

EVALUATION OF THE RATIONALE BEHIND NEW REGULATION 153 GROUNDWATER STANDARDS FOR F3 AND F4 PETROLEUM HYDROCARBONS

Hydrocarbons are one of the most common contaminants in the environment and as such it is critical that the standards set by regulatory groups and what the laboratory measures reflect the true risk of these contaminants in soil, groundwater and sediment systems. The new standards first presented to the industry December 29th, 2009 represent years of work by MOE to update the science behind the values to best accomplish this goal. Although these standards clearly are for use on Brownfield sites for Record of Site Condition filings, they become the default criteria applied to many other sites.



In the June 29th, 2010 document *Soil, Ground and Sediment Standards for Use under Part XV.1 of the Environmental Protection Act*¹, Ontario Ministry of Environment (MOE) has set the standard at 500 ug/L for all property uses and site conditions for F3 (C16-C34) and F4 (C34-C50) hydrocarbons in groundwater. This is a drop from the 1000 ug/L it is today in a potable water setting. MOE's 560 page Rationale Document² indicates that the chemical and physical properties for hydrocarbons used to derive the new standard were obtained from the TPH Working Group in Volume 3 -*Selection of Representative TPH Fractions Based on Fate and Transport Considerations*².

It might seem obvious that heavy hydrocarbons will not dissolve in water and therefore won't transport through groundwater systems in the dissolved phase. Alberta states in their updated standards in 2008: "*Subsurface distribution in groundwater not required for F3 and F4 due to low aqueous solubility*"³

If it's not possible to have dissolved F3 and F4 hydrocarbons you would expect all lab results to be non-detect right? Unfortunately, as QPs and laboratories have learned with low level PAH analysis, the inclusion of sediment in samples during the sampling procedures can bias results high, well beyond solubility limits. Furthermore, once a groundwater sample for CCME PHCs is submitted to the lab with particulate, it is currently not possible to analyze just dissolved hydrocarbons since filtration will cause losses due to adsorption on the filter.

Maxxam reviewed the solubility data in the TPH Working Group document and has summarized it below:

	Water Solubility (ug/L)		Water Solubility (ug/L)
C5-C6 Aliphatic	36,000	C12-C16 Aliphatic	0.76
C5-C7 Aromatic	220,000	C12-C16 Aromatic	5,800
C6-C8 Aliphatic	5,400	C16-C21 Aliphatic	0.0025
C7-C8 Aromatic	130,000	C16-C21 Aromatic	650
C8-C10 Aliphatic	430	C21-C35 Aliphatic	not listed
C8-C10 Aromatic	65,000	C21-C35 Aromatic	6.6
C10-C12 Aliphatic	34	> C35 (aliphatic or aromatic)	not listed
C10-C12 Aromatic	25,000		

This clearly shows that aromatic hydrocarbons are much more water soluble than aliphatic hydrocarbons and that only aromatic hydrocarbons in the F3 range could possibly be found above the laboratory reporting limit of 100 ug/L. It also suggests that it's not possible to have any detectable concentrations of dissolved aromatics or aliphatics in the F4 fraction.

The more alkylated aromatics are, the less water soluble they become. This suggests that base aromatic hydrocarbons (non alkylated PAH) drive the water solubility limit of 650 ug/L listed by TPHWG. We understand that this 650 ug/L value was the key driver behind the 500 ug/L standard for F3 and F4 (aliphatic + aromatic) hydrocarbons. It's worthy to note that MOE regulates specific Polynuclear Aromatic Hydrocarbons (PAHs) based on their individual chemical, physical and toxicological properties and that the CCME soil method allows for the subtraction of specific PAHs from the F3 and F4 fractions if analyzed by GC/MS.

To put all of this to the test, Maxxam took 2mL of commercially available motor oil, added it to approximately 1L of water in a separatory funnel and allowed it to sit for 48 hours. After 48 hours, three aliquots of 250mL of water (and any dissolved hydrocarbons) were removed from the bottom of the vessel and analyzed for F3 and F4 hydrocarbons. The experiment was completed in triplicate. All results for the analysis came back < 100 ug/L for these fractions.

Under free product conditions in a controlled setting, we were unable to capture any dissolved hydrocarbons in the C16-C50 range. Although this was a simple test, it is a clear indication that if you are seeing levels of F3 and F4 hydrocarbons greater than 500 ug/L, it is likely the inclusion of sediment that is causing the exceedence, making it even more important now to ensure wells are properly developed and technology such as low flow sampling is used in silty conditions.

1. Ontario Ministry of Environment. Soil, Ground Water and Sediment Standards for Use under Part XV.1 of the Environmental Protection Act. June 29, 2010.
2. Guftason et al. Selection of Representative TPH Fractions Based on Fate and Transport Considerations – Volume 3. TPH Working Group. 1997.
3. Alberta Tier 1 Soil and Groundwater Remediation Guidelines, August 2008 pg C-50