Permit Guidance 12 Final	**National Pollutant Discharge Elimination System (NPDES); BADCT Limits for Volatile Organic Compounds**	
	Statutory references: ORC 6111.01, 6111.03, 6111.04 Rule references: OAC 3745-1-05, 3745-33-07	Ohio EPA, Division of Surface Water Revision 0, November 8, 2010 Revision 1, September 27, 2019
This internal guidance does not affect requirements found in referenced rule or statute.		

Background and Purpose

Ohio's Antidegradation rule (OAC 3745-1-05) requires that new discharges be treated to levels associated with the Best Available Demonstrated Control Technology (BADCT). The rule specifically defines BADCT for domestic sewage and federal categorical industries. For cleanups of response action sites contaminated by VOCs, BADCT is defined as treatment capable of meeting 5 ug/l as a 30-day average for each chemical.

The purpose of this guidance is to define which chemicals are considered VOCs subject to this treatment standard.

Treatment Used

The process of remediation requires that groundwater or contaminated surface waters are pumped from their location to a receiving water to meet appropriate health standards for the site waters. If VOC compounds are present, the discharge is usually treated to remove the VOC compounds.

VOCs are normally separated from water by physical/chemical processes such as air stripping or carbon adsorption. The effectiveness of these methods is determined by two physical/chemical properties of the VOC compound - The Henry's Law Constant and the water solubility of the chemical.

Air stripping is designed to remove VOCs based on a ratio of their water solubility (the tendency of the chemical to stay in solution) to vapor pressure (the tendency to volatilize). This ratio is the Henry's Law Constant. Chemicals with lower Henry's Law Constants require greater stripping column heights and greater air pressures than those with higher Henry's Law Constants.

Carbon adsorption is designed to remove organic chemicals by adsorbing trace materials that have low water solubilities. Because most of these chemicals do not dissolve easily in water, they will adsorb to carbon at high rates. Granular activated carbon (GAC) removes VOCs that adsorb to carbon because the VOCs are carbon-based; the lower the solubility of the VOC in water, the higher the rate of adsorption will be. Therefore, water solubility is used to predict which chemicals will adsorb well to GAC.

Treatment Criteria for BADCT Standard

The literature on Henry's Law Constants and strippability lists a range of values from 0.001 to 0.01 atm-m3/mole as the lower limit for air stripping. The consensus of published reports is that MTBE, with a Henry's Law Constant of 5.8 E-04, does not respond well to air stripping. Air stripping columns appear to be able to remove 1,2-dichloroethane, with a constant of 9.8E-04. Chloroform, with a value of 3.7E-03 atm-m3/mole appears to be effectively removable by air stripping. Likewise, the BTEX compounds, with Henry's Law constants ranging from 5.5E-03 to 7.9E-03 are readily removed by air stripping. Thus 1E-03 (0.001) atm-m3/mole appears to be a safe threshold value for efficient air stripping.

Organic chemicals with high water solubilities will adsorb to carbon, but at a much lower rate than less soluble chemicals. These more soluble chemicals cannot be expected to meet the BADCT standard because of this. The literature indicates that chloroform and methylene chloride, with solubilities of 7,920 and 13,000 mg/l, respectively, are both difficult to remove using granular activated carbon. Thus, the upper limit of water solubility for GAC removal is approximately 8,000 mg/l. Note that the solubility of a volatile organic compound varies inversely with the organic partition coefficient, Koc, which measures the chemical's affinity for carbon. Figure 1 shows the relationship between those two values for some common VOCs. While we could express the threshold for effective carbon sorption in terms of a minimum Koc, the solubility limit may be a better measure because that data is more readily available and generally more precisely measured.

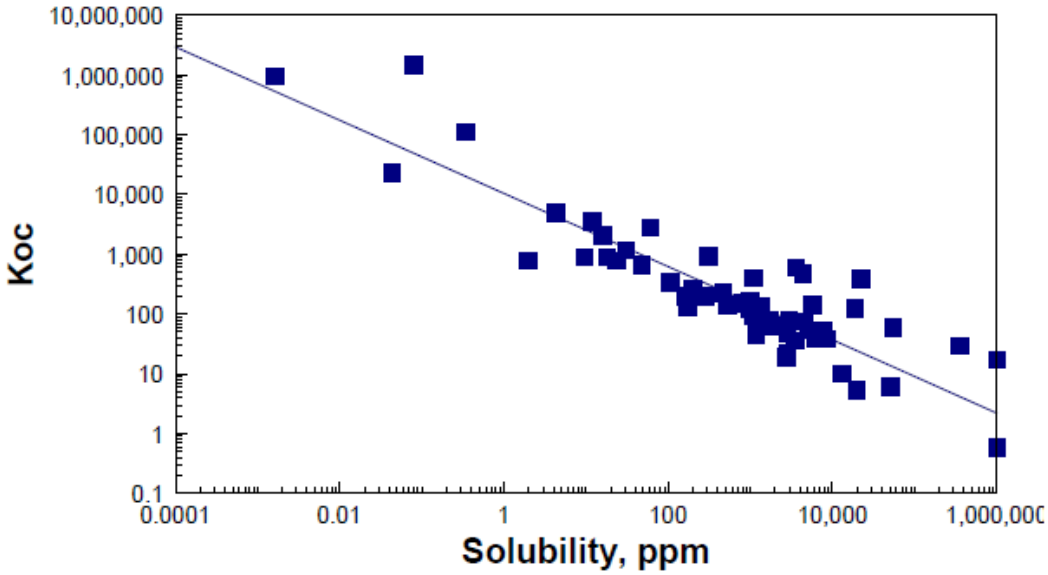

Figure 1. Relationship between aqueous solubility and organic partitioning coefficient for VOCs.

Evaluation of Chemicals

Approximately 80 chemicals were evaluated for inclusion in this guidance. In addition to the physical/chemical parameters listed above, the analytical quantification level (QL) for each

chemical was also reviewed to make sure that the QL was, or was likely to be, less than or equal to 5 ug/l. The QLs used were those listed in DSW Limits Below Quantification Level guidance document at www.epa.ohio.gov/dsw/guidance/guidance.aspx. The attached list of chemicals are those evaluated that meet the three criteria:

1. Henry's Law Constant > 1E-03, or
2. water solubility < 8,000 mg/l, and
3. analytical QL ≤ 5 ug/l

The chemicals in Table 1 are not a complete list of VOCs. These are the chemicals initially evaluated by DSW and DERR. Any chemical that meets one of the first two criteria, and meets the third criterion is covered by this BADCT. Those chemicals in Table 1 with shaded Henry's Law Constants are considered to be strippable. Those chemicals with shaded water solubility values will be sufficiently adsorbed to activated carbon to meet this limit.

Limits in NPDES permits and discharge authorizations under CERCLA records of decision need to contain 30-day limits of 5 ug/l for any chemical subject to the antidegradation rule. Maximum limits of 10 ug/l are typically also included in these documents.

Xylenes represent a special case. The three xylene isomers (o-xylene, m-xylene, p-xylene) are not always able to be separated by USEPA-approved analytical methods. If this is the case, limits for total xylene of 15 ug/l (30-day average) may be used as BADCT. Maximum limits are typically set at 20 ug/l in this case.

For chemicals that meet the treatability criteria but have analytical QLs greater than 5 ug/l, the 30-day limit should be set at the QL, because detections at this level are not expected, given the treatability data. Maximum limits should be based on a measure of the standard analytical error at the QL (3 standard deviations above the QL). To determine these values, consult the DSW QL Guidance Document, USEPA analytical methods [40 CFR 136 or SW-846, as appropriate], or quality assurance documents and information from Ohio EPA Division of Environmental Services.

Chemicals not listed in Table 1 that meet the treatability criterion for water solubility, but not for Henry's Law Constant are not considered VOCs. These chemicals are treatable by carbon adsorption but may or may not be treatable to the BADCT level defined for VOCs. To develop treatment technology limits for these chemicals using Best Professional Judgment, the following sources should be consulted:

- Treatability information from DERR's remedial response program database
- Wastewater treatability information published by U.S. EPA (available in CO-DSW)
- New source performance standards for the Organic Chemicals, Plastics and Synthetic Fibers Industry [40 CFR Part 414].

Chemicals that do not meet either treatability criterion must be considered case-by-case. Water soluble organic chemicals that are not strippable must generally be treated using a biological process, either standard biological treatment processes, or specialized biological treatment towers or columns. NPDES limits will be based on Permit-to-Install information on treatability (or similar information for CERCLA sites), Ohio water quality criteria, and projections of CBOD

concentrations and their potential impacts on the receiving water.

For More Information, Contact:

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Table 1. Chemicals Specifically Considered VOCs Under OAC 3745-1-05(A)(3)(f)

Shaded values in the Henry's Law column are those chemicals that can be air-stripped from water. Shaded values in the water solubility column are those that are amenable to carbon adsorption. All values are from DERR's database of chemical constants.

CAS #	Chemical	Henry's Law Constant (atm-m3/mole)	Water Solubility at 25C (mg/l)
000071-43-2	Benzene	5.55E-03	1790
000108-86-1	Bromobenzene	2.08E-03	410
000074-97-5	Bromochloromethane	1.46E-03	16700
000075-27-5	Bromodichloromethane	2.12E-03	1290
000075-25-2	Bromoform	5.35E-04	3100
000074-83-9	Bromomethane (Methyl bromide)	6.24E-03	15200
000104-51-8	n-Butylbenzene	1.59E-02	11.8
000135-98-8	sec-Butylbenzene	1.76E-02	17.6
000098-06-6	tert-Butylbenzene	1.32E-02	29.5
000075-15-0	Carbon Disulfide	1.44E-02	1190
000056-23-5	Carbon Tetrachloride	2.76E-02	793
000108-90-7	Chlorobenzene	3.77E-03	498
000075-00-3	Chloroethane	1.11E-02	5680
000067-66-3	Chloroform	3.67E-02	7950
000108-60-1	bis-2-Chloroisopropylether	1.30E-04	1700
000074-87-3	Chloromethane (Methyl chloride)	8.82E-03	5320
000095-49-8	2-Chlorotoluene	3.57E-03	347
000106-43-4	4-Chlorotoluene	4.38E-03	1.06
000124-48-1	Dibromochloromethane	7.83E-04	2700
000096-12-8	1,2-Dibromo-3-chloropropane	1.47E-04	1230

000106-43-4	1,2-Dibromoethane	6.67E-04	4150
000095-50-1	1,2-Dichlorobenzene	1.90E-03	156
000541-73-1	1,3-Dichlorobenzene	2.63E-03	125
000106-46-7	1.4-Dichlorobenzene	2.40E-03	76
000075-71-8	Dichlorodifluoromethane	3.43E-01	280
000075-34-3	1,1-Dichloroethane	5.62E-03	5060
000107-06-2	1,2-Dichloroethane	1.18E-03	8520
000075-35-4	1,1-Dichloroethylene	2.61E-02	2250
000156-59-2	cis-1,2-Dichloroethyene	4.08E-03	3500
000156-60-5	trans-1,2-Dichloroethylene	9.38E-03	6300
000078-87-5	1,2-Dichloropropane	2.82E-03	2800
000142-28-9	1,3-Dichloropropane	1.82E-01	2750
000563-58-6	1,1-Dichloropropene	5.00E-02	749
000542-75-6	trans-1,3-Dichloropropene	3.55E-03	2800
000100-41-4	Ethylbenzene	7.88E-03	169
000087-68-3	Hexachlorobutadiene	1.03E-02	3.2
000067-72-1	Hexachloroethane	3.89E-03	7.7
000110-54-3	n-Hexane	1.81E+00	10
000098-82-8	Isopropylbenzene (Cumene)	1.15E-02	61.3
000099-87-6	4-Isopropyltoluene (Cymene)	1.10E-02	23.4
000075-09-2	Methylene Chloride	3.25E-03	13000
000076-01-7	Pentachloroethane	1.94E-03	480
000103-65-1	n-Propylbenzene	1.05E-02	52.2
000100-42-5	Styrene	2.75E-03	310
000630-20-6	1,1,1,2-Tetrachloroethane	2.42E-03	1100
000079-34-5	1,1,2,2-Tetrachloroethane	3.67E-04	2960
000127-18-4	Tetrachloroethylene	1.77E-02	200
000108-88-3	Toluene	6.64E-03	526
000087-61-6	1,2,3-Trichlorobenzene	1.25E-03	18
000120-82-1	1,2,4-Trichlorobenzene	1.42E-03	49
000071-55-6	1,1,1-Trichloroethane	1.72E-02	1500
000079-00-5	1,1,2-Trichloroethane	8.24E-04	4420
000079-01-6	Trichloroethylene	9.85E-03	1100
000075-69-4	Trichlorofluoromethane	9.70E-02	1100
000096-18-4	1,2,3-Trichloropropane	3.43E-04	1750
000095-63-6	1,2,4-Trimethylbenzene	6.16E-03	57
000108-67-8	1,3,5-Trimethylbenzene	8.77E-03	48.2
000075-01-4	Vinyl chloride	2.78E-02	8800
00095-47-6	o-Xylene	5.18E-03	1780
000108-38-3	m-Xylene	7.18E-03	1610
000106-42-3	p-Xylene	7.53E-03	1620

Table 2. Chemicals Reviewed in Developing this Guidance Document

Shaded values in the Henry's Law column are those chemicals that can be air-stripped from water. Shaded values in the water solubility column are those that are amenable to carbon adsorption. All values are from DERR's database of chemical constants.

Chemical	Henry's Law Constant (atm-m3/mole)	Water Solubility at 25C (mg/l)
Acetone	3.97E-05	1000000
Acetonitrile	3.45E-05	1000000
Acrylonitrile	1.38E-04	74500
Aniline	1.90E-05	36000
Benzene	5.55E-03	1790
Biphenyl	4.08E-04	6.94
Bromobenzene	2.08E-03	410
Bromochloromethane	1.46E-03	16700
Bromodichloromethane	2.12E-03	1290
Bromoform	5.35E-04	3100
Bromoethane	6.24E-03	15200
2-Butanone (MEK)	5.69E-05	223000
n-Butylbenzene	1.59E-02	11.8
sec-Butylbenzene	1.76E-02	17.6
tert-Butylbenzene	1.32E-02	29.5
Carbon Disulfide	1.44E-02	1190
Carbon Tetrachloride	2.76E-02	793
Chlorobenzene	3.77E-03	498
Chloroethane	1.11E-02	5680
Chloroform	3.67E-02	7950
bis-2-Chloroisopropylether	1.30E-04	1700
Chloromethane	8.82E-03	5320
2-Chlorotoluene	3.57E-03	347
4-Chlorotoluene	4.38E-03	1.06
Dibromochloromethane	7.83E-04	2700
1,2-Dibromo-3-chloropropane	1.47E-04	1230
Dibromomethane	8.22E-04	11900
1,2-Dibromoethane	6.67E-04	4150
1,2-Dichlorobenzene	1.90E-03	156
1,3-Dichlorobenzene	2.63E-03	125
1.4-Dichlorobenzene	2.40E-03	76
Dichlorodifluoromethane	3.43E-01	280

Chemical	Henry's Law Constant (atm-m3/mole)	Water Solubility at 25C (mg/l)
1,1-Dichloroethane	5.62E-03	5060
1,2-Dichloroethane	1.18E-03	8520
1,1-Dichloroethylene	2.61E-02	2250
cis-1,2-Dichloroethyene	4.08E-03	3500
trans-1,2-Dichloroethylene	9.38E-03	6300
1,2-Dichloropropane	2.82E-03	2800
1,3-Dichloropropane	1.82E-01	2750
1,1-Dichloropropene	5.00E-02	749
1,3-Dichloropropene	3.55E-03	2800
1,3-Dinitrobenzene	3.74E-07	533
2,3-Dinitrotoluene	9.26E-08	220
2,4-Dinitrotoluene	1.30E-07	270
2,5-Dinitrotoluene	9.26E-08	220
2,6-Dinitrotoluene	7.47E-07	182
1,4-Dioxane	4.80E-06	1000000
Ethylene glycol	6.00E-08	1000000
Ethylbenzene	7.88E-03	169
Hexachlorobutadiene	1.03E-02	3.2
Hexachloroethane	3.89E-03	7.7
n-Hexane	1.81E+00	10
2-Hexanone	8.74E-07	1750
Isobutyl Alcohol	9.78E-06	55000
Isopropylbenzene (Cumene)	1.15E-02	61.3
4-Isopropyltoluene	1.10E-02	23.4
Methyl tert-butyl Ether (MTBE)	5.87E-04	51000
Methylene Chloride	3.25E-03	13000
Naphthalene	4.83E-04	3.1
Nitrobenzene	2.40E-05	2090
Nitroglycerine	4.33E-08	1380
Pentachloroethane	1.94E-03	480
n-Propylbenzene	1.05E-02	52.2
Styrene	2.75E-03	310
1,1,1,2-Tetrachloroethane	2.42E-03	1100
1,1,2,2-Tetrachloroethane	3.67E-04	2960
Tetrachloroethylene	1.77E-02	200
Tetrahydrofuran	7.05E-05	1000000
Toluene	6.64E-03	526
1,2,3-Trichlorobenzene	1.25E-03	18
1,2,4-Trichlorobenzene	1.42E-03	49
1,1,1-Trichloroethane	1.72E-02	1500

Chemical	Henry's Law Constant (atm-m3/mole)	Water Solubility at 25C (mg/l)
1,1,2-Trichloroethane	8.24E-04	4420
Trichloroethylene	9.85E-03	1100
Trichlorofluoromethane	9.70E-02	1100
1,2,3-Trichloropropane	3.43E-04	1750
1,2,4-Trimethylbenzene	6.16E-03	57
1,3,5-Trimethylbenzene	8.77E-03	48.2
Vinyl acetate	5.11E-04	20000
Vinyl chloride	2.78E-02	8800
o-Xylene	5.18E-03	1780
m-Xylene	7.18E-03	1610
p-Xylene	7.53E-03	1620