

**COMMONWEALTH OF PENNSYLVANIA
PA DEPARTMENT OF ENVIRONMENTAL PROTECTION
BUREAU OF CLEAN WATER**

**RATIONALE FOR THE DEVELOPMENT OF AMBIENT WATER
QUALITY CRITERIA FOR PROTECTION OF HUMAN HEALTH**

**Acetone, Barium, Boron, Chloroform, Formaldehyde, Methyl ethyl
ketone, Metolachlor, Resorcinol, 1,2,3-trichloropropane, 1,2,4-
trimethylbenzene, 1,3,5-Trimethylbenzene, Chlorophenoxy herbicide
(2,4-D), and Xylene**

February 2022

Executive Summary

Section 303 of the federal Clean Water Act (CWA) requires states to periodically, but at least once every three years, review and revise as necessary their water quality standards. The CWA directs states to adopt criteria for toxic pollutants “the presence of which in the affected waters could reasonably be expected to interfere with a state’s designated uses.” 33 U.S.C. § 303(c)(2)(B).

In 2015, the U.S. Environmental Protection Agency (USEPA) published updated human health criteria exposure inputs, which included increased values for body weight (from 70 kg to 80 kg), drinking water intake (from 2 liters to 2.4 liters), and fish intake (from 17.5 g/day to 22.0 g/day). The Pennsylvania Department of Environmental Protection (Department) adopted these updated criteria exposure inputs in its 9th triennial review of water quality standards (WQS). These updates have prompted the Department to evaluate its agency-derived human health toxics criteria contained in 25 Pa. Code Chapter 93 (relating to water quality standards). The Department reviewed all 18 agency-derived human health toxics criteria and is recommending updated human health criteria for the following 11 toxics substances: acetone, barium, boron, formaldehyde, methyl ethyl ketone, metolachlor, resorcinol, 1,2,3-trichloropropane, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, and xylene. The Department is also recommending updated human health criteria for chloroform and chlorophenoxy herbicide (commonly known as 2,4-D) based on the current USEPA Section 304(a) water quality criteria recommendations for these substances.

The federal water quality standards regulation at 40 CFR 131.11(b)(1) requires states to adopt numeric water quality criteria that are based on section 304(a) criteria recommendations developed by the United States Environmental Protection Agency (USEPA), section 304(a) criteria recommendations modified to reflect site-specific conditions, or other scientifically-defensible methods.

Updated Exposure Inputs

The Department incorporated the USEPA's 2015 recommendations for body weight, drinking water intake, and fish consumption into the Commonwealth's water quality standards during its 9th triennial review. In 2015, USEPA also updated the methodology used to determine the bioaccumulation in fish, in addition to other toxicity factors (reference dose and cancer slope factors). Below is a summary of the USEPA recommendations.

Body Weight

The default body weight has been increased to 80 kilograms (176 pounds). This is the mean body weight for adults ages 21 and older. The new weight is based on data from the Centers for Disease Control and Prevention's National Health and Nutrition Examination Survey (NHANES), from 1999 to 2006. The previous default body weight was 70 kilograms (154 pounds) and was based on NHANES data from 1988 to 1994.

Drinking Water

The default drinking water intake assumption is increased to 2.4 liters per day (81.2 fl. oz./day). This is based on NHANES data collected from 2003 to 2006 for the 90th percentile of water consumption in adults ages 21 and older. The water intake rate is based on consumer-only estimates of direct and indirect water ingestion. The previous recommended default drinking water intake rate was 2 liters per day. The data used was from adults surveyed in the United States Department of Agriculture, 1994-1996 Continuing Survey of Food Intake by Individuals (CSFII) and the National Cancer Institute study of the 1977-1978 Nationwide Food Consumption Survey.

Fish Consumption

The recommended default fish consumption rate has been increased to 22 grams per day (0.78 oz./day). This rate represents the consumption of freshwater and shellfish from inland and near shore waters for adults 21 years of age and older, based on NHANES data from 2003 to 2010. The previous fish consumption rate was 17.5 grams per day based on the consumption rate of freshwater and estuarine fish for the adult population from 1994-1996 CSFII data.

