Report for 2001ME2401B: Seed Project to Determine the Fate of MtBE in Groundwater in Maine.

- Water Resources Research Institute Reports:
  - 2. Schmitt, C. and J.M. Peckenham (2002) Source Water Protection: Linking Surface Water Quality to the Watershed. Handbook, Univ. of Maine 85 p. (includes information on MtBE)
- Conference Proceedings:
  - 1. Peckenham, J.M. (2002) The occurrence and persistence of MtBE in groundwater inWindham, Maine, NE FOCUS Conf. On Groundwater Issues, October 3, 2002.

Report Follows:

Seed Project to Determine the Fate of MtBE in Groundwater in Maine

John M. Peckenham
University of Maine

Problem and Research Objectives:

Methyl tert-butyl ether (MtBE) was added to gasoline to lower VOC emissions from automobiles. In 1991 Maine opted into the use of reformulated gasoline that had 8% to 12% MtBE. In 1998, the State of Maine (1998) determined that 16% of public water supplies contained detectable concentrations of MtBE and reduced MtBE in gasoline from 12% to 2%. The effect of decreasing the MtBE content in gasoline on groundwater supplies in unknown. This made a unique opportunity to assess the residual effects of MtBE on groundwater quality.

This project initiated the determination of the residual risks posed to groundwater supplies by MtBE. We expected to detect changes in the distribution of MtBE (magnitude and detection rate) since 1998 (post-RFG). The geographical distribution of MtBE is a function of gasoline composition, spills, atmospheric transport, dilution/dispersion, and microbial transformation (Johnson *et al*., 2000, Squillace *et al.*, 1999). This study provided time-sensitive data to quantify how water resources recover from ambient MtBE contamination and thus provide the basis for a more exhaustive research proposal to be submitted to an appropriate agency in the near future.

MtBE was added to gasoline in Maine from circa 1986 through 1998. The use of greater than 5% by volume MtBE was banned in 1999. This research assessed the changes in the distribution of MtBE in groundwater monitoring wells in Windham, Maine, from 1998/1999 versus 2001 (2 data years). This builds on a detailed town-wide study completed in 1999 (Nielsen and Peckenham, 2001).

Methodology:

Site Selection. We sampled 19 existing groundwater monitoring wells in Windham, Maine where baseline data are available (Figure 1). MtBE contamination has been detected in 35% of wells in Windham sampled in 1998 and 1999 (Nielsen and Peckenham, 2001).

Sampling Methods. This study used existing monitoring wells installed by the USGS in the Windham aquifer (Nichols and Silverman, 1998). Sampling will was based on the with USGS National Water Quality Assessment protocols for sampling ground- water wells (Koterba *et al*., 1995). Modifications of the USGS protocols were incorporated to use the USEPA low-flow (minimal drawdown) sampling procedures (Puls and Barcelona, 1995). The monitoring-well sampling equipment setup was simplified from the USGS protocols. A submersible pump with teflon-lined tubing was used purge wells by the USGS field personnel. Once field personnel collected a water quality sample, a clean polyethylene bailer was lowered to the top of the water table to collect a sample. A new bailer and line was used for each well.

Samples for MtBE and BTEX analyses were collected directly from the bailer into four 40 ml glass VOA vials with teflon septum tops and no air space (acidified to pH<2).

QA/QC Methods. Samples will be kept on ice and driven to the Geochemistry and Environmental Engineering Laboratory of the George Mitchell Center, Orono, Maine, for analysis. Quality-assurance samples consisted of 10% duplicate samples, plus equipment blanks, trip blanks, spiked samples, source-solution blanks, and ambient blanks (trip blank vials opened and exposed to the ambient air during sampling, then closed and sent in for analysis). Laboratory quality assurance and quality control were consistent with good laboratory practices and USEPA QA/QC guidelines. The laboratory currently operates under both USEPA and state approved laboratory plans.

Sample Analysis. Samples will be analyzed for MtBE and gasoline-range organic compounds using modified USEPA Methods (SW-846) and specialized laboratory methods including Standard Methods (5000 and 6000) and Church *et al.* (1997).

Principal Findings and Significance:

The 2001 sampling data for selected wells in Windham, Maine, substantiate the persistence of MtBE in groundwater (Table I). The characteristics of the occurrences of MtBE, however, have changed since 1998. The characteristics include the statistical attributes, as well as, the spatial attributes.

