

To: DEQ Water Quality Staff**Date:** November 28, 2014**From:** Jennifer Wigal, *Surface Water Management Section Manager*
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Andrea Matzke, *WQ Standards and Assessment Section***Subject:** Implementation Instructions for the Water Quality Criterion 1,2 Diphenylhydrazine
(CAS #: 122-66-7)

This memo clarifies how 1,2 diphenylhydrazine concentrations in effluent and surface water are measured to determine compliance with water quality criteria.

Criteria Summary

Oregon water quality standards include numeric criteria for 1,2 diphenylhydrazine to protect human health (See table below). There are no corresponding aquatic life criteria.

Chemical	Human Health Criteria		Aquatic Life Criteria (Freshwater)		Aquatic Life Criteria (Saltwater)	
	Water + Org (µg/L)	Org Only (µg/L)	Acute (µg/L)	Chronic (µg/L)	Acute (µg/L)	Chronic (µg/L)
1,2 Diphenylhydrazine	0.014	0.020	---	---	---	---

Key Issues

According to the 1990 ATSDR¹, under aerobic conditions, 1,2-diphenylhydrazine in wastewater effluent rapidly decomposes into other chemicals and has a half-life in water as short as 15 minutes. One of the decomposition chemicals is azobenzene. Due to the fact that accurate modeling regarding decomposition information is unavailable and potentially highly variable, DEQ proposes to measure “azobenzene” as the primary estimate for determining the amount of 1,2-diphenylhydrazine in a water sample. 1,2-diphenylhydrazine has additional metabolites (e.g. aniline, benzidine, 2-hydroxyazobenzene, 2-aminophenol, 2-alkoxyamine, 2-acetamidophenol, 4-hydroxyazobenzene, 4-aminophenol, 4-acetamidophenol and 4-alkoxyamine), but DEQ is not proposing to analyze these chemicals at this time unless sample interference, excessive costs, or other factors would favor the use of other decomposition products in lieu of azobenzene. The presence of these other metabolites may also indicate that the sample originally contained 1,2-diphenylhydrazine which has since decomposed.

¹ Agency for Toxic Substances and Disease Registry.
<http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=952&tid=198>

Recommended Analytical Method

The recommended analytical method for azobenzene is EPA 625.

1,2-diphenylhydrazine rapidly decomposes in the injection port of the Gas Chromatograph to azobenzene. However, the 2009 ATSDR addendum² states that the decomposition of 1,2-diphenylhydrazine into its metabolites is highly dependent upon environmental conditions such as pH and the presence of other compounds. High Performance Liquid Chromatography (HPLC) is typically used in cases where the compound is susceptible to decomposition, but at this time, no methods for this compound by HPLC have been promulgated by EPA. Though adequate analytical procedures exist for GC/MS, the current methods for sample collection, preservation and storage, though improved, are still insufficient for this compound. The biggest concern at this time is that regardless of the efficiency of the analytical technique, the sampling and preservation techniques may not be appropriate to keep 1,2-diphenylhydrazine from decomposing prior to extraction.

To determine the applicable quantitation limits for individual permit holders, please refer to Schedule B of the applicable permit. For older permits without quantitation limits in their Schedule B, please refer to Revision 3.0 of the [Reasonable Potential Analysis for Toxic Pollutants IMD](#) to determine applicable quantitation limits.

Implementation Instructions for NPDES Permits

1,2 diphenylhydrazine is listed as a monitoring requirement in 40 CFR 122, Appendix D for certain industrial and domestic sources. Appendix D also includes a parenthetical, “as azobenzene” adjacent to 1,2 diphenylhydrazine which further substantiates the use of azobenzene as a surrogate.

When evaluation of 1,2 diphenylhydrazine is indicated as part of the permit application or renewal process, the permit writer will require monitoring for azobenzene using EPA Method 625 as part of the Tier 1 monitoring process. These results will be used as a surrogate to evaluate 1,2 diphenylhydrazine and determine if it is a pollutant of concern (POC).

If identified as a POC, additional Tier 2 monitoring of the ambient and potentially effluent condition will be required. Although this monitoring will typically be conducted using azobenzene, the permit writer may consult the DEQ laboratory and consider the use of alternative decomposition metabolites when conducting additional analysis and determining *reasonable potential*.

The RPA Workbook has been configured for the use of azobenzene in the various determination processes. If other metabolites are to be used, the permit writer should contact Surface Water Management for technical assistance in making changes to the workbook and conducting the evaluation.

Conclusion

In summary, 1,2 diphenylhydrazine is difficult to analyze given its rapid decomposition rate in water. Instead, azobenzene, which is a decomposition product of 1,2 diphenylhydrazine, should

² Agency for Toxic Substances and Disease Registry.
http://www.atsdr.cdc.gov/toxprofiles/1,2-diphenylhydrazine_addendum.pdf

be analyzed as an estimate of this chemical. Analytical results from azobenzene analysis will be directly compared to the applicable water quality criterion for 1,2-diphenylhydrazine.