

Monitoring Water Supply Wells for VOCs Around Solid Waste Disposal Facilities NR 507.19 and NR 507.20



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Description: This document clarifies ch. NR 507, Wis. Adm. Code, monitoring requirements for volatile organic chemicals (VOCs) in water supply wells

Relevant Code Citations: NR 507.19(3); NR 507.20; NR 507 Appendices II and III; NR 809.24; NR 809.25; NR 809.725 (1) Tables B and G; NR 140.16; NR 716.13(2), NR 812.06.

Applicability: This guidance primarily is intended for staff use in establishing monitoring requirements associated with Plans of Operation for landfills regulated under ch. NR 507, Wis. Adm. Code. In addition, it may be applicable to landfills for which corrective action is necessary or cases where NR 507 and NR 716 may both be applicable. It specifically addresses monitoring private wells around landfills. Recommendations in this guidance are not directly applicable to landfill monitoring wells.

Although the recommendations contained in this guidance may have general applicability to private well monitoring at remediation sites, it is not intended for use at LUST sites or sites with known contaminant plumes from sources other than landfills. The specific contaminant list, considerations for method selection, and sensitivity needs may be different than what is discussed in this document.

Problem Statement: Detection monitoring for Volatile Organic Compounds (VOCs) may involve analysis of private water supplies in the monitoring network. When pollutants in water supply wells exceed the enforcement standards (ESs) in NR 140, the Safe Drinking Water Act (SDWA) Maximum Contaminant Levels or MCLs are also exceeded for the regulated compounds. When contaminant concentrations exceed their Preventative Action Limits (PALs), the Department's concern becomes both protecting groundwater quality and protecting the health of people drinking water from those wells. Thus, the same results may be used to determine compliance with monitoring requirements, to issue public health advisories, and for well compensation determinations. The regulations reflect that concern for public health by requiring the procedures in NR 809 to be followed for private water (e.g. homeowner) supplies. NR 507.20 (1) (a) and (b) state that water supply well samples shall be collected, handled and analyzed in accordance with the procedures specified in chapter NR 809 and analyzed in accordance with plans approved by the Department. As currently implemented, this Code provision has caused some confusion for staff and in the regulated community and as a result, the data reported is not always adequate.

Although NR 507 indicates that water supply wells shall be analyzed according to the Safe Drinking Water Act procedures identified in NR 809, various Plans of Operation list solid waste methodology for private well analyses. The volatile organic compound list in NR 507 Appendix III includes substances that are not regulated under the Safe Drinking Water Act (SDWA). Laboratories performing drinking water analyses may only be prepared to report the compounds regulated under SDWA. On the other hand, laboratories performing the analyses using solid waste methodology may report the appropriate compounds, but their detection limits may be too high to determine whether the drinking water MCLs have been exceeded. This document clarifies

requirements for methodology, the compound list for VOCs and detection limits as well as providing recommendations for ensuring that monitoring data meets its intended purposes.

Compound List: Without any additional information, when laboratories process requests for volatile organics by drinking water methods, they typically analyze the samples for the drinking water regulated analytes. Therefore, a key to having the appropriate compounds reported is to communicate the list of compounds expected. Ideally, plans of operation will clearly indicate the requirement to report the compounds listed in NR 507 Appendix III for VOC determinations for all water supply wells, whether they be public or private supplies (NR 507.19 (3)). Table 1 lists the compounds found in the September 1998 revision to NR 507 Appendix. Compounds in the Appendix III list that are not included in SDWA regulations are in italics and underlined in Table 1 and include:

Acetone
Carbon Disulfide
1,2-Dichlorobenzene
Fluorotrichloromethane
Methyl ethyl ketone (MEK)
Methyl tert-butyl ether (MTBE)

It is important to note that 1,2,4-Trichlorobenzene is not included in Appendix III but is an SDWA-regulated compound with an MCL of 0.07 mg/L (70 µg/L). It may be appropriate to add this compound to the monitoring list when site-specific conditions indicate that this may be a compound of concern (e.g. other chlorinated benzenes are present in groundwater or leachate). This compound should not be added automatically to compound list.

The Environmental Monitoring Team recommends that staff clearly communicate the expected compound list to the facilities and their laboratories. It may be convenient to send the Table as an attachment to pertinent correspondence or include the compound list in Table 1 in the Plan of Operation.

