of DNT at Badger, the initiative to do so would not be taken without some impetus from environmental regulators.

Health effects. DNT can affect the blood, nervous system, liver, kidneys, and male reproductive system in both humans and animals, and is a suspected human carcinogen. Several studies suggest that the minor isomers are toxicologically similar to 2,4- and 2,6-DNT. All DNT isomers are capable of inducing cyanosis secondary to methemoglobin formation, and all isomers have shown mutagenic effects in short-term studies. [vi]

Technical grade DNT, which is a mixture of the six isomers, is known to cause cancer in animals. All six isomers have shown mutagenic effects in short-term studies. Published studies indicate that the four less common isomers of DNT are "as toxic or more toxic than 2,4-DNT and 2,6-DNT".[vii]

Fate and Transport. It is important to note that the four less common forms of DNT may be more persistent in the environment than 2,4- and 2,6-DNT. The 2,3-DNT isomer has not been shown to biodegrade. No studies have been conducted to demonstrate that 3,4-DNT, 3,5-DNT, or 2,5-DNT will biodegrade in soils or groundwater. [viii]

Once in the environment, DNT can be transferred to plants via root uptake from soil or irrigation with contaminated water, although no direct measurements have been found.[ix] According to the U.S. Environmental Protection Agency, both 2,4- and 2,-6 Dinitrotoluene are quite soluble in water and expected to "accumulate readily" in plants via root uptake from soils.[x] At the Milan Army Ammunition Plant (TN), possible routes of exposure for cattle included the ingestion of pasture grass and corn silage, as well as incidental ingestion of soil while grazing in pasture areas.[xi]

In 1996, plant scientists and environmental engineers with the U.S. Army Corps of Engineers Waterways Experiment Station completed a 115-day outdoor phytoremediation study at the Volunteer Army Ammunition Plant (TN) to quantify the clean-up ability of native aquatic and wetlands plants. A component of the initial groundwater, 2,4-DNT was found in plant tissue.[xii] A scientific study by the Civil Engineering Department of Auburn University assessed the feasibility of using the aquatic plant parrot feather to remediate 2,4-DNT contaminated soils. This plant species was shown to be capable of the uptake and biotransformation of 2,4-DNT from contaminated soils.[xiii]

Wildlife present at Badger may be impacted by contaminated surface water, sediment and soils through direct contact and ingestion exposure routes. Army researchers found that data for the toxicity of DNT to terrestrial wildlife must be inferred from tests conducted with laboratory mammals because tests have not been conducted with wildlife species. In subacute toxicity studies, small mammals exposed to DNT all developed methemoglobinemia and anemia. The effects of chronic exposure to 2,4-DNT include liver damage, jaundice, and reversible anemia. Bats fed a technical-grade mixture of DNT or 2,6-DNT for 1 year developed liver cancer.[xiv] A study of the mammalian toxicity of munitions compounds concluded that 3,5-DNT was the "most potent of all DNT isomers" in oral acute doses to rats and mice.[xv]

Soil contaminants may be carried to aquatic environments and wetlands through storm water run-off, erosion and through the air as fugitive dust. Most of the DNT isomers have been evaluated in terms of their potential toxicity to freshwater aquatic organisms. Results of these studies indicate that the 2,3-DNT, 2,5-DNT, and 3,4-DNT isomers are about 10 times more toxic than the 2,4-DNT, 2,6-DNT, or 3,5-DNT isomers.[xvi]

Equity. With new enforceable groundwater rules in place, we believe that it is appropriate to now require corresponding testing of soils and sediments for residual DNT and associated products of degradation/biotransformation. This field data is essential to accurately and thoroughly assess potential risks to the environment, ecological systems, animal and human health and to effectively evaluate proposed remedies that will have long-term implications for affected communities and their environment. We believe that this recommendation is further consistent with NR 720 which requires the evaluation of risks to terrestrial ecosystems and to human health through the food chain, including consumption of fish and wild game, and through dermal contact, inhalation, and incidental ingestion.

Thank you for your time and consideration of our request. Please call if you have any questions or would like to discuss this further. You may reach me by phone at (608)643-3124. We look forward to your reply.

