



Evaluation of the Applicability of PCE WQS and a Proposed Alternative Approach

For Discussion Purposes Only

Objective/Purpose

The following white paper has been developed to facilitate discussion between Georgia's Department of Environmental Protection (GADEP) and Ashland on surface water cleanup standards for the Tara Shopping Center, HSI Site Number 10798 (Site). GADEP has indicated that the proposed remedial approach will need to comply with the GADEP's water quality standard (WQS) and achieve a tetrachloroethylene (PCE) concentration of 3.3 micrograms per liter ($\mu\text{g/l}$) in the drainage ditch that flows into an unnamed tributary to the Flint River.

This white paper examines the PCE standard, its application to the Site, and recent USEPA revisions to the PCE exposure assumptions that directly impact this standard. On the basis of these recent revisions, the document provides discussion of the updated science, an evaluation of site-specific conditions and an alternative for application of the criteria to this site.

Regulatory Basis for Georgia Water Quality Standard for Tetrachloroethylene

Georgia's Department of Environmental Protection's Rule 391-3-6-.01 established the organizational and administrative procedures to be followed in the administration and enforcement of the Georgia Water Quality Control Act to carry out the purposes and requirements of the Act, and of the Federal Water Pollution Control Act Amendments of 1972. The Water Quality Standards Regulation (40 CFR 131) describes the State requirements and procedures for developing, reviewing, revising, and adopting WQS, and the U. S. Environmental Protection Agency (EPA) requirements and procedures for reviewing, approving, disapproving, and promulgating water quality standards as authorized by section 303(c) of the Clean Water Act. Under section 510 of the Act, States must develop water quality standards at least as stringent as required by the Water Quality Standards Regulation. The WQS for PCE of 3.3 $\mu\text{g/l}$ meets this requirement for in stream concentrations as listed by the EPA as toxic priority pollutants pursuant to Section 307(a)(1) of the Federal Clean Water Act that shall not exceed criteria under **annual average or higher stream flow conditions** for protection of human health from consumption of aquatic organisms.

The EPA published the *Ambient Water Quality Criteria for Tetrachloroethylene* in October 1980, based on the available database at that time. The 1980 document presented concentrations of PCE that were protective of freshwater aquatic species in the surface water body, and that were considered safe for human health from ingestion of water and aquatic organisms.

Five different aquatic species were tested in acute and chronic bioassays to derive the AWQC for PCE in the 1980 document. The results of these tests indicated that for freshwater organisms, the rainbow trout is the most sensitive, and the bluegill and fathead minnow are approximately as sensitive as the cladoceran *Daphnia magna*. One other freshwater aquatic species tested, an alga, was more resistant to PCE than the fishes or cladoceran. Estimated and measured bio-concentration factors for the two fish species ranged from 39 for the rainbow trout to 49 for the bluegill. In the bluegill, equilibrium was reached within 21 days, and the depuration rate was rapid with a half-life of less than one day.

The October 1980 document for PCE indicated that acute and chronic toxicity to freshwater aquatic species occurs at concentrations as low as 5,280 micrograms per liter ($\mu\text{g/l}$) and 840 $\mu\text{g/l}$, and would occur at lower concentrations among species that are more sensitive than those tested. In 2009, EPA published a compilation of its national recommended AWQC for 150 constituents. These AWQC are EPA's current recommended Section 304(a) criteria, reflecting the latest scientific knowledge. Notably, PCE currently does not have an AWQC for the protection of aquatic species.

In the October 1980 document, PCE was suspected of being a human carcinogen, and this health effect was the basis for the development of the AWQC for the protection of humans, and concentrations of PCE corresponding to an incremental lifetime cancer risk level of 1×10^{-6} were estimated. Exposure assumption included drinking two liters of water and consuming 6.5 grams of fish and shellfish per day. Concentrations were derived assuming a lifetime exposure to PCE occurring from the consumption of both drinking water and aquatic life inhabiting the water. Approximately nine percent of the PCE exposure was a result of consumption of aquatic organisms with an average bio-concentration factor of 30.6. The remaining 91 percent of PCE exposure was due to drinking water. The bio-concentration factor of 30.6 was a weighted bio-concentration factor based on the edible portion of all freshwater and estuarine aquatic organisms consumed by humans adjusted for the lipid weighted average for all fish and shellfish consumed. Concentrations also were derived assuming a lifetime exposure to PCE occurring from consumption solely of aquatic life inhabiting surface water. The recommended AWQC for consumption of water and aquatic organisms was 0.8 $\mu\text{g/l}$, and if consumption is limited to aquatic organisms only, the AWQC was 8.85 $\mu\text{g/l}$. The November 2002 (EPA 2002) recommended AWQC for consumption of water and aquatic organisms was 0.69 $\mu\text{g/l}$, and if consumption is limited to aquatic organisms only, the AWQC was 3.3 $\mu\text{g/l}$. These changes were based on a revised ingestion rate of 17.5 grams of fish and shellfish per day, and not a revised bio-concentration factor.