The results of this seed project indicate that the mean concentration of MtBE in the groundwater in Windham, Maine, has increased significantly since 1998. The concentrations of MtBE ranged from values less than detection (0.1 µg/L) to 38.7 µg/L. The rate of detection (percentage of wells with detectable MtBE for each sample event) for 2001 (42%) was nearly the same as overall rate (43%) and both were greater than 1998 (20%) (Figure 2).

The mean concentrations of MtBE for the same set of wells has increased from 0.225 µg/L to 3.01 µg/L. This mean was calculated by setting less than detection limit values to equal 0.5 times the detection limit. The mean increased even when the highest concentration, 38.7 µg/L, was excluded from the estimate of the mean.

The median concentrations of MtBE for the same set of wells has decreased from 0.1 µg/L to 0.05 µg/L. This median was calculated by setting less than detection limit values to equal 0.5 times the detection limit. This estimate of the median implies that there are more low-level detections of MtBE with a fewer number of high concentration. However, if the median is calculated based on samples above the detection limit only then the median exhibits a steady increase from <1.0 µg/L in 1998 to 4.2 µg/L in 2001.

The statistcal characteristics of the MtBE detections suggest that MtBE is still widespread in the groundwater with perhaps a greater occurrence at low concentrations. The

detection of significant concentrations in a few wells suggests that the MtBE content in gasoline is still sufficiently high to cause marked groundwater contamination.

The spatial association were analyzed using the same land-use criteria as Nielsen and Peckenham (2001): urban, low-density residential, and undeveloped. The distribution of MtBE based on these spatial landscape categories exhibited marked differences between 1998 and 2001 (Figures 3 and 4). In particular, there was a broadening of the detection ranges in the undeveloped units while the urban units exhibit little or no change.

In summary:

- The mean detectable concentration of MtBE has increased since 1998.
- The range of detection is greater in 2001 than 1998.
- There is a broader spatial occurrence in 2001 compared to 1998.
- Detections are associated with any type of land use.

References:

Church, C.D., Isabelle, L.M., Pankow, J.F., Rose, D.L., Tratnyek, P.G., 1997. Method for determination of methyl tert-butyl ether and its degradation products. Environ. Sci. Technol. 31(12):3723-3726.

Johnson, R., J. Pankow, D. Bender, C. Price, and J. Zogorski, 2000. MtBE, To what extent will past releases contaminate community water supply wells? Environ. Sci. Tech., May News:2A-9A.

Koterba, M., F. Wilde, and W. Lapham, 1995. Ground water data-collection protocols and procedures for the National Water-Quality Assessment Program collection and documentation of water quality samples and data, U.S.G.S. OF 95-399.

Maine Department of Human Services, Maine Department of Environmental Protection, and Maine Geological Survey, 1998. The presence of MtBE and other gasoline compounds in Maine's drinking water, A preliminary report October 13, 1998.

Neil, C., 1998. Significant Sand and Gravel Aquifer Map, Windham, Maine. Maine Geol. Surv., Augusta, ME.

Nichols, W. J. and P.N. Silverman, 1998. Hydrologic data for the Presumpscot River Basin, Cumberland and Oxford Counties, Maine 1995 to 1996. USGS OF98-265.

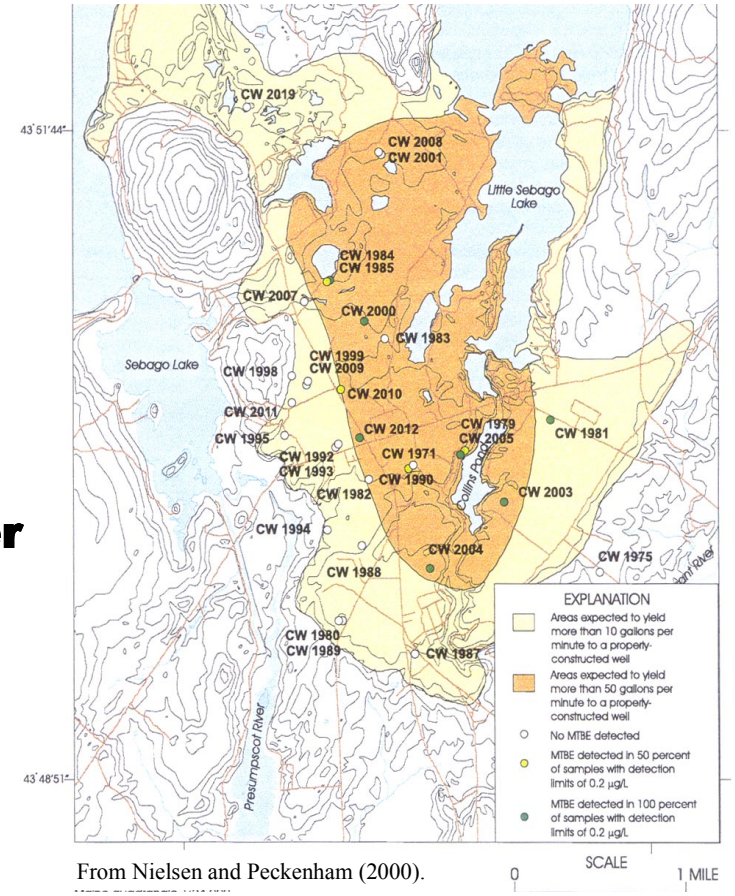
Nielsen, M. G. and J. M. Peckenham (2000) Methyl tert-Butyl Ether (MTBE) in ground water, air, and precipitation in an urbanized area in Maine, USGS Water Res. Inv. Rpt., 00-4048, 28p.

Puls, R. and M. Barcelona, 1995. Low flow (minimal drawdown) ground-water sampling procedures, U.S. EPA, EPA/540/S-95/504.

Squillace, P. J., J. S. Zogorski , W.G. Wilbur, and C. V. Price, 1999. Preliminary assessment of the occurrence and possible sources of MtBE in groundwater in the United States, 1993-94. Environ. Sci. Tech. 30:1721-1730.

Location of Wells in Windham, Maine

Sand and Gravel Aquifer Boundaries from Neil (1998).



From Nielsen and Peckenham (2000).

Figure 1. Study location in Windham, Maine.

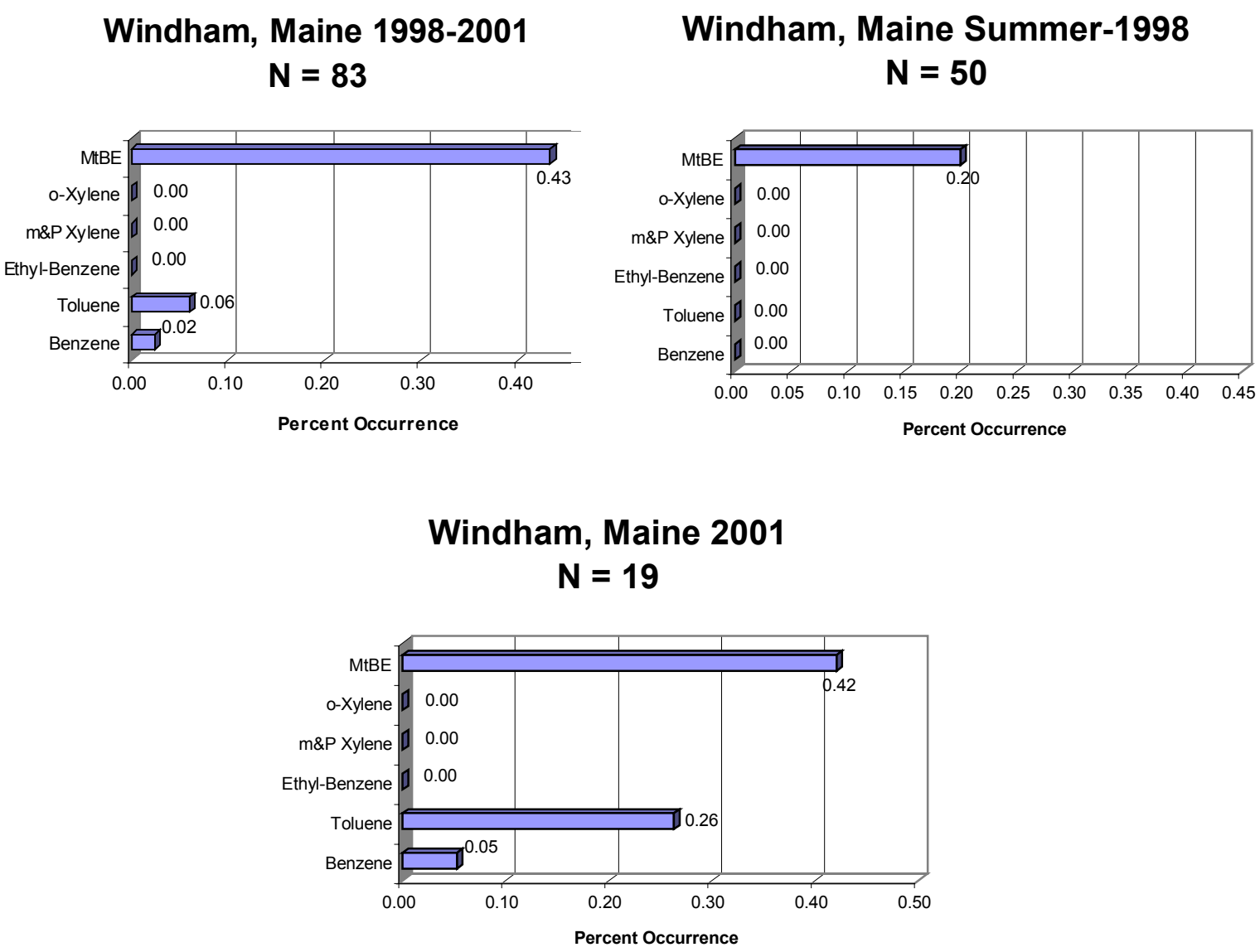
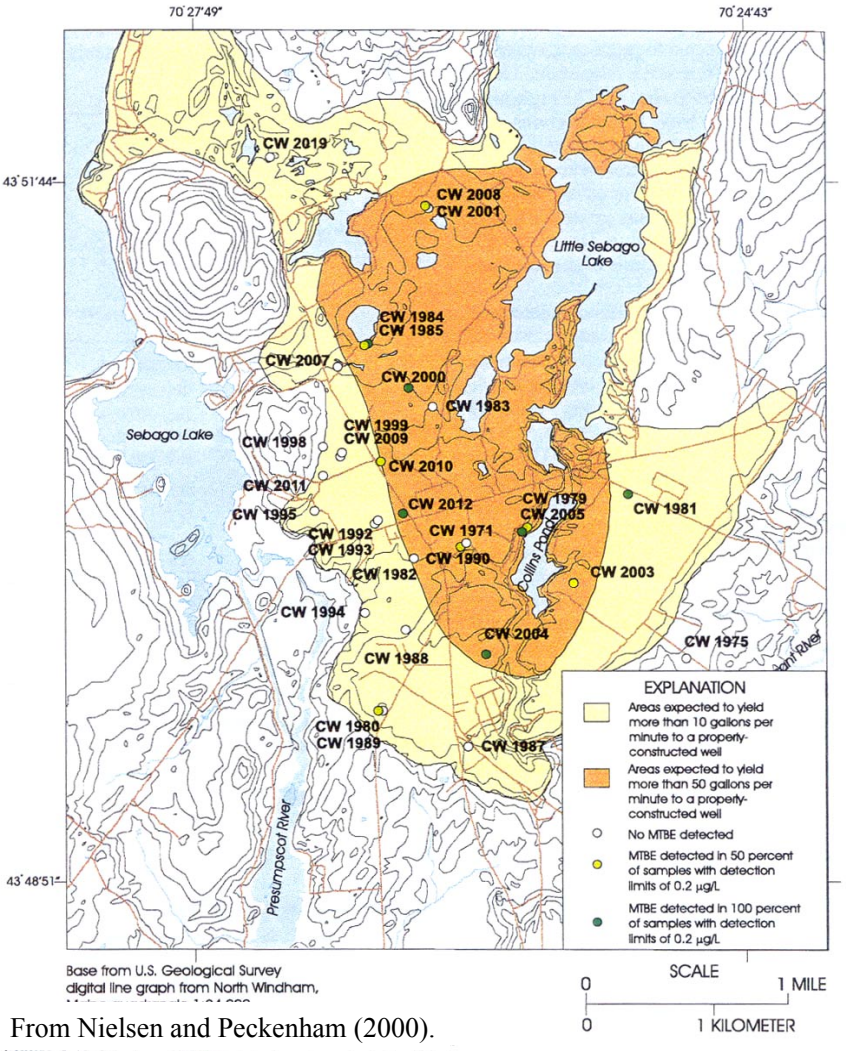


Figure 2. Frequency of occurrence for MtBE in groundwater samples for 1998 through 2001.

Spatial Frequency of Occurrence of MtBE in Windham, Maine

Sand and Gravel Aquifer Boundaries from Neil (1998).



From Nielsen and Peckenham (2000).

Figure 3. Spatial and temporal distribution of MtBE detectections in groundwater wells.

