Evidence for Biodegradation of Gasoline Products in Groundwater Below Gas Stations

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Background

Methyl-Tert-Butyl-Ether (MTBE) leakage from gasoline underground storage tanks (UST) is a worldwide problem. In the groundwater, pollutants may undergo processes of natural attenuation (NA) including volatilization, dilution, sorption, and microbial degradation.

The latter is the most important process since it is the only one that breaks down or transforms the pollutants **(Figure 1)**. Contaminated aquifers rapidly become anoxic due to rapid consumption of oxygen by microbial respiration and slow oxygen recharge in the groundwater. Therefore, anaerobic biodegradation is the dominant process in these sites.

Monitored Natural Attenuation (MNA) was tested as an alternative for a spill below Nir Galim (NG) gas station situated in the southern part of the Israel coastal aquifer **(Figure 2)**.

Research Objectives

- ❑ Determine whether biodegradation of MTBE occurs naturally in the polluted coastal aquifer groundwater below Nir Galim gas station
- ❑ Determine the biodegradation rate at this specific site

Methods indicating *In Situ* Biodegradation in the Aquifer

- ❑ Water geochemistry - Consumption of oxygen, reduction of nitrate, iron and sulfate associated with anaerobic respiration in the groundwater;
- ❑ Organic compound quantification – Disappearance of pollutants and appearance of transformation products (field and microcosm experiments);
- ❑ Compound Specific Isotopic Analysis (CSIA) - Fractionation of carbon in the pollutants while biodegraded (field and microcosm experiments);

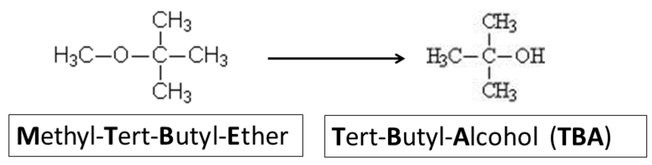

Figure 1: Common groundwater pollutant originating from gas stations. MTBE biodegrades to TBA under both aerobic and anaerobic conditions

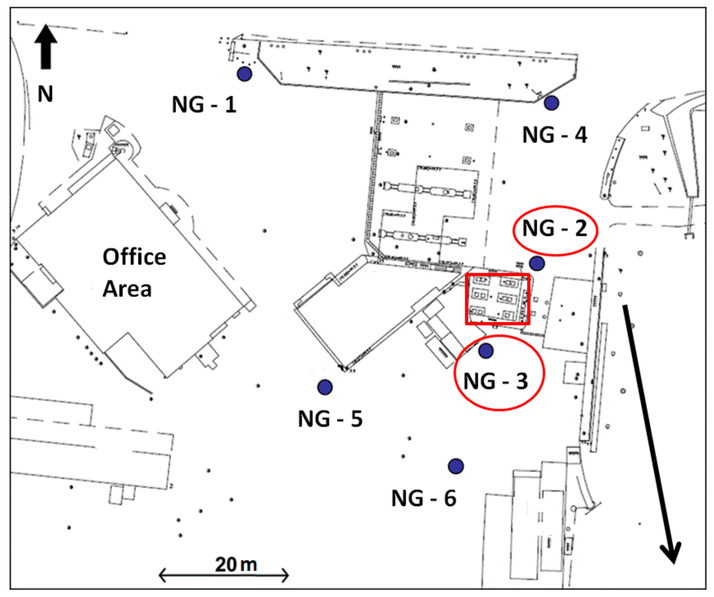

Figure 2: Nir Galim gas station map, six monitoring wells are shown here.
The red square represents the underground storage tank, the black arrow represents the groundwater flow direction.

* Data presented here are taken from NG2 and NG3 (red cycle).