The regulations state that application of this criteria is to occur during annual average or high flow conditions. Based on results from the SW sampling, the current sampling has historically been biased towards low flow conditions.

Uptake, Bioaccumulation, and Metabolism of Tetrachloroethylene

The uptake of PCE in fish is dependent on a variety of biological, chemical, and physical factors. Bottom dwelling fish, such as suckers and catfish, have a greater tendency to be exposed to PCE concentrations at the groundwater/surface water transition zone than would fish that occupy the pelagic, or open water, zone. These fish species tend to feed in the bottom sediments, and would be attracted to an upwelling zone, with uptake occurring from ingestion of prey and sediments, and exposure to concentrations in the surface water. Because of the low bioconcentration factor (ratio of concentration of constituent in fish to concentration of constituent in the water body; takes into account uptake by fish from water passing across gills) for PCE, the rapid depuration rate, and a half-life of less than one day (as measured in the bluegill), uptake of PCE is not considered to be significant in a fishery (EPA 1980). Relative to bioaccumulation (ratio of concentration of constituent in fish to concentration of constituent in the water body; takes into account uptake by fish from water, sediments passing across gills, and consumption of food items), the EPA uses a log K_{ow} of 4.0 as the cutoff in determining whether an organic compound will bioaccumulate. Because PCE has a log K_{ow} of less than 4.0, it is not considered an organic compound that will bioaccumulate from concentrations in sediments or food items. The ATSDR (1997) notes that monitoring data on tetrachloroethylene in water and associated aquatic organisms is in agreement with the bioconcentration factors.

When released to surface water, the main removal process for PCE is through volatilization, with the aquatic half-life ranging from hours to days depending on wind and mixing conditions. Therefore, uptake of PCE by fish within a surface water body would be a function of PCE concentrations within the sediment/surface water zone for bottom dwelling fish species, and in the vertical concentration gradients existing to the surface for the pelagic fish species. Because bioaccumulation is insignificant for PCE, the concentration in fish species would

be expected to be independent of the age of the fish, but dependent on the habitat the fish occupies in the surface water body, and the time the fish spent within an area of high PCE concentration in the surface water.

PCE belongs to the chlorinated aliphatics class of chlorinated organic solvents that are gases or volatile liquids that rapidly cross biological membranes and concentrate in fatty tissue Carey et. al. 1998). They are metabolized by two ubiquitous enzyme systems, the cytochrome P450s, principally cytochrome P450III_{E1}, and the glutathione-S-transferases. The chlorinated aliphatics containing double bonds or protons are oxidized to potential reactive electrophiles that are rapidly eliminated following hydrolysis or conjugation with glutathione. Direct conjugation of these molecules with glutathione similarly leads to rapid excretion. The volatility of these solvents also facilitates elimination from biological systems in an unchanged form. As a result of the volatility and rapid metabolism of these chemicals, they do not accumulate or biomagnify in biological systems. PCE is not expected to significantly bioconcentrate in aquatic organisms based on reported and estimated bioconcentration factors (Irwin 1997). Further, the biological half-life of PCE metabolites (as measured as total trichloro-compounds) is 144 hours. The biological half-life for fat stores was 71.5 hours (Irwin 1997).

Application of Water Quality Standards for Tetrachloroethylene

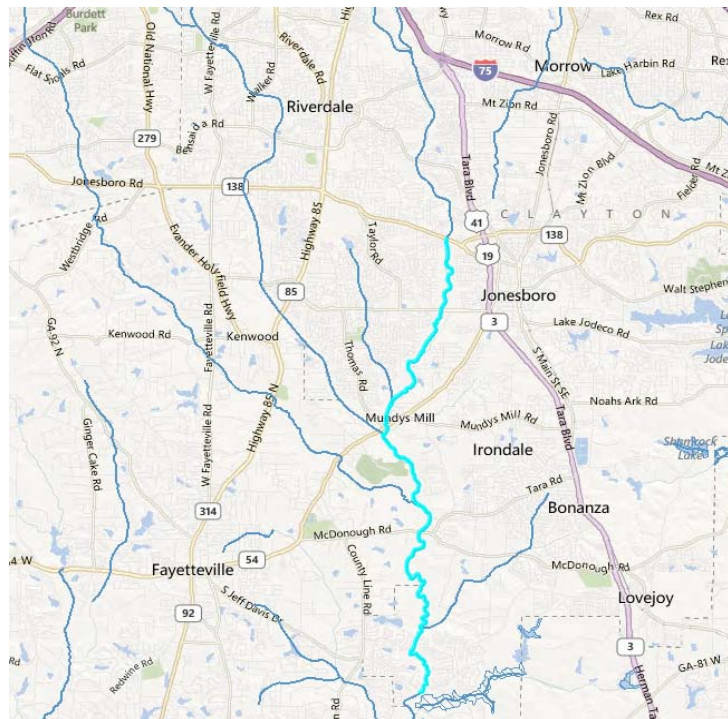
The calculation of the 3.3 µg/l for ingestion of aquatic organisms only was based on the 2000 methodology for calculating human health AWQC (EPA 2000). The specific equations used in the 2000 methodology are provided below.

2000 Methodology Calculations	
<i>Linear Approach</i>	
Using cancer potency, q1*:	Using Reference Dose:
For consumption of water and organisms:	For consumption of water and organisms:
$AWQC [\mu g/L] = \frac{(10^{-6}/q1^*) \bullet 70 \text{ kg} \bullet 1000 \mu g/mg}{(2 \text{ L/d} + (0.0175 \text{ kg/d} \bullet BCF [L/kg]))}$	$AWQC [\mu g/L] = [RfD [mg/kg-d] \bullet RSC \bullet (70 \text{ kg/} 2 \text{ L/d} + (0.0175 \text{ kg/d} \bullet BCF [L/kg]))] \bullet 1000 \mu g/mg \text{ or } (- RSC)$
For consumption of organisms only:	For consumption of organisms only:
$AWQC [\mu g/L] = \frac{(10^{-6}/q1^*) \bullet 70 \text{ kg} \bullet 1000 \mu g/mg}{0.0175 \text{ kg/d} \bullet BCF [L/kg]}$	$AWQC [\mu g/L] = [RfD [mg/kg-d] \bullet RSC \bullet (70 \text{ kg/} (0.0175 \text{ kg/d} \bullet BCF [L/kg]))] \bullet 1000 \mu g/mg \text{ or } (- RSC)$
<i>Nonlinear Approach</i> (Presented for information only- no criteria in matrix based on nonlinear approach currently)	
For consumption of water and organisms:	
$AWQC [\mu g/L] = POD/UF \bullet RSC \bullet (BW/DI + (FI \bullet BCF))$	
For consumption of organisms only:	
$AWQC [\mu g/L] = POD/UF \bullet RSC \bullet (BW/(FI \bullet BCF))$	
AWQC = Ambient water quality criteria = national recommended water quality criteria q1* = Cancer potency factor kg-d/mg or per mg/kg-day RSD = Risk specific dose $10^{-6}/q1^*$ mg/kg-day RfD = Reference dose mg/kg-d DI = Drinking water intake 2 L/day BW = Human body weight 70 kg FI = Fish intake 0.0175 kg/day BCF = Bioconcentration factor L/kg UF = Uncertainty factor (unitless) RSC = Relative source contribution (percentage of subtraction) POD = Point of departure mg/kg-day	

The cancer potency factor, q1*, of 3.98×10^{-2} per milligrams per kilogram-day (mg/kg-day)⁻¹ used in the 2000 methodology was based on the then current toxicological criteria available in 2000. Since 2000, the EPA has updated the cancer potency factor for PCE (EPA 2012), which currently is 2.1×10^{-3} (mg/kg-day)⁻¹. Using the

current cancer potency factor for PCE, the AWQC for consumption of aquatic organisms would be $62.2 \mu\text{g/l}$. Based on the regulatory procedures established for Georgia WQS, the most appropriate and applicable in stream WQS would be $62.2 \mu\text{g/l}$. Based on the Risk Reduction Standards GADEP Rule 391-3-19-.07, the in stream WQS would be $622 \mu\text{g/l}$ based on an acceptable upper bound estimated excess cancer risk of less than or equal to 1×10^{-5} . The WQS for PCE is based on the consumption of aquatic organisms, and utilizes a fish intake rate of 0.0175 kilograms per day (kg/day). A fish consumption rate of 0.0175 kg/day equals about 0.6 ounces per day or three 6-ounce meals per month, based on a recreational fisherman activity patterns.

Section 305(b) of the Clean Water Act requires States to assess and describe the quality of its waters every two years in a report called the 305(b) report. Section 303(d) of the Clean Water Act requires States to submit a list of all of the waters that are not meeting their designated uses and that need to have a TMDL(s) written for them. The reach of the Flint River that includes Jonesboro evaluated as part of the draft 2012 integrated 305(b) and 303(d) water quality assessment program, Highