Evaluating total petroleum hydrocarbons in drinking water samples

Petroleum Remediation Program

This guidance discusses the use of the total petroleum hydrocarbons (TPH) fractionation methodology for petroleum impacted drinking water where the program has identified a completed exposure pathway, as an additional level of protection following routine (existing) sampling and risk assessment.

1. Test groundwater/perform chemical analysis to identify specific chemicals. Follow Petroleum Remediation Program (PRP) guidance document Groundwater sample collection and analysis procedures. To the extent feasible, ensure analytical reporting limits are not above the individual Minnesota Department of Health (MDH) human-health based water guidance values. If J-flagged data are available for individual analytes, they are typically used the same way as other quantified results (i.e., non-J-flag data). Analyze for:

    a. Diesel range organics (DRO) and gasoline range organics (GRO) – only run as part of the investigative process. The DRO/GRO results are used to determine if a water plume is a mixture of petroleum products. The GRO/DRO data will help inform what type of chemical testing refinements (volatile organic compounds [VOC], semi-volatile organic compounds [SVOC], polycyclic aromatic hydrocarbons [PAH]) are warranted in future sampling events. The DRO/GRO results are not used to assess human health risks.

    b. Volatile Organic Compounds (VOCs) and semi-volatile organic compounds (SVOCs)
    Acceptable methods: most recent version of U.S. Environmental Protection Agency (EPA) method 8260 (VOCs) and 8270 (SVOCs) or for lower reporting limits EPA method 524.2 (VOCs) and 525.2 (SVOCs).

    c. Polycyclic aromatic hydrocarbons (PAHs)
    Acceptable methods: most recent version of EPA method 8270 (8270 SIM preferred).

2. Compare concentrations of chemicals from Step 1b and 1c with their corresponding MDH human-health based water guidance values (HRL/HBV/RAA) and assess additivity to evaluate risk if multiple chemicals are present. The additivity calculation is performed for chemicals that have the same health endpoint. The MDH human health-based water guidance table and additivity calculator are available on the MDH website:
www.health.state.mn.us/communities/environment/risk/guidance/gw/table.html.
Evaluate carcinogenic PAHs using MDH's Guidance for Evaluating the Cancer Potency of Polycyclic Aromatic Hydrocarbon (PAH) Mixtures in Environmental Samples:
https://www.health.state.mn.us/communities/environment/risk/docs/guidance/pahguidance.pdf

    a. If any contaminant concentrations (individually or as a mixture) exceed MDH human health-based water guidance values, treat the water, or provide an alternative supply.

    b. If no drinking water guidance values are exceeded, proceed to Step 3.

3. If a completed exposure pathway is present and water does not exceed any current HRL/HBV/RAA, use fractionation methods to characterize petroleum residuals.

a. Perform volatile petroleum hydrocarbons (VPH) and/or extractable petroleum hydrocarbons (EPH) analysis (Massachusetts Department of Environmental Protection methods).

b. Determine if exceedances exist based on **Table 1**, which uses a surrogate and component approach for evaluating exposure risk. A surrogate drinking water value (MDH HRL/HBV/RAA or MPCA calculated value) is used to compare against specific TPH fractions (e.g., the drinking water value for n-hexane is compared against the concentration of the low aliphatic fraction). Individual component chemicals are only used for evaluating the low aromatic fraction. The component chemical concentrations for evaluating the low aromatic fraction may need to be determined using the latest version of EPA method 8260 instead of VPH/EPH methods because EPA method 8260 can achieve lower reporting limits.

c. The reporting limits for the low aliphatic and medium aromatic fractions may not be low enough to compare against the surrogate drinking water values. J-flag data may need to be used to evaluate these fractions.

d. An additivity calculation should be performed to sum hazard estimates across all relevant fractions. An internal additivity calculator is available to MPCA staff that automatically performs this calculation. For the sake of completeness, this calculation includes summation across all six fractions, but, depending on the source of the mixture and weathering and transport, exposure may not include all fractions.

e. Risk characterization for some petroleum residuals (medium aliphatic, high aliphatic, and high aromatic fractions) does not consider the higher relative water intake rates of infants. If any detections occur for these fractions, even if below the drinking water guidance values, households should be notified that alternate sources of water are recommended for bottle-fed infants (children up to 1 year or 12 months of age).

Table 1. Drinking water guidance values for evaluating TPH fractions

Analytical fraction			Surrogate or component	Parameter	Drinking water value (µg/L)[1]	Value type
Aliphatics	Low	C5-C8	surrogate	n-hexane	**MDH table**	MDH Chronic
	Medium	C9-C18	surrogate	mid-range aliphatic hydrocarbons	40	MPCA Chronic[2]
	High	C19-C36	surrogate	white mineral oil	1000	MPCA Chronic[2]
Aromatics	Low	C6-C8	component	benzene	**MDH table**	MDH Cancer
					MDH table	MDH Chronic
			component	toluene	**MDH table**	MDH Chronic
			component	ethylbenzene	**MDH table**	MDH Chronic
			component	xylenes	**MDH table**	MDH Chronic
	Medium	C9-C10	surrogate	trimethylbenzenes	**MDH table**	MDH Chronic
	High	C11-C22	surrogate	pyrene	**MDH table**	MDH Chronic

1 – This table is predominantly based on drinking water values developed by MDH. Go to the MDH water guidance table to retrieve the most up-to-date chronic and/or cancer value.

2 – Where a value from MDH was not available, MPCA calculated a value with MDH input. MDH and MPCA will collaborate in the future to update these values as new data become available and mixtures risk assessment practices evolve.