Results

- ○ Geochemical data show simultaneous reduction of manganese, iron and sulfate in the two most contaminated wells, for example NG2 (**Figure 3).**
- ○ Over a period of one year, a strong enrichment in $\delta^{13}C$ was detected. Values shifted from -30‰ to 14.1‰ and -6.7‰ in wells NG2 and NG3 respectively **(Figure 4).**
- ○ Microcosm experiments confirmed this strong enrichment using groundwater taken from NG2 and NG3. Isotopic analysis of samples from this experiment yielded a fractionation factor (ε) of -17.2±0.5 ‰ under both sulphate reducing and methanogenic conditions **(Figure 5).**
- ○ Estimated degradation efficiency **(Table 1)**:
  - Natural attenuation rate is ~1.8 ($Year^{-1}$)
  - Biodegradation rate (based on isotope fractionation) is ~0.5 ($Year^{-1}$).
  - Biodegradation is responsible for 57 - 72% of MTBE's natural attenuation process.

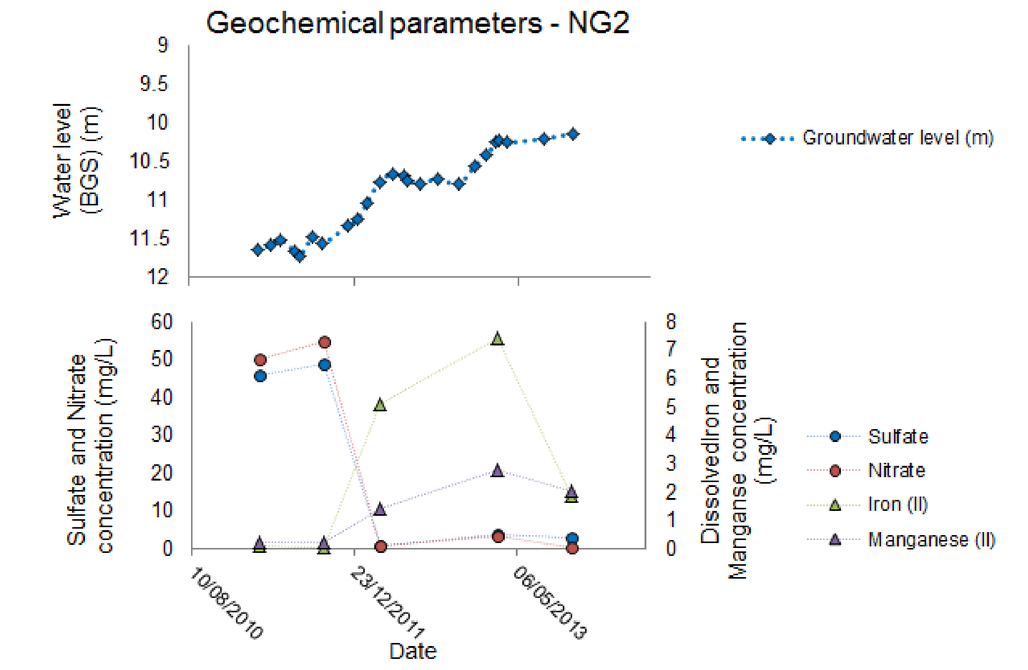

Figure 3: Geochemical data measured by the GSI from NG2. Electron excerptor concentration change with time.