Bioaccumulation Factors

The criteria have been updated using bioaccumulation factors (BAFs) as recommended in the USEPA human health criteria methodology (USEPA 2000). BAFs will account for the uptake and retention of a chemical by an aquatic organism from all surrounding

media (e.g., water, food, sediment). Criteria were previously calculated with bioconcentration factors (BCFs) that only accounted for direct water contact. In order to account for the variation in bioaccumulation due to the aquatic trophic position of an organism, USEPA is recommending that BAFs be determined and applied to three trophic levels of fish. USEPA used field-measured BAF's and laboratory-measured bioconcentration factors, along with octanol-water partition coefficients available from peer-reviewed databases to develop the national BAFs. USEPA verified the calculated BAFs using a peer-reviewed model called Estimation Program Interface Suite (EPI Suite).

Health Risk Factors

USEPA has updated the health risk factors using the most current toxicity information. The toxicity values for both non-carcinogenic and carcinogenic effects were used. USEPA's *Integrated Risk Information System* (IRIS) is the primary source for reference dose (RfD) and cancer slope values. For some pollutants, USEPA has used other sources provided by USEPA's Office of Water, Office of Pesticide Programs, and international and state agencies.

Relative Source Contribution

USEPA has updated the Relative Source Contribution (RSC) to reflect chemical-specific exposure. The RSC, which is only applied to threshold non-carcinogens, will range from 20 to 80 percent as recommended in USEPA's human health methodology (USEPA 2000). Unless adequate exposure pathway data is available, USEPA uses an RSC of 20 percent, which assumes that the major portion of total exposure comes from other sources. The RSC protects against particular pollutant exposures from other foods, marine fish consumption, dermal exposure, and respiratory exposures. The use of the RSC is to ensure that an individual's total exposure from all sources of a pollutant does not exceed the criteria.

Criteria Development

Criteria for the protection of Human Health from Toxic Substances

The Department develops human health-based criteria in accordance with its Water Quality Toxics Management Strategy – Statement of Policy. Human health criteria development considers various exposure pathways including exposures from drinking water and fish consumption and may include exposures from inhalation or dermal absorption.

Evaluation of Available Recommendations and Scientific Data

The Department has reviewed and considered the available scientific data and recommendations in accordance with 25 Pa. Code Chapter 16 (relating to water quality toxics management strategy – statement of policy) and Chapter 93. Human health criteria are based on one of two approaches – either threshold level or non-threshold level toxic effects (carcinogens). When no criteria have been developed by USEPA for a

substance identified or expected in a discharge, the Department will develop criteria following USEPA's standard toxicological procedures outlined in the *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (USEPA 2000) as amended and updated (25 Pa. Code §16.32(c)(2)). As further stated in §16.32(d), the sources the Department uses to obtain relevant risk assessment values for protection for threshold level toxic effects to human health as are follows:

- (1) Verified references doses, listed in the EPA agency-wide supported data system known as IRIS and other EPA approved data sources referred through IRIS
- (2) Maximum Contaminant Level Goals (MCLGs)
- (3) The EPA's CWA § 304(a) health criteria listed under the National Toxics Rule in 40 CFR 131.36 (57 FR 80848, December 22, 1992) (relating to toxics criteria for those States not complying with CWA section 303(c)(2)(B)), as amended and updated and other final criteria published by the EPA and the Great Lakes Initiative Clearinghouse.
- (4) Teratology and other data that have been peer-reviewed may provide information for criteria development.

In accordance with this policy, the Department has evaluated its human health toxics criteria for acetone, acrylamide, benzyl chloride, barium, 2-butoxyethanol, boron, chloroform, cyclohexylamine, formaldehyde, methyl ethyl ketone, metolachlor, resorcinol, strontium, 1,2,3-trichloropropane, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 2,4-D and xylene.

