Site Investigation Scoping: Identifying Contaminants of Concern, Wis. Admin. Code § NR 716.07

Purpose

This guidance can help select the appropriate chemicals for analysis in a Wis. Admin. Code ch. NR 716 site investigation. Identifying the potential contaminants of concern is an important first step in any site investigation and is needed to comply with the following regulatory requirements:

- Scope and develop a workplan for a site investigation based on knowledge of the type of contamination (Wis. Admin. Code §§ NR 716.07 and 716.09(2)(f)).
- Select and use laboratory methods that are suitable for the type and anticipated levels of contamination (Wis. Admin. Code § NR 716.13).

In Wisconsin, responsible parties (RPs) and their environmental consultants are required to evaluate all relevant factors in scoping a site investigation under Wis. Admin. Code NR § 716.07 to ensure that the scope and detail of the field investigation are appropriate for the complexity of the site or facility. Wis. Admin. Code §§ NR 716.09 and NR 716.15 require RPs to develop and submit to the department both a site investigation (SI) work plan and report which evaluate the "history of the site or facility, including industrial, commercial or other land uses that may have been associated with one or more hazardous substance discharges at the site or facility."

This guidance was developed to assist RPs and consultants identify the types of hazardous substances and/or environmental pollution that may be appropriate to include in the SI workplan and report based on a site or facility's history and use. Table 1 of this guidance summarizes substances commonly associated with certain types of industry and/or land use. This table functions as a general guide for department staff, RPs, and consultants, and should not be used as a definitive list of substances that will always be present or absent at a site.

It is important to note that inclusion of a type of industry or land use on the table does not mean a discharge of a hazardous substance or environmental pollution has or has not occurred at a facility or site. The table is simply a guide to present common substances that may be associated with a particular industry or land use. Analysis for all parameters listed in the table for a specific site activity is not required. However, if listed parameters are not included in the SI workplan and report, consultants may wish to provide an explanation of why a given parameter was omitted. For example, if an RP is addressing contamination at a dry-cleaning facility, the department expects the RP to sample for tetrachloroethene (PCE). Further, if an RP is submitting an SI workplan for a shooting range, the department expects the RP to include sampling for lead in the work plan.

Contaminants with and without Numeric Cleanup Standards

The potential contaminants of concern for a site may include chemicals that currently do not have promulgated numeric cleanup standards. This is often the case for emerging contaminants such as per and poly-fluoroalkyl substances (PFAS). Contaminants resulting from environmental pollution and/or a hazardous substance discharge to the environment must be assessed in an investigation even if they do not have a cleanup standard.

Contaminants with and without Numeric Cleanup Standards

When there is evidence of environmental pollution and/or a discharge of a hazardous substance, the DNR has authority to require that the RP address the discharge and/or pollution and can require that the RP develop site-specific cleanup levels for contaminated environmental media, per Wis. Admin. Code § NR 722.09.

In Wisconsin law, the definitions of "environmental pollution" and "discharge" of a "hazardous substance" are not the same as the definition of a hazardous substance in the federal Superfund law and in some other states' laws. In Wisconsin:

"**Environmental pollution**" means the contaminating or rendering unclean or impure the air, land or waters of the state, or making the same injurious to public health, harmful for commercial or recreational use, or deleterious to fish, bird, animal or plant life. See Wis. Stats. § 292.01(4).

"**Discharge**" means, but is not limited to, spilling, leaking, pumping, pouring, emitting, emptying or dumping. See Wis. Stats. § 292.01(3).

"**Hazardous substance**" means any substance or combination of substances including any waste of a solid, semisolid, liquid or gaseous form which may cause or significantly contribute to an increase in mortality or an increase in serious irreversible or incapacitating reversible illness or which may pose a substantial present or potential hazard to human health or the environment because of its quantity, concentration or physical, chemical or infectious characteristics. This term includes, but is not limited to, substances which are toxic, corrosive, flammable, irritants, strong sensitizers or explosives as determined by the department. See Wis. Stats. § 292.01(5).

What are "emerging contaminants?"

Emerging contaminants are generally substances that may be found in the environment – the air, land or water – and where the state or federal regulatory authorities may have: (a) limited health or toxicological data; (b) limited sampling and analytical protocols; and/or (c) no promulgated, numeric cleanup standard to assist in adequately assessing and responding to these substances.

Emerging contaminants are important because the risk they pose to human health and the environment is not yet fully understood and systems may not be in place to address them.

For additional information, see EPA's "Emerging Contaminants and Federal Facility Contaminants of Concern" web page at https://www.epa.gov/fedfac/emerging-contaminants-and-federal-facility-contaminants-concern.

Reporting discovery of a hazardous substance discharge, including emerging contaminants:

Hazardous substances and environmental pollution may include emerging contaminants. In Wisconsin, persons responsible for the discharge of a hazardous substance to the air, land or waters of the state **shall notify the department immediately**, conduct a site investigation, determine the appropriate clean-up standards for the hazardous substance or environmental pollution in each media impacted (e.g., soil, groundwater, surface water and sediment), and conduct the necessary response actions. See Wis. Stats. §§ 292.11(2) and 292.11(3). Notification must be done in compliance with Wis. Admin. Code ch. NR 706; submittal of a Phase II environmental assessment or site investigation report does not satisfy the requirement to "immediately" notify the department.

Laboratory Methods

Per Wis. Admin. Code § NR 716.13(2), all laboratory analyses must be completed by a Wisconsin certified lab meeting the criteria outlined in Wis. Admin. Code ch. 149. Work with the laboratory to select the appropriate sampling methods for the contaminant of concern at a site, the appropriate reporting limits, and to establish the correct sample preparation and hold times.

The EPA's *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods Compendium (SW-846) – Chapter 2: Choosing the Correct Procedure* provides further information.

In most cases, the list of chemicals reported by the lab for a method should be kept broad in the initial sampling until the sources and contaminants of a concern have been defined. The analytes reported by the lab may be narrowed to specific subsets of parameters based on the results from the initial sampling (i.e. full VOCs list vs specific VOC list).

Additional Information on Potential Sources

This section provides information on the common sources of contamination for chemicals in Table 1.

Metals: Metals are naturally occurring and can be found at elevated concentrations in combustion residuals, waste streams from certain manufacturing operations (e.g. chromium plating), and discharges of products containing metals (e.g. leaded gasoline).

RCRA 8: This is a prescribed list of metals that includes: arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), selenium (Se) and silver (Ag). Professional judgement should be exercised when determining whether the full suite of analytes in the RCRA 8 list should be considered based on site activity and potential sources. Analysis for all RCRA 8 metals is often appropriate for evaluating discharges of combustion residuals.

Arsenic: Inorganic arsenic compounds were mainly used to preserve wood. Organic arsenic compounds are used as pesticides, primarily for cotton and orchards, and are in residual products of coal combustion. The most common forms of arsenic in the environment are arsenite (As+3) and arsenate (As+5).

Mercury: Mercury impacts are most often associated with emissions from the burning of fossil fuels and where mercury-based compounds were used as fungicides in agriculture.

Discharges of elemental mercury can also occur. Elemental mercury is a shiny, silver-white metal that is a liquid at room temperature, and was used in older thermometers, fluorescent light bulbs and some electrical switches. When spilled, elemental mercury breaks into smaller mobile droplets and can evaporate to become an invisible, odorless, toxic vapor.

Hexavalent Chromium: Hexavalent chromium was used historically in the chrome plating of metals, as an ingredient in dyes and pigments, in the leather tanning process, and as a wood preservative.

Chromium primarily exists as two oxidation states, trivalent Cr(III) and hexavalent Cr(VI). Hexavalent chromium is a much more toxic and soluble form of chromium and will often reduce to the more stable and less soluble form, Cr(III), when electron donors are available.

Cyanide: Cyanide is a chemical compound that contains one carbon and one nitrogen atom. Cyanide may be used in electroplating, treatment and cleaning of metals, and as an insecticide for fumigating enclosed spaces. Cyanide may also be found in water discharged from organic chemical industries, iron and steel works, and wastewater treatment.

VOCs: Volatile Organic Compounds (VOCs) are a class of contaminants commonly associated with discharges of solvents, petroleum fuels, oils, and other hydrocarbons. The list of VOCs reported by the laboratory is typically left broad during site discovery and initial site investigation activities but, can be narrowed to a specific list of parameters based on site history and the results from the initial sampling.

n-nonane: A component in petroleum fuel (~0.4% in gasoline, ~0.4% in diesel and ~2% in kerosene), paint thinners (1 to 6%), mineral spirits (~10%), and Stoddard solvents (1 to 5%). Most hydrocarbons in Stoddard solvent and mineral spirits will not be detected in a standard VOC scan[1]. When investigating discharges of mineral spirits and Stoddard solvent, analysis for n-nonane is recommended to determine the degree and extent of contamination. Upon request, some laboratories will report n-nonane in their VOC analysis.