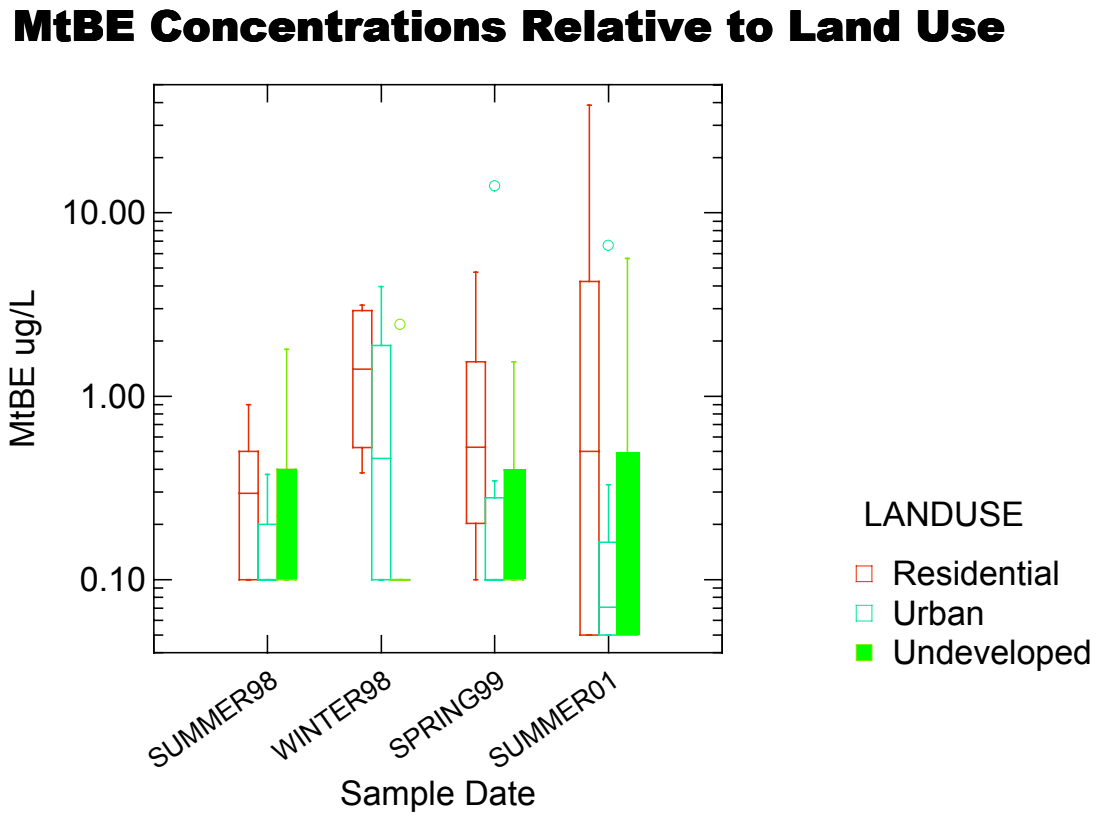


Figure 4. Spatial and statistical summary of MtBE detections in groundwater wells by land-use class.

Table I. Analytical results for MtBE analyses 1998-2001. Note that < means less than detection limit and E is estimated concentration. Data for 1998 and 1999 from Nielsen and Peckenham (2001).

		Sample Date		MtBE (ug/L)	
Well ID	**USGS ID**	**Aug-98**	**Nov-98**	**May-99**	**Aug-01**
ARL-1	CW 1971	<0.2		<0.2	<0.1
CPW-1	CW 1979	<0.2		0.203	0.500
MTW-1	CW 1980	<0.2			0.490
CHA-2	CW 1985	<0.5	<0.2	E0.102	<0.1
KEL-1	CW 1987	<0.2		<0.2	<0.1
ARL-2	CW 1990	<0.2		0.226	E0.01
Bent-1	CW 1992	<0.2		<0.2	<0.1
Bent-2	CW 1993	<0.2		<0.2	<0.1
Key 1	CW 1999	<0.2		<0.2	<0.1
SSW-1	CW 2000	<0.4	0.459	0.346	0.160
MPW-1	CW 2001	<0.8	<0.2	<0.2	<0.1
UWW-1	CW 2003	<1.0	0.723	0.467	E0.05
TCBY-1	CW 2004	<0.7	3.140	0.596	38.700
CPW-2	CW 2005	<1.8	2.730	1.540	4.220
MPW-2	CW 2008	<0.2		<0.2	5.650
Key 2	CW 2009	<0.2		<0.2	<0.1
MDW-1	CW 2010	<0.2		1.890	0.330
CBW-1	CW 2012	<0.75	3.960	14.000	6.640
BRW-1	CW-2011	<0.4	<0.2	<0.2	<0.1
Mean			2.202	2.409	7.086
			RFG use	*post-RFG*	
median			2.730	0.532	4.220