Development of Human Health Criteria

In accordance with the USEPA *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (USEPA 2000) and using the updated exposure input values for body weight, drinking water intake, and fish consumption, the Department derived human health criteria for the toxic substances described above using the following calculation:

$$AWQC = RfD \times RSC \times (BW \div [DWI + (FI \times BAF)])$$

Where:

AWQC = ambient water quality criteria

RfD = published reference dose for each substance

RSC = Relative Source Contribution, default (0.2)

BW = Body Weight, default (80 kg)

DWI = Drinking Water Intake, default (2.4 L)

FI = Fish consumption rate for aquatic trophic levels 2, 3 and 4, default (0.022 kg/day)

BAF = Bioaccumulation factor for aquatic trophic levels 2, 3, and 4, default (1, if substance does not bioaccumulate)

Comparisons of DEP Current and Updated Agency-Derived Human Health Criteria

Of the 18 toxic substances evaluated, 13 substances warrant a change in current water quality criteria listed in 25 Pa. Code Chapter 93, Table 5. The origins and applications of the current water quality criterion as well as the criteria recommendations for each of these 13 toxic substances is described in the tables and summaries below.

Table 1. More Stringent Criteria

| | Pollutant | CAS No. | DEP Current (ug/L) | DEP Recommended (ug/L) |
|---|------------------------|----------------|---------------------------|-------------------------------|
| 1 | Barium | 07440393 | 2400 | 1000 |
| 2 | Boron | 07440428 | 3100 | 1000 |
| 3 | Methyl ethyl ketone | 00078933 | 21000 | 4000 |
| 4 | 1,2,3-trichloropropane | 00096184 | 210 | 30 |
| 5 | 1,2,4-trimethylbenzene | 00095636 | 72 | 10 |
| 6 | 1,3,5-trimethylbenzene | 00108678 | 72 | 10 |
| 7 | 2,4-D | 00094757 | 1400 | 1300 |
| 8 | Xylene | 01330207 | 70000 | 1000 |

Of the 18 toxic substances evaluated by the Department, eight substances will have a more stringent criterion than previously listed in 25 Pa. Code Chapter 93, Table 5.

1) Barium

The current barium criterion is 2,400 ug/L and was adopted/updated in the Department's 5th triennial review of WQS (2000).

There are currently 51 Bureau of Clean Water (BCW) National Pollutant Discharge Elimination System (NPDES) permits with effluent limitations for barium. Of these 51 permits, 39 facilities have reported results through the Department's Electronic Discharge Monitoring Report (eDMR) system. Most of the permits contain only monitor and report requirements and have had no violations since 2018.

Staff analyzed Department-collected surface water sample data for barium. Data was retrieved from the Water Quality Portal, which is sponsored by the United States Geological Survey (USGS), USEPA and the National Water Quality Monitoring Council (NWQMC). A total of 19,794 samples were collected between 1998-2020. Sample results ranged from below a lower reporting limit of 2 ug/L to 2,410 ug/L.

Staff recalculated the criterion using the USEPA IRIS RfD of 0.2 mg/kg/day (2005), an RSC of 0.2, a BAF of 1, and the new exposure inputs. The new value is 1,321 ug/L before rounding. After accounting for significant figures, the criterion value is rounded to 1,000 ug/L.

2) Boron

The current boron criterion is 3,100 ug/L and was adopted/updated in the Department's 5th triennial review of WQS (2000).

There are currently 43 BCW NPDES permits with effluent limitations for boron. Of these 43 permits, 30 facilities have reported results through the Department's eDMR system. Most of the permits contain only monitor and report requirements and have had no violations since 2018. One permit with numeric limits (PA0046680) has had violations.

Staff analyzed Department-collected surface water sample data for boron. Data was retrieved from the Water Quality Portal, which is sponsored by the USGS, USEPA and NWQMC. A total of 15,949 samples were collected between 2010-2020. Sample results ranged from below a lower reporting limit of 13.2 ug/L to 1,345 ug/L.

This criterion was based on a 1989 RfD (0.09 mg/kg/day) and old methodologies that did not include fish intake, a BAF or an RSC. Staff recalculated the criterion using the current USEPA IRIS RfD of 0.2 mg/kg/day (2004), an RSC of 0.2, a BAF of 1, and the new exposure inputs. The new value is 1321 ug/L before rounding. After accounting for significant figures, the criterion value is rounded to 1,000 ug/L.