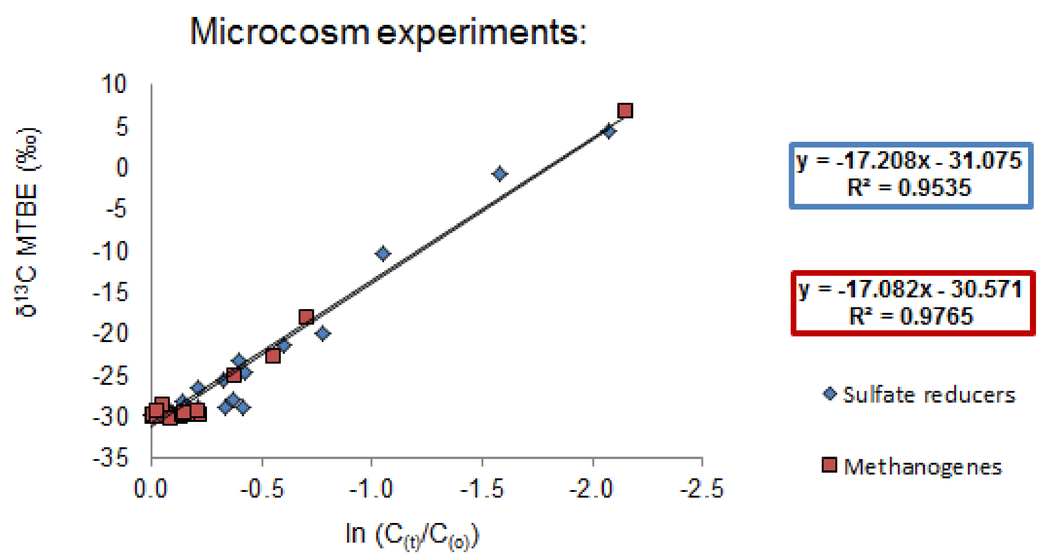

Figure 5: ln of the remaining fraction of MTBE vs. $\delta^{13}C$ MTBE, the slope represents the enrichment factor (ε).

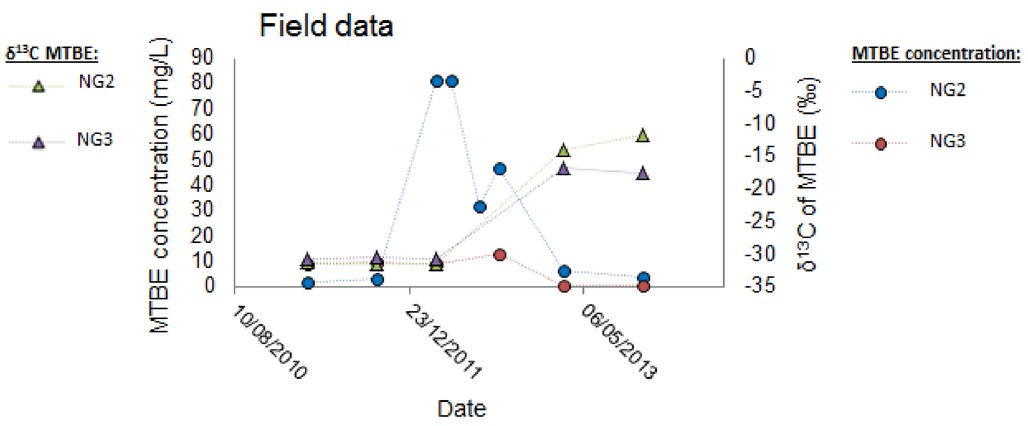

Figure 4: MTBE concentrations and its isotopic fractionation over time measured in NG2 and NG3 groundwater.

Parameter		Isotope	Concentration	Isotope	Concentration
		NG2		NG3	
f	$f = C/C_0 = \mathrm{EXP}\left(\frac{\Delta\delta 13_C}{\varepsilon(‰)}\right)$	0.32	0.05	0.46	0.05
Amount decreased (%)	$B = (1-f) * 100$	68	94	54	94
λ time ($year^{-1}$)	$\lambda_{time} = -\frac{ln(f)}{t}$	0.7	1.8	0.5	1.8

Table 1: Preliminary results calculating natural attenuation of MTBE in wells NG2 and NG3. These calculations were done based on two time points March 2012 and October 2013, assuming first order kinetics.

Conclusions

Over a period of one year, a strong enrichment in $\delta^{13}C$ was detected, indicating anaerobic biodegradation of MTBE in wells NG2 and NG3. Microcosm experiments confirmed this strong enrichment using groundwater taken from both wells, yielding a fractionation factor (ε) of -17.2±0.5 ‰ under both sulphate reducing and methanogenic conditions.

This calculated ε ,from the microcosm experiment, allows us to estimate the biodegradation rate (~0.5 $Year^{-1}$) of MTBE and to assess that biodegradation is the main process (between 57 - 72%) contributing to the natural attenuation processes, Further research is needed in order to validate these estmations.