Sincerely,

Laura Olah, Executive Director

cc: John Holst, Ho-Chunk Nation
Bill Wenzel, Badger Oversight Management Commission
Ron Lins, Community Chair, Badger Restoration Advisory Board

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[i] In May 2011, the WDNR forwarded CSWAB's petition to the Wisconsin Division of Public Health for health advisory levels and/or interim groundwater standards for 4-amino-2-nitrotoluene, 4-amino-3-nitrotoluene, 2-amino-4-nitrotoluene, 2-amino-6-nitrotoluene, 2-amino-3-nitrotoluene, and 3-amino-4-nitrotoluene. All of these compounds have been detected in groundwater at Badger. They may result from biotransformation of DNT.

[ii] Extracts from soil were tested utilizing reversed phase high performance liquid chromatographic method with UV detection according to SW846 Method 8330. Gas chromatography-electron capture detector (GC-ECD) has also been used to test soils for nitroaromatic, nitramine, and nitrate ester explosives (U.S. Army Corps of Engineers, August 1999). According to the Geneva International Centre for Humanitarian Demining, modern methods for soil sampling and chemical residue analysis developed for environmental pollution assessments (EPA SW846, 2002) can be used for landmine soil residue assessments. Soil analysis for this purpose can be performed via high pressure liquid chromatography (EPA SW846 Method 8330), or by gas chromatography with either a electron capture detection (EPA SW846 Method 8095), thermionic detector (Hewitt et al., 2001), nitrogen/phosphorus detector (Hewitt and Jenkins, 1999; Kjellstrom and Sarholm, 2000), or mass spectroscopy.

[iii] Thomas F. Jenkins, Daniel C. Leggett, and Thomas A. Ranney, U.S. Army Corps of Engineers, *Vapor Signatures from Military Explosives Part 1. Vapor Transport from Buried Military-Grade TNT*, December 1999.

[iv] Soil samples were analyzed for explosives-related residues by GC-ECD using SW-846 Method 8095 (draft).

[v] Thomas F. Jenkins et al, U.S. Army Corps of Engineers, Engineer Research and Development Center, *Characterization of Explosives Contamination at Military Firing Ranges*, July 2001.

[vi] Lynda Knobeloch, Ph.D., Senior Toxicologist, Bureau of Public Health, Wisconsin Department of Health and Family Services, SCIENTIFIC SUPPORT DOCUMENTATION FOR CYCLE 9 REVISIONS OF NR 140.10 GROUNDWATER ENFORCEMENT STANDARD & PREVENTIVE ACTION LIMIT RECOMMENDATIONS, May 2009.

[vii] Linda Knobeloch, Ph.D., Wisconsin Division of Public Health, *Drinking Water Health Advisory for Dinitrotoluenes*, June 14, 2007.

[viii] Shirley F. Nishino and Jim C. Spain, Air Force Research Laboratory, Tyndall AFB, *Florida Technology Status Review: Bioremediation of Dinitrotoluene (DNT)*, pages 2 and 5, February 2001.

[ix] U.S. Agency for Toxic Substances and Disease Registry, *Toxicological Profile for 2,4- and 2,6-Dinitrotoluene*, December 1998.

[x] U.S. Environmental Protection Agency, *Drinking Water Health Advisory 2,4 Dinitrotoluene and 2,6-Dinitrotoluene*, January 2008.

[xi] USATHAMA, Milan Army Ammunition Plant, Remedial Investigation Report, Appendix S: Screening Level Evaluation of Human Exposures and Risks Via Ingestion of Crops and Beef from Milan Army Ammunition Plant, December 1991.

[xii] Miller, J.L., Best, E.P.H. and Larson, S.L., *Degradation of explosives in groundwater at the Volunteer Army Ammunition Plant in flow-through systems planted with aquatic and wetland plants*, 1997.

[xiii] SR Todd, CR Lange, *Phytoremediation of 2,4-dinitrotoluene contaminated soils using parrot feather (Myriophilum brasiliense)*, 1996.

[xiv] U.S. Army Medical Bioengineering Research and Development Lab, *Organic Explosives and Related Compounds: Environmental and Health Considerations*, Technical Report 8901, 1989.

[xv] Ellis, Harry V., III et al, Midwest Research Institute for the Environmental Protection Research Division U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, Maryland, *Mammalian Toxicity of Munitions Compounds. Phase I. Acute Oral Toxicity, Primary Skin and Eye Irritation, Dermal Sensitization, Disposition and Metabolism and Ames Tests of Additional Compounds*, 1978.

[xvi] U.S. Army Medical Bioengineering Research and Development Lab, *Organic Explosives and Related Compounds: Environmental and Health Considerations*, Technical Report 8901, Appendix F: Ecotoxicity Profiles for Munitions Compounds, 1996.