3) Methyl ethyl ketone

The current methyl ethyl ketone criterion is 21,000 ug/L and was adopted/updated in the Department's 5th triennial review of WQS (2000).

Currently, there is one BCW NPDES permit with an effluent limitation for this pollutant. There is no eDMR system data on this permit.

Staff analyzed Department-collected surface water sample data for methyl ethyl ketone. Data was retrieved from the Water Quality Portal, which is sponsored by the USGS, USEPA and NWQMC. A total of 61 samples were collected between 1999-2009. Sample results ranged from 2.1 ug/L to 5 ug/L.

Staff recalculated the criterion using the USEPA IRIS RfD of 0.6 mg/kg/day (2003), an RSC of 0.2, a BAF of 1, and the new exposure inputs. The new value is 3,964 ug/L before rounding. After accounting for significant figures, the criterion value is rounded to 4,000 ug/L.

4) 1,2,3-trichloropropane

The current 1,2,3-trichloropropane criterion is 210 ug/L and was adopted/updated in the Department's 5th triennial review of WQS (2000).

There are currently two BCW NPDES permits with effluent limitations for this pollutant. Both permits contain numeric limits and have had no violations since 2018.

Staff analyzed Department-collected surface water sample data for 1,2,3-trichloropropane. Data was retrieved from the Water Quality Portal, which is sponsored by the USGS, USEPA and NWQMC. A total of 72 samples were collected between 1999-2015. Sample results ranged from below a lower reporting limit of 0.25 ug/L to 2 ug/L.

Staff recalculated the criterion using the USEPA IRIS RfD of 0.004 (2009), an RSC of 0.2, a BAF of 1, and the new exposure inputs. The new value is 26 ug/L before rounding. After accounting for significant figures, the criterion value is rounded to 30 ug/L.

5) 1,2,4-trimethylbenzene

The current 1,2,4-trimethylbenzene criterion is 72 ug/L and was adopted/updated in the Department's 8th triennial review of WQS (2013).

There are currently two BCW NPDES permits with effluent limitations for this pollutant. Both permits contain monitor and report requirements.

Staff analyzed Department-collected surface water sample data for 1,2,4-trimethylbenzene. Data was retrieved from the Water Quality Portal, which is sponsored by the USGS, USEPA and NWQMC. A total of 72 samples were collected between 1999-2015. Sample results ranged from below a lower reporting limit of 0.21 ug/L to 2 ug/L.

Staff recalculated the criterion using the USEPA IRIS RfD of 0.01 (2016), an RSC of 0.2, a BAF of 439 (BCF from USEPA 1994), and the new exposure inputs. The new value is 13.2 ug/L before rounding. After accounting for significant figures, the criterion value is rounded to 10 ug/L.

6) 1,3,5-trimethylbenzene

The current 1,3,5-trimethylbenzene criterion is 72 ug/L and was adopted/updated in the Department's 8th triennial review of WQS (2013).

There are currently two BCW NPDES permits with effluent limitations for this pollutant. Both permits contain monitor and report requirements.

Staff analyzed Department-collected surface water sample data for 1,3,5-trimethylbenzene. Data was retrieved from the Water Quality Portal, which is sponsored by the USGS, USEPA and NWQMC. A total of 72 samples were collected between 1999-2015. Sample results ranged from below a lower reporting limit of 0.25 ug/L to 2 ug/L.

Staff recalculated the criterion using the USEPA IRIS RfD of 0.01 (2016), an RSC of 0.2, a BAF of 439 (BCF from USEPA 1994), and the new exposure inputs. The new value is 13.2 ug/L before rounding. After accounting for significant figures, the criterion value is rounded to 10 ug/L.