1,4-Dioxane: Used primarily as a stabilizer in solvents like 1,1,1-trichlorethane and trichloroethene, and as a solvent in lacquers, paints, resins, and in surfactants and detergents. It is known to be present in greases, dyes, paint stripping, antifreeze, cosmetics, shampoos, pharmaceuticals, and pesticides. 1,4-dioxane should be looked for in the site discovery and initial investigation for any of these types of sites. (Note, liquid detergents [e.g. Dawn and Liquinox] contain some 1,4-dioxane and use of these detergents should be avoided during sampling and analysis). For more information, see USEPA 1,4-Dioxane Factsheet[2].

SVOCs: Semi-volatile Organic Compounds (SVOCs) encompass a broad range of potential contaminant sources including phenols, cresols, extractable pesticides, and PAHs. This broad suite of chemicals is typically analyzed during site discovery and initial site investigation activities. Once the results from the initial sampling are available, the SVOCs reported by the lab can be narrowed to a specific list of parameters based on the initial findings.

PAHs: Polycyclic aromatic hydrocarbons (PAHs) refer to a large class of organic compounds that contain only carbon and hydrogen, and are comprised of two or more fused aromatic rings. PAHs are seldom found separately; rather, they occur as complex mixtures in the environment. PAHs are primarily classified as petrogenic or pyrogenic.

- Petrogenic PAHs are generated from geological processes and are associated with fossil fuels. Petrogenic PAHs can be found at discharges of unprocessed coal and crude oil, and refined petroleum products (e.g. gasoline, diesel, motor oil, home heating oil, lubricants and asphalt).
- Pyrogenic PAHs are generated by high temperature combustion of organic matter. Pyrogenic PAHs can form from natural sources (e.g. forest and grass fires), but mainly come from anthropogenic sources; such as residential wood burning, engine exhausts, coal-fired power plant emissions, coke-oven emissions, coking plant byproduct, creosote, and coal tar.

There are hundreds of chemicals comprising the PAH class, but the specific number remains unknown. A total of 18 PAHs are typically analyzed for in soil and groundwater. Remediation and Redevelopment's program guidance RR-087[3], *Calculating Soil RCLS for PAHs* includes a list of the 18 PAHs typically analyzed.

[1] At sites where GRO and VOCs are both collected, it is typically noted that GRO results > sum of the VOCs. This shows that the standard VOC analysis leaves out many compounds, one of which is often n-nonane.

[2] https://www.epa.gov/sites/production/files/2014-03/documents/ffrro_factsheet_contaminant_14-dioxane_january2014_final.pdf

[3] http://dnr.wi.gov/files/PDF/pubs/rr/RR087.pdf

PCBs: Polychlorinated Biphenyls (PCBs) are a group of synthetic chemicals comprised of carbon, hydrogen, and chlorine. PCBs were manufactured from 1929 to 1979 for their non-flammability, chemical stability, and electrical insulation. Although no longer manufactured, PCBs may be present in products produced before 1979 (e.g. transformers and capacitors, hydraulic oils, oil-based paint, carbonless copy paper, caulking, adhesives and tapes), and found as contaminants at sites with these products, or where improper management or disposal of waste containing PCBs occurred.

PCBs are typically discussed in terms of congeners and Aroclors. A PCB congener is a single, uniquely well-defined compound, of which there are 209. PCBs were typically manufactured as a mixture of congeners and sold under trade names. The most common was the Aroclor series, of which there are 16 common name Aroclor mixtures. Laboratory analysis for PCBs can be done to identify congeners or Aroclors. For more information, see U.S EPA PCB Website[4].

PFAS: Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) are a large class (thousands of compounds) of synthetic organic chemicals comprised of a fluorinated carbon chain with a functional group at the end of the carbon chain. The specific name of a PFAS is determined by the length of its carbon chain, whether the carbon chain is fully (per) or partially (poly) fluorinated, and the type of functional group. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are two of the commonly referenced PFAS.