Detection Limits and Reporting: Although NR 140.16(2) includes language about selecting a method that will meet the PALs, it does not explicitly state maximum acceptable detection limits. When private wells are monitored around landfills, the facility should select a laboratory that can meet the detection limit requirements for drinking water. Staff should clearly communicate this expectation to facilities and laboratories performing this monitoring. NR 809.25(17) specifies maximum acceptable detection limits of 0.5 µg/L for all regulated VOCs, except vinyl chloride, EDB and DBCP. NR 809.25(17) requires the vinyl chloride detection limit to be no higher than 0.3 µg/L. The maximum detection limits allowed for EDB and DBCP are 0.01 µg/L and 0.02 µg/L, respectively (NR 809.21(6)). Both NR 809 and NR 140 require reporting to the detection limit. As with other groundwater reporting, the laboratory's actual LOD and LOQ should be reported with the results and results between LOD and LOQ should be appropriately flagged. NR 507.20 (3) also requires that the information on the Groundwater Monitoring Inventory Form 3300-67 in Appendix V be completed for all private wells.

Methodology: NR 507.20(1) indicates that water supply well samples must be collected, handled, and analyzed in accordance with the procedures specified in NR 809. The only distinction made between private and public water supplies in this section of the NR 507 relates to documentation so the provision about sampling and analysis should be applied to all water supply wells¹. This affords private well owners the same level of data quality as public water supplies when the monitoring is associated with landfill monitoring. The list of volatiles with their associated drinking water methodology is found in Table 1. If, in preparing a Plan of Operation for a facility with private well monitoring, specific methods are referenced, the methods references should be consistent with those found in Table 1. It is important to note that the NR 809 Table B requires separate methods for 1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-chloropropane (DBCP) because the VOC

¹ When the purpose for monitoring private water supplies that are not covered by the Safe Drinking Water Act (NR 809) is something other than landfill monitoring, NR 812 is the applicable administrative rule. NR 812 differs significantly from NR 809.

methods are unable to detect these compounds at the drinking water MCL. These two compounds are regulated as synthetic organic contaminants rather than VOCs in the SDWA..

The Environmental Monitoring Team recommends that the Plan of Operation be modified to indicate SDWA methods are required under NR 507.20(1) for monitoring water supply wells. (For remediation sites, the appropriate code reference is NR 716.13(2).) Various existing Plans of Operation specify the same VOC methods for private wells as those used for other monitoring wells at the landfill. Most commonly, these methods citations are either 8021 or 8260 from SW-846. Method 8260 is the preferred method choice when the facility or DNR staff know that the private wells contain significant VOC or petroleum hydrocarbon contamination. Facilities may request that the Plan of Operation continue to allow SW-846 methods rather than SDWA methods to avoid confusion or error or to save money. This request may be considered provided that other drinking water requirements are met.

Operationally, VOC methods 8021 and 8260 are very similar to drinking water methods 502.2 and 524.2 respectively, but there may be differences in the quality of results obtained. The SDWA VOC methods do not require matrix spike analysis because they assume that samples are clean, finished water without matrix effects. Many laboratories designate specific instrumentation for drinking water samples and pay close attention to hygiene practices to minimize risk of sample contamination and to maintain required sensitivity. In some laboratories, the drinking water and the SW-846 VOC methods are identical, only the names are changed to satisfy reporting requirements. Analyses for method blanks should demonstrate that laboratory contamination sources are adequately controlled.

If private water supply wells potentially contain significant concentrations of petroleum hydrocarbons (TPH), GC/MS methods should be selected to assure that accurate results are obtained for methyl-tert-butyl ether (MTBE). Recent literature indicates that when VOCs are determined by GC methods, MTBE results may be biased high or be false positives when high concentrations of TPH are also present.

Sample Collection and Handling: A minimum of four additional 40 mL vials per sample are necessary to provide for the separate determination of EDB and DBCP. Although NR 809 specifies collecting the samples in 60 mL vials, both DNR and EPA recognize that it may be more practical to use 40 mL vials because they are in ready supply. EPA's addendum to method 551.1 explains the allowance to use the smaller vials and the circumstances under which smaller sample volumes may be used. As with VOC samples, samples from wells that are not chlorinated must be preserved to a pH less than 2 and cooled to 4°C². The recommended cooling procedure is to place the samples on ice immediately after collection. Samples should be shipped with sufficient ice to assure that ice is still present when the laboratory receives the samples.

Laboratory certification criteria and procedures for safe drinking water in NR 149.21(1)(a) require laboratories to reject samples that are improperly preserved. This provision in the drinking water regulations provides some assurance that sample results are not biased (low) by poor sample handling practices, an important consideration when determining whether human health standards have been exceeded. Sample rejection also serves as timely notification to the facility or consultant that re-sampling is necessary. NR 140.16(4) allows the Department to reject groundwater results when the analytical method requirements are not met (preservation requirements are included in the methods). Staff must consider carefully whether to accept results for samples that are improperly preserved, particularly those that are not cooled properly. If the sample results are unacceptable, re-sampling is recommended.

Certification Requirements: Private well samples, which are required to be taken by DNR's Waste and Materials Management or Remediation and Redevelopment programs, must be analyzed by a laboratory certified under NR 149 for VOCs. Although certification in the safe drinking water test category for VOCs is strongly recommended, it is not required.

² If the water supply well is chlorinated, the preservation procedure must include dechlorination with either sodium thiosulfate for methods 502.2, 524.2 and 504.1 or ammonium chloride for methods 551 and 551.1. Following dechlorination, these samples must be acid preserved and cooled to 4°C.

Summary of Recommendations:

The Environmental Monitoring Team recommends that staff:

1. Provide facilities and consultants with the list of compounds required. This may be done as an attachment to correspondence or Plan of Operation documentation.
2. Modify Plans of Operation to reference the Safe Drinking Water methods if analytical methods are specified in the Plan. Strict reading of the Code indicates that the Safe Drinking Water methods are the methods required for monitoring private water supplies.
3. Consider allowing solid waste methods included in SW-846 if other drinking water requirements are met.
4. Communicate the detection limits requirements to facilities. The maximum detection limits for compounds included in both NR 507 and NR 809 are:

Vinyl Chloride	0.3 ug/L
EDB	0.01 ug/L
DBCP	0.02 ug/L
Other SDWA VOCs	0.5 ug/L

5. Evaluate method blank results. Method blanks should demonstrate that laboratory contamination is controlled. If QC flags indicates that blanks contain contaminants of concern, carefully evaluate the results to determine if the data is of sufficient quality for its intended use.
6. Remind facilities that analyses EDB and DBCP require additional sample bottles because it is a separate analysis from VOCs.

Contact DNRWasteMaterials@Wisconsin.gov for further information.

***Disclaimer:** This document is intended solely as guidance and does not contain any mandatory requirements except where requirements found in statute or administrative rule are referenced. Any regulatory decisions made by the Department of Natural Resources in any matter addressed by this guidance will be made by applying the governing statutes and administrative rules to the relevant facts.*

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Table 1

Note: This table may change as NR 507, NR 140, NR 809 and 40 CFR 141 are revised.