7) Chlorophenoxy herbicide (2,4-D)

The current 2,4-D criterion is 1400 ug/L and was adopted in the Department's 9th triennial review of WQS. USEPA disapproved this criterion due to the rounding of the value. The calculated criterion before rounding was 1371 ug/L. USEPA chose to round the criterion to 1300 ug/L rather than 1400 ug/L. The current criterion is less stringent than USEPA's 304(a) recommendation. Therefore, the criterion value of 1300 ug/L is being recommended to be consistent with USEPA.

The Department has not collected surface water quality data for this parameter, and there no NPDES permits with limits for 2,4-D.

8) Xylene

The current xylene criterion is 70,000 ug/L and was adopted/updated in the Department's 5th triennial review of WQS (2000).

There are currently 55 BCW NPDES permits with effluent limitations for xylene. Of these 55 permits, 16 facilities have reported results through the Department's eDMR system. All of the permits except one contain monitor and report requirements and have had no violations since 2018. The one permit with numeric limits has reported some minor exceedances.

Data was retrieved from the Water Quality Portal, which is sponsored by the USGS, USEPA and NWQMC. While the Department has not collected surface water quality data for this parameter, samples have been collected by USGS and the Delaware River Basin Commission (DRBC). A total of 335 samples were collected between 1988-2021. Sample results ranged from 0.1 ug/L to 5.2 ug/L, but most results were less than the method detection limit. Method detection limits ranged from 0.06 ug/L to 3 ug/L.

Staff recalculated the criterion using the USEPA IRIS RfD of 0.2 (2003), an RSC of 0.2, a BAF of 1, and the new exposure inputs. The new value is 1,321 ug/L before rounding. After accounting for significant figures, the criterion value is rounded to 1,000 ug/L.

Table 2. Less Stringent Criteria

| | Pollutant | CAS No. | DEP Current (ug/L) | DEP Recommended (ug/L) |
|---|------------------|----------------|---------------------------|-------------------------------|
| 1 | Acetone | 00067641 | 3500 | 6000 |
| 2 | Formaldehyde | 00050000 | 700 | 1000 |
| 3 | Metolachlor | 51218452 | 69 | 700 |
| 4 | Resorcinol | 01084603 | 2700 | 3000 |
| 5 | Chloroform | 00067663 | 5.7 | 60 |

The Department has recalculated the toxicity of the following five toxic substances which will result in a less stringent criterion than currently listed in 25 Pa. Code Chapter 93, Table 5.

9) Acetone

The current acetone criterion is 3,500 ug/L and was adopted/updated in the Department's 5th triennial review of WQS (2000).

There are currently 17 BCW NPDES permits with effluent limitations for acetone. Of these 17 permits, nine facilities have reported results through the Department's eDMR system. Most of the permits contain numeric limits and have had no violations since 2018.

Staff analyzed Department-collected available surface water sample data for acetone. Data was retrieved from the Water Quality Portal, which is sponsored by the USGS, USEPA and NWQMC. A total of 71 samples were collected between 1999-2010. The majority of samples were collected from Delaware River basin tributaries. Sample results ranged from 1.2 ug/L to 65.8 ug/L.

Staff recalculated the criterion using the current USEPA IRIS RfD of 0.9 mg/kg/day (2003), an RSC of 0.2, a BAF of 1, and the new exposure inputs. The new criterion value is 5,945 ug/L before rounding. After accounting for significant figures, the criterion value is rounded to 6,000 ug/L.

10) Formaldehyde

The current formaldehyde criterion is 700 ug/L and was adopted/updated in the Department's 5th triennial review of WQS (2000).

Currently, there are 10 BCW NPDES permits with an effluent limitation for this pollutant. Most, if not all, of the permits are for fish hatcheries. Of these ten permits, nine facilities have reported results through the Department's eDMR system. Most of the permits contain numeric limits and have had no violations since 2018.

The Department has not collected surface water quality data for this parameter.

Staff recalculated the criterion using the USEPA IRIS RfD of 0.2 mg/kg/day (1990), an RSC of 0.2, a BAF of 1, and the new exposure inputs. The new value is 1,321 ug/L before rounding. After accounting for significant figures, the criterion value is rounded to 1,000 ug/L.

11) Metolachlor

The current metolachlor criterion is 69 ug/L and was adopted/updated in the Department's 7th triennial review of WQS (2008).

Currently, there are no BCW NPDES permits with an effluent limitation for this pollutant.

The Department has not collected surface water quality data for this parameter.

The RfD used in the criterion calculation did not come from USEPA's IRIS. It was based on newer information contained in a USEPA Registration Eligibility Decision (RED) document for metolachlor (USEPA 1995). According to the RED document, a cancer potency factor was recommended in 1991 but later retracted in 1994. The Department included a safety factor of 10 due to the lack of a cancer potency factor in development of the 69 ug/L criterion. The RfD of 0.10 mg/kg/day was based on a No Observed Effect Level (NOEL) of 9.7 mg/kg/day and an uncertainty factor of 100. The NOEL was from a one-year feeding study in dogs.

Staff recalculated the criterion using the RED RfD of 0.10 mg/kg/day, an RSC of 0.2, a BAF of 1, and the new exposure inputs. The Department removed its cancer safety factor of 10 based on the information contained in USEPA's RED for metolachlor. In 1994, the Health Effects Division Peer Review Committee recommended a margin of exposures (MOE) approach for metolachlor since there was no supportable mutagenicity concern and in light of new information on the relative metabolism of metolachlor. The MOE was calculated from a NOEL of 15 mg/kg/day. Since the RfD is based on a NOEL of 9.7 mg/kg/day, cancer concerns are adequately addressed. The new criterion value is 700 ug/L after rounding.

12) Resorcinol

The current resorcinol criterion is 2,700 ug/L and was adopted/updated in the Department's 8th triennial review of WQS (2013).

Currently, there is one BCW permit with an effluent limitation for this pollutant. The permit contains only monitor and report requirements.

DEP has not collected surface water quality data for this parameter.

Staff recalculated the criterion using the previous RfD of 0.4 mg/kg/day, RSC of 0.2, BAF of 3.162 (based on a BCF from INDSPEC Chemical Corp), and the new exposure inputs. The RfD used in the criterion calculation did not come from USEPA's IRIS. It was based on toxicity information from the *Concise International Chemical Assessment Document 71* for resorcinol, which was published by the International Program on Chemical Safety (IPCS). The Rfd was based on a no-observed-adverse-effect-level (NOAEL) from a 1992 National Toxicology Program (NTP) study on rats that was adjusted to convert the 5 day/week exposure regime of the study (50 mg/kg/day for 5 days/week) into a daily exposure value (36 mg/kg/day 7 days/week). The new value is 2,595 ug/L before rounding. After accounting for significant figures, the new value is 3,000 ug/L.

13) Chloroform

The current chloroform criterion of 5.7 ug/L was evaluated by the Department during its 9th triennial review of WQS. During that rulemaking, an error was identified in the proposed criterion value, which was not consistent with USEPA's 304(a) criterion recommendation. The Department removed the criterion recommendation from the 9th triennial review pending additional review and consideration. Following additional review, the Department has determined that USEPA's 304(a) criterion recommendation for chloroform is appropriate for this Commonwealth. A criterion value of 60 ug/L is being recommended to be consistent with USEPA.

Table 3. Criteria that will not change

| | Pollutant | CAS No. | DEP Current (ug/L) | DEP Recommended (ug/L) |
|---|------------------|----------------|-------------------------------|---------------------------------------|
| 1 | Acrylamide | 00079061 | 0.07 | 0.07 |
| 2 | 2-Butoxy ethanol | 00111762 | 700 | 700 |
| 3 | cyclohexylamine | 000108918 | 1000 | 1000 |
| 4 | strontium | 07440246 | 4000 | 4000 |
| 5 | Benzyl Chloride | 000100447 | 0.2 | 0.2 |

There are five toxic substances that had no change in criterion value based upon review of the current RfD recommendations for each substance, recalculation using the updated exposure inputs, and observance of significant figures. Therefore, these five substances do not require any change to the current criteria.

Conclusion

The Department recommends the Board adopt the updated criteria for the 13 toxic substances as described in this rationale document.

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