PFAS are produced and used for their properties including oil and water repellency, temperature resistance, and friction reduction. PFAS have been found at high concentrations at sites where the chemicals were manufactured and disposed, fire training areas that use Aqueous Film Forming Foam (AFFF), and disposal areas for waste containing PFAS (e.g. tannery materials treated with PFAS). PFAS also have the potential to be contaminants at sites which used them in their manufacturing process (e.g. coatings for textiles, paper products and cookware, and a range of industrial applications; aerospace, photographic imaging, semiconductor, automotive, construction, electronics and aviation). For more information, see ITRC PFAS Factsheets[5].

Dioxin/Furan: Dioxin and furans refer to a family of toxic chemicals with similar chemical structure. Most are not created intentionally but are formed during chlorine bleaching of pulp and paper, copper smelting, chemical manufacturing, cement kiln burning, coal-fired electricity generation, manufacturing of chlorine-containing chemicals and polyvinyl chloride, and incineration of waste. Dioxins are highly toxic and take a long time to break down in the environment. For more information, see the U.S. EPA Dioxin Website[6], ASTDR Dioxin Website[7] and ASTDR Furan Website[8].

Glycol: Glycol is class of organic compounds in the alcohol family, where two hydroxyl (−OH) groups are attached to different carbon atoms. The term glycol is often applied to the simplest member of the class, ethylene glycol. Ethylene glycol is a prominent component in de-icing fluids and antifreeze, and is also used as a moisturizer in funeral homes.

Ammonia: Ammonia is a compound comprised of one nitrogen and three hydrogen atoms. Approximately 90% of the ammonia that is commercially produced is used as fertilizer. The other 10% is used as corrosion inhibitor, household cleaner, refrigerant, and in the pulp and paper, metallurgy, rubber, and textile and leather industries.

[4] https://www.epa.gov/pcbs/learn-about-polychlorinated-biphenyls-pcbs
[5] https://pfas-1.itrcweb.org/fact-sheets/
[6] https://www.epa.gov/dioxin
[7] https://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=63
[8] https://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=194

Nitrate: Nitrate is a compound comprised of one nitrogen and three oxygen atoms. A majority of nitrate in the environment comes from breakdown of inorganic (ammonium and urea) fertilizers. Other uses included herbicides, insecticides, food preservative for cured meats and beverages, and munitions or explosives.

Phosphorus: Phosphorus is an element that is most commonly associated with fertilizer. Other uses include detergents, pesticides, and steel production, explosives, and pyrotechnics.

Pesticides: This includes a wide range of herbicides, fungicides, and pesticides. For the Dept. of Agriculture, Trade and Consumer Protection's standard list of pesticide analytes, refer to DATCP's website[9]. There are many lab method(s) to consider depending on the pesticide source, so it is important to work with the laboratory to select the appropriate method(s) for a specific site.

GRO and DRO: Do not have regulatory standards. However, they may by useful parameters during site discovery and investigation to determine if a discharge has occurred, and to estimate the extent of contamination. After initial site screening and discovery are complete, analyses for other specific parameters are typically needed to determine the extent of contamination over cleanup standards and to select cleanup goals and remedial alternatives.

> **GRO:** Gasoline Range Organics (GRO) quantifies the total hydrocarbons within the range of C_6 - C_{10} and a boiling point range between approximately 60°C and 220°C. GRO is a good screening tool to identify impacts associated with discharges of gasoline, chlorinated solvents, ketones, ethers, mineral spirits, Stoddard solvents, and napthas.
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> **DRO:** Diesel Range Organics (DRO) quantifies the total hydrocarbons within the range of C_{10} - C_{28} and a boiling point range between approximately 170°C and 430°C. DRO is a good screening tool to identify impacts associated with discharges of diesel fuel, chlorinated solvents, phenols, phthalate esters, polycyclic aromatic hydrocarbons, kerosene, fuel oils, and heavier oils.

