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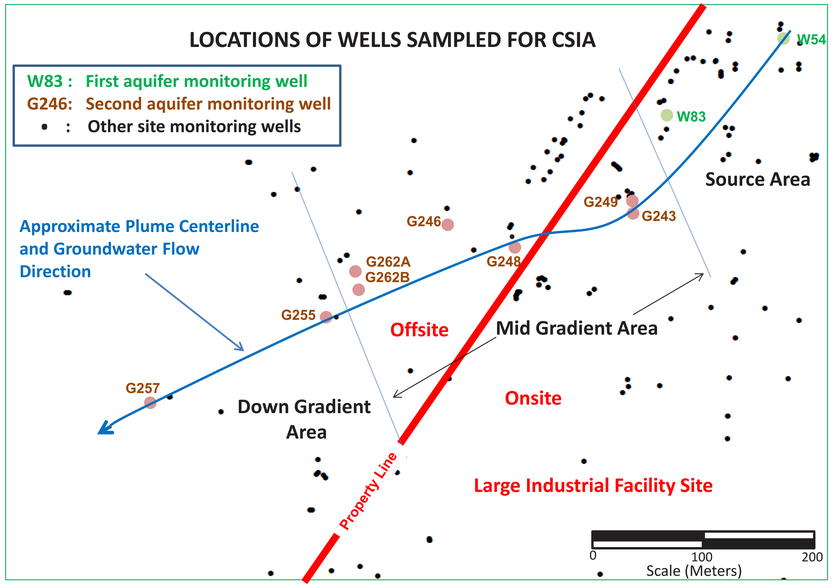
Use of CSIA to Understand Risk at Complex Petroleum Impacted Sites

Frank Muramoto, PG, CHG (AECOM, Long Beach, CA) | Jun Lu, PhD, PG, CHG, CEG (China Aerospace Kaitian Environmental Technology Co. Ltd., Changsha, China)

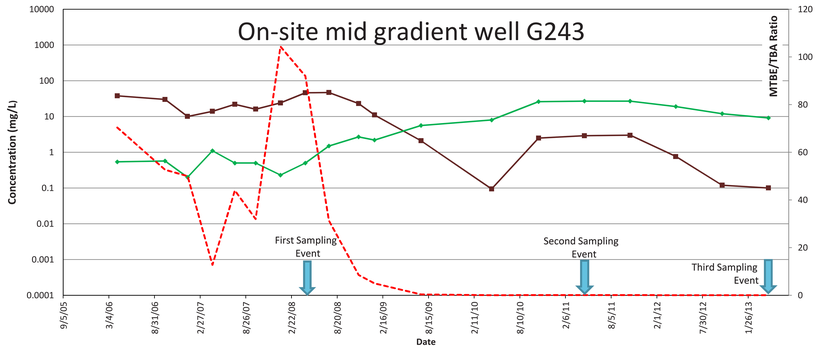
Introduction and Approach

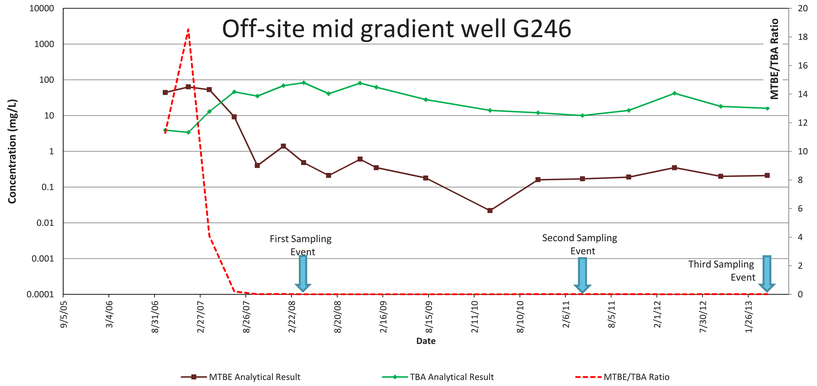
At petroleum refining facilities, the subsurface is typically impacted by light non-aqueous phase liquid (LNAPL) related to historical releases and incidentally by release(s) during ongoing operations. To effectively manage these sites, understanding the distribution and character of LNAPL and associated dissolved impacts in the subsurface are critical. At this facility, methyl tert-butyl ether (MTBE) was stored and used in gasoline blends in the late 1980s through early 2000s. During this period, neat MTBE was released to the subsurface and dispersed into the existing LNAPL. Consequently, the MTBE-containing LNAPL served as a continuous source of dissolved phase MTBE in groundwater on site and off site.

To better understand risks associated with the off-site dissolved phase MTBE plume, Compound-Specific Isotope Analysis (CSIA) was identified as an advanced technique for implementation so that a more robust site management plan be implemented.

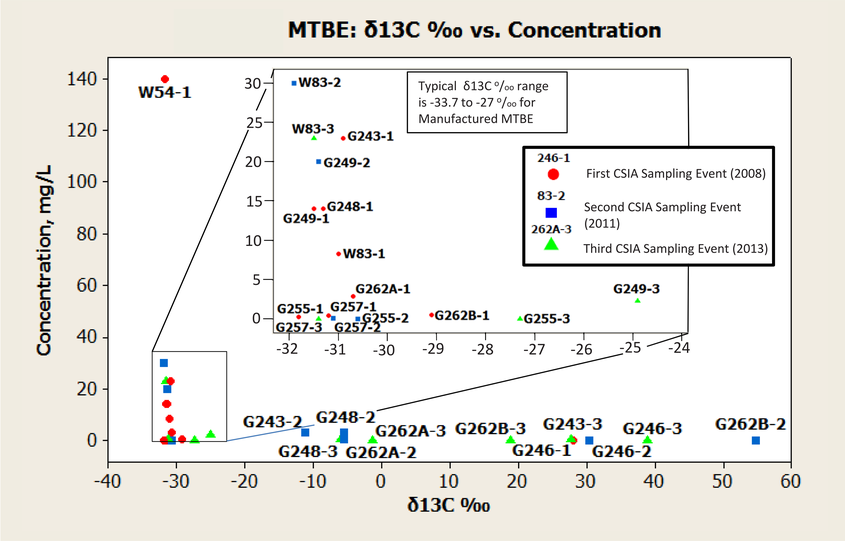


Results





Over time, decreases in MTBE concentrations with corresponding increases in TBA concentrations are evident in the data. The time of onset of the decrease in MTBE/TBA ratio varied among the wells sampled. The earliest change in MTBE/TBA ratio seen was in well G246. The temporal trends of MTBE and TBA are consistent with biotransformation of MTBE to TBA. CSIA sampling events are shown with the blue arrows.



Three rounds of CSIA were conducted (2008, 2011, and 2013). The CSIA analyses demonstrate progressive $^{13}\delta C$ enrichment over time. The initial sampling from well G243 and upgradient source area wells contained $^{13}\delta C$ values in the range of manufactured MTBE, suggesting that MTBE biodegradation was generally not significant prior to 2008. Initial sampling of well G246 showed $^{13}\delta C$ value of 27.8 ‰, with subsequent $^{13}\delta C$ values of 30.5 and 39‰ in 2011 and 2013, respectively, showing enrichment of $^{13}\delta C$ over time. The enrichment of $^{13}\delta C$ provides direct evidence of biodegradation

Conclusions

The study utilized three rounds of CSIA analyses to better understand risks associated with off-site migration of MTBE. The results of CSIA data confirmed biodegradation of MTBE over time. These findings are invaluable in understanding of the effectiveness of monitored attenuation and helped to formulate a strategy for risk management of the off-site MTBE plume.