NR 507 Appendix III Contaminant	CAS #	NR 140 PAL ($\mu\text{g/L}$)	NR 809 Status (MCL in $\mu\text{g/L}$)	SDWA Methods
<i>Acetone</i>	67-64-1	200	--	524.2
Benzene	71-43-2	0.5	5	502.2, 524.2
Bromodichloromethane	75-27-4	0.06	TTHM MCL = 100	502.2, 524.2
Bromomethane	74-83-9	1	Unregulated	502.2, 524.2
Bromoform (Tribromomethane)	75-25-2	0.44	TTHM MCL = 100	502.2, 524.2
<i>Carbon disulfide</i>	75-15-0	200		524.2
Carbon tetrachloride	56-23-5	0.5	5	502.2, 524.2
Chlorobenzene	108-90-7	20	100	502.2, 524.2
Chloroethane	75-00-3	80	Unregulated	502.2, 524.2
Chloroform (Trichloromethane)	67-66-3	0.6	TTHM MCL = 100	502.2, 524.2
Chloromethane	74-87-3	0.3	Unregulated	502.2, 524.2
Dibromochloromethane	124-48-1	6	TTHM MCL = 100	502.2, 524.2
<i>1,2-Dibromo-3-chloropropane (DBCP)</i>	96-12-8	0.02	0.2	504.1, 551, 551.1
<i>1,2-Dibromoethane (EDB)</i>	106-93-4	0.005	0.05	504.1, 551, 551.1
<i>1,2-Dichlorobenzene</i>	95-50-1	60		502.2, 524.2
1,3-Dichlorobenzene	541-73-1	125	Special 809.26	502.2, 524.2
1,4-Dichlorobenzene	106-46-7	15	75	502.2, 524.2
Dichlorodifluoromethane	75-71-8	200	Special 809.26	502.2, 524.2
1,1-Dichloroethane	75-34-3	85	Special 809.26	502.2, 524.2
1,2-Dichloroethane	107-06-2	0.5	5	502.2, 524.2
1,1-Dichloroethylene	75-35-4	0.7	7	502.2, 524.2
cis-1,2-Dichloroethylene	156-59-2	7	70	502.2, 524.2
trans-1,2-Dichloroethylene	156-60-5	20	100	502.2, 524.2
1,2-Dichloropropane	78-87-5	0.5	5	502.2, 524.2
1,3-Dichloropropene (cis)	10061-01-5	*0.02	Special 809.26	502.2, 524.2
1,3-Dichloropropene (trans)	10061-02-6	*0.02	Unregulated	502.2, 524.2
Ethylbenzene	100-41-4	140	Unregulated	502.2, 524.2
<i>Fluorotrichloromethane</i>	75-69-4	698		502.2, 524.2
Methylene bromide	74-95-3		Unregulated	502.2, 524.2
Methylene chloride (Dichloromethane)	75-09-2	0.5	5	524.2
<i>Methyl ethyl ketone (MEK)</i>	78-93-3	90		502.2, 524.2
<i>Methyl tert-butyl ether (MTBE)</i>	1634-04-4	12		502.2, 524.2
**Naphthalene	91-20-3	8	Unregulated	524.2*
Styrene	100-42-5	10	100	502.2, 524.2
Tetrachloroethylene	127-18-4	0.5	5	502.2, 524.2
Tetrahydrofuran	109-99-9	10		502.2, 524.2
Toluene	108-88-3	200	1000	502.2, 524.2
1,1,1-Trichloroethane	71-55-6	40	200	524.2
1,1,2-Trichloroethane	79-00-5	0.5	5	502.2, 524.2
Trichloroethylene (TCE)	79-01-6	0.5	5	502.2, 524.2
Vinyl chloride	75-01-4	0.02	0.2	502.2, 524.2
Xylenes (total)	***	1000	10000	502.2, 524.2

* PAL applies to the sum of the concentrations of 1,3-Dichloropropene (cis) and 1,3-Dichloropropene (trans).

** Naphthalene is also a polynuclear aromatic hydrocarbon (PAH). If other semi-volatile compounds or specifically PAHs are included in the monitoring plan, it may be appropriate to eliminate this compound from VOC monitoring.

*** CAS #s include 95-47-6 for o-Xylene, 108-38-3 for m-Xylene, and 106-42-3 for p-Xylene, or 1330-20-7 for unspecified Xylene



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Pursuant to ch. 227, Wis. Stats., the Wisconsin Department of Natural Resources has finalized and hereby certifies the following guidance document.

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DOCUMENT TITLE

Monitoring Water Supply Wells for VOCs Around Solid Waste Disposal Facilities

PROGRAM/BUREAU

Waste and Materials Management

STATUTORY AUTHORITY OR LEGAL CITATION

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DATE SENT TO LEGISLATIVE REFERENCE BUREAU (FOR PUBLIC COMMENTS)

November 18, 2019

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December 11, 2019

DNR CERTIFICATION

I have reviewed this guidance document or proposed guidance document and I certify that it complies with sections 227.10 and 227.11 of the Wisconsin Statutes. I further certify that the guidance document or proposed guidance document contains no standard, requirement, or threshold that is not explicitly required or explicitly permitted by a statute or a rule that has been lawfully promulgated. I further certify that the guidance document or proposed guidance document contains no standard, requirement, or threshold that is more restrictive than a standard, requirement, or threshold contained in the Wisconsin Statutes.

December 11, 2019

Signature

Date