[9] https://datcp.wi.gov/Documents/ACCPAnalytesLabs.pdf

Table 1
Potential Contaminants of Concern

Current & Historical Site Activity	Metals and CN		Organics											Inorganics				Other			Screening	
	Metals	Cyanide	VOCs	VOC (n-nonane)	VOC (1,4-Dioxane)	CVOCs	PVOCs	SVOCs	PAHs	PCBs	PFAS	Dioxin/Furan	Glycol	Ammonia	Nitrate	Phosphorus	Asbestos	Pesticides	Radiation	Explosives	GRO (C_6 - C_{10})	DRO (C_{10} - C_{28})
Adhesives			•					•		•	•		•									
Agricultural[1]	• As, Hg, Pb													•	•	•		•				
Airports			•	•	•						•		•								•	•
Anti-fogging films											•											
Auto/Boat Manufacturing or Repair	• RCRA 8[2]		•						•	•											•	•
Cement Additives	• RCRA 8[2]								•		•		•									
Chemical Production[3]								See Note 3														
Cleaning Products (Industrial & Household)			•								•			•		•						
Combustion (e.g. coal, oil, or wood)	• RCRA 8[2], Al, Co, Cu, Zn								•			•										
Cosmetics and Personal Care Products	• RCRA 8[2]		•		•			•			•		•									
Dry Cleaning [4]			•	•	•	•					•											
Electrical Transformers			•	•						•											•	•
Electronic Industry (Production, Recycling)	• RCRA 8[2]		•							•	•										•	•
Etching	• RCRA 8[2]		•								•			•								
Fire Training & Products	• RCRA 8[2]		•						•		•										•	•
Funeral Home/Morturary			•					•					•								•	•
Furniture Refinishing	• RCRA 8[2]		•	•	•						•										•	
Manufactured Gas Plant (MGP)	• As, Cr, Hg	•	•					•		•				•							•	•
Medical	• RCRA 8[2], Co		•					•			•	•							•			
Metal Casting (Foundry)	• RCRA 8[2], Al, Zn		•						•		•											
Metallurgical Processes (e.g. smelting, plating, refining)	• RCRA 8[2], Al, Co, Cu, Zn,	•	•					•		•	•	•		•	•	•						
Mining Industry	• RCRA 8[2], U, Al, Fe, Ni, Cu, Zn	•	•								•			•	•					•		
Paint and Printing (surface coatings, paint, varnish, inks, enamels)	• RCRA 8[2]		•		•	•	•	•	•	•	•					•					•	•
Pesticides	• RCRA 8[2]		•								•							•				
Petroleum & Refineries																						
Fuel Oil and Diesel Fuel			•	•			•		•		•											•
Gasoline (including E-85 Fuel)	• Pb[5]		•				•				•										•	
Kerosene and Aviation Fuel			•				•				•										•	•
Mineral Spirits and Stoddard Solvent			•	•			•				•										•	
Waste Oil	• RCRA 8[2], Cu, Ni, Ag, Zn		•	•			•		•	•	•										•	•
Photographic Industry	• RCRA 8[2]		•		•	•					•											
Plastics, Resins, and Rubber	• RCRA 8[2]		•								•											
Pulp and Paper, Cardboard Packaging	• Hg									•	•	•		•	•	•						
Railroad - Line and Switch/Maint Yard	• RCRA 8[2]		•					•													•	•
Semiconductor Industry	• RCRA 8[2]		•		•	•					•											
Shooting Ranges/Gun Clubs	• See ITRC, 2005[6]								•											•		
Tannery	• Cr							•			•											
Textiles, stain and water repellants	• RCRA 8[2], Cu, Ni, Co		•	•							•	•										
Tombstone (Cemetery Monument) Maker			•																			
Waste																						
Junk/Salvage Yard	• RCRA 8[2]	•	•	•	•			•		•			•				•				•	•
Landfills and other waste disposal	• RCRA 8[2]	•	•	•	•	•	•	•	•	•	•	•		•	•						•	•
Wood Treatment / Preservation	• As, Cr, Cu		•	•				•	•			•									•	•

[1] Agricultural: The DATCP oversees cleanup of fertilizer and non-household pesticides, per Wis. Stat. § 94.73 and Wis. Admin. § ATCP 35.

[2] RCRA 8: Analysis of the full suite of metals in the RCRA 8 list may not always be necessary.

[3] Chemical Production: Potential contaminants of concern will be specific to the process and type of chemicals manufactured at the site.

[4] Dry cleaning solvents were often tetrachlorethene (PCE) or Stoddard solvent.
Other dry cleaning industries include formal ware, uniform rental, drapery cleaners, commerical rug cleaning, stain treatment, and water proofing.

[5] The DATCP's Tank System Site Assessment (TSSA) defines analyses to close certain underground storage tanks. TSSA is not equivalent to a NR 716 Site Investigation.

[6] ITRC, 2005 *Environmental Management at Operating Outdoor Small Arms Firing Ranges* Table 2-1 provides a summary of the metals potentially found at ranges.