

GUIDANCE SUMMARY

The attached water quality program guidance “PAH Group of 10 Calculation of Concentration Using Toxicity Equivalent Factors” is being made available for public review at this time. This draft guidance was written to inform Wisconsin Department of Natural Resources (WDNR) staff, permittees, and others about determining compliance with effluent limits for polycyclic aromatic hydrocarbons (PAH) using the new proposed method to calculate the concentration of the PAH group of 10 compounds.

This technical guidance was developed by WDNR in response to a comment raised during the public notice of a recent WPDES permit reissuance that contained PAH limits for the discharge from an oil and water separator. The WDNR is now soliciting input from external stakeholders on this guidance. Once this 21 day notice period is complete, all comments will be considered, revisions will be made to the guidance as needed, and final guidance will be made available to internal and external stakeholders.

The legal authority for regulating the discharge of pollutants into waters of the state is contained in ch. 283, stats., the Wisconsin Pollutant Discharge Elimination System (WPDES) permit program. There isn't a specific legal reference applicable to this guidance. This is simply a refinement of how the PAH concentration may be calculated with the use a multiplier to normalize the toxicity of 10 PAH compounds. The concentration of each PAH compound is multiplied by a toxicity equivalent factor (TEF) that has been derived by EPA and others.

Comments related to this draft guidance should be sent Paul Luebke, wastewater specialist in the Bureau of Water Quality, at the following email address:

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**BUREAU OF WATER QUALITY
PROGRAM GUIDANCE
WPDES**

**PAH Group of 10 Calculation of Concentration
Using Toxicity Equivalent Factors**

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Guidance Number: 3400-2015-01

Wisconsin Department of Natural Resources

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. This guidance does not establish or affect legal rights or obligations, and is not finally determinative of any of the issues addressed. This guidance does not create any rights enforceable by any party in litigation with the State of Wisconsin or the Department of Natural Resources. 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.

APPROVED:

Susan L. Sylvester, Director
Bureau of Water Quality

Date

Introduction

This technical guidance establishes the method for staff in the water quality program to calculate the concentration of the polycyclic aromatic hydrocarbon (PAH) group of 10 compounds for determining compliance in WPDES permits that regulate contaminants from petroleum products. Need for the guidance was triggered by a comment received during the 2014 reissuance of the Dane County Regional Airport WPDES permit (WI-0048747-04) on the PAH effluent limits for the oil and water separators. In response to a comment, the Department implemented a new method for the summation of the PAH group of 10 compounds. The guidance is necessary to allow consistent application of the new method for determining compliance with the PAH limit, and to improve the accuracy in calculating the PAH group of 10 concentration. Any WPDES permit with PAH limits could be impacted. The method will provide relief in determining compliance with the effluent limit.

Background Information

Point source wastewater discharges containing PAH compounds in are usually regulated using best professional judgment (BPJ) technology based limitations. The BPJ limits are based on an oil and water separator treatment process and activated carbon adsorption, where applicable, as the best available economically achievable treatment technology. When naphthalene is present an air stripping process is used to establish those BPJ limits. The BPJ limits meet site specific water quality standards for most Wisconsin waters.

There are three BPJ limits applicable to the PAH compounds.

- Benzo(a)pyrene is limited separately with a limit of 0.1 µg/L.
- Naphthalene is limited separately with a limit of 70 µg/L.
- A group of 10 PAH compounds are regulated together with a limit of 0.1 µg/L applicable to the sum of the detected amounts of each of the following:
 1. Benzo(a)anthracene
 2. Benzo(b)fluoranthene
 3. Benzo(k)fluoranthene
 4. Benzo(g,h,i)perylene
 5. Chrysene
 6. Dibenzo(a,h)anthracene
 7. Fluoranthene
 8. Indeno(1,2,3-cd)pyrene
 9. Phenanthrene
 10. Pyrene

These three limits for PAH compounds are currently included in the groundwater remediation general permit (WI-0046566-06), the petroleum contaminated water general permit (WI-0046531-05), and other site specific individual WPDES permits when there's a need for a PAH limit, such as those with oil and water separators. For the PAH group of 10, permits generally allow compliance to be demonstrated by a no detect of all of the 10 compounds or by reporting the sum of the PAH group of 10 detected amounts equal to or less than 0.1 µg/L.

At one time ch. NR 105, Wis. Adm. Code had a water quality criterion for benzo(a)pyrene, and a group criterion for the 10 of the other 16 PAH compounds that have a similar atomic structure to benzo(a)pyrene. The other 6 PAH compounds are excluded from the PAH group limit because they are not believed to exhibit the same toxicity due to their dissimilar atomic structure. In the most recent version of ch. NR 105, the criteria for these PAH compounds did not meet the new set of guidelines for the number of species with toxicological data. Therefore, in 1997 the PAH criteria were removed from ch. NR 105. Alternatively, secondary water quality values for PAH's may be used based on available toxicological data and a safety factor to protect aquatic life.

PAH Toxicity Equivalent Factor

The method for calculating the PAH group of 10 concentration will reflect a toxicity equivalent factor (TEF) based on benzo(a)pyrene in order to normalize the toxicity. PAH compounds are a human health concern because they're suspected carcinogens. Benzo(a)pyrene is the most toxic of the PAH compounds

based on toxicological testing. The other PAH compounds had previously been considered to be equivalent in toxicity. But, most of the other PAH compounds are considerably less toxic. To prevent an over estimation of the toxicity for the PAH group of 10 a toxicity equivalent factor (TEF), also referred to as a relative potency factor (RPF), was established for each compound relative to benzo(a)pyrene. Use of a TEF in the summation of PAH group of 10 compounds is a more precise and scientifically valid methodology than a simple summation of the 10 compounds without taking into account the relative toxicity of each compound.

Permittees with PAH limits may have compliance issues with the PAH group of 10 because the summed concentration exceeds the 0.1 µg/L limit, even when all the individual compounds are <0.1 µg/L. This has occurred at sites where the oil and water separator is located near combustion sources, such as jet engines at airports. By using the TEF in calculating the concentration of the PAH group of 10, permittees that were in apparent violation may now be found in compliance due to the more precise method of calculating the concentration. This isn't a new concept, as a similar TEF approach is used to evaluate compliance with limitations for dioxin related equivalent compounds, as described in s. NR 106.115, Wis. Adm. Code - "additivity of dioxins and furans".

Summary of TEF Method

To calculate the concentration for the PAH group of 10, multiply the concentration of each PAH compound by the corresponding TEF value from the table below and then sum the results.

For reference to the TEF or RPF used in the table below several documents were reviewed. Some of the PAH compounds have a few different TEF or RPF values reported. The values in the "PAH Toxicity Equivalent Factors" table include the EPA values (shown in bold), except when EPA didn't have a value; in which case a literature value was chosen from the reference documents. The values are subject to change in the future if better information becomes available.

PAH Toxicity Equivalent Factors

	PAH Compounds	TEF - Toxicity Equivalent Factor	10 Summed Compounds with 0.1 µg/L Limit	Individual Compounds with Limits
1	Acenaphthene	--	--	--
2	Acenaphthylene	--	--	--
3	Anthracene	--	--	--
4	Benzo(a)anthracene	0.1	Benzo(a)anthracene	--
5	Benzo(a)pyrene	1	--	Benzo(a)pyrene 0.1 µg/L
6	Benzo(b)fluoranthene	0.1	Benzo(b)fluoranthene	--
7	Benzo(g,h,i)perylene	0.01	Benzo(g,h,i)perylene	--
8	Benzo(k)fluoranthene	0.01	Benzo(k)fluoranthene	--
9	Chrysene	0.001	Chrysene	--
10	Dibenzo(a,h)anthracene	1	Dibenzo(a,h)anthracene	--
11	Fluoranthene	0.001	Fluoranthene	--
12	Fluorene	--	--	--
13	Indeno(1,2,3-cd)pyrene	0.1	Indeno(1,2,3-cd)pyrene	--
14	Naphthalene	--	--	Naphthalene 70 µg/L
15	Phenanthrene	0.001	Phenanthrene	--
16	Pyrene	0.001	Pyrene	--

This guidance for calculating the concentration for the PAH group of 10 may be implemented in existing permits immediately. A permit modification to use the new calculation method is unnecessary. The PAH limit isn't changing. The only change being made is how the summation of the 10 PAH compounds is calculated and may be reported by the permittee.

In future permits the following three paragraphs related to the regulation of PAH's may be included:

1.1.1.1 PAH Group of Ten

Polycyclic aromatic hydrocarbons (PAH's) shall include a summation of the following ten individual compounds: benzo(a)anthracene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, indeno(1,2,3-cd)pyrene, phenanthrene, and pyrene. Compliance with the monthly average PAH limit can be demonstrated by reporting a no detect of all of these PAH compounds, or by reporting the sum of the PAH individual compounds equal to or less than 0.1 µg/L. If a PAH compound is detected between the level of detection (LOD) and level of quantitation (LOQ) the value shall be reported on the DMR, but it is not considered an exceedance if the LOQ is greater than 0.1 µg/L.

In determining compliance with the 0.1 µg/L limit, the permittee may use the toxicity equivalent factors shown below. For calculating the concentration for the PAH group of 10, multiply the concentration of each PAH compound by the corresponding TEF value and then sum the results. For results <LOD, a zero may be used for the concentration. Refer to the permit standard requirement for the reporting of monitoring results.

	PAH Compounds	TEF - Toxicity Equivalent Factor
1	Benzo(a)anthracene	0.1
2	Benzo(b)fluoranthene	0.1
3	Benzo(g,h,i)perylene	0.01
4	Benzo(k)fluoranthene	0.01
5	Chrysene	0.001
6	Dibenzo(a,h)anthracene	1
7	Fluoranthene	0.001
8	Indeno(1,2,3-cd)pyrene	0.1
9	Phenanthrene	0.001
10	Pyrene	0.001

1.1.1.2 Benzo(a)pyrene

The PAH compound benzo(a)pyrene is regulated separately. Compliance can be demonstrated by reporting no detect, or by reporting a detected amount equal to or less than 0.1 µg/L.

1.1.1.3 Naphthalene

The PAH compound naphthalene is regulated separately. Compliance can be demonstrated by reporting no detect, or by reporting a detected amount equal to or less than 70 µg/L.

References

1. "Development of a Relative Potency Factor (RPF) Approach for Polycyclic Aromatic Hydrocarbon (PAH) Mixtures". Table 3.1 on page 45 lists the RPF for several of the PAH compounds.
http://cfpub.epa.gov/ncea/iris_drafts/recordisplay.cfm?deid=194584
2. At EPA's web site Ecotox toxicity equivalent factors can be found by searching for documents containing "PAH TEF".
<http://cfpub.epa.gov/ecotox/>
3. There's also a paper in the International Journal of Environmental Research and Public Health that included TEF's for PAH compounds. While this study is on exposure to PAH's in the air, the same conclusions can be made for PAH's in water, sediment and fish.
<http://www.mdpi.com/1660-4601/7/5/1889>
4. The Minnesota Department of Health has "Guidance for Evaluating the Cancer Potency of Polycyclic Aromatic Hydrocarbon (PAH) Mixtures in Environmental Samples", dated October 31, 2014.
<http://www.health.state.mn.us/divs/eh/risk/guidance/pahguidance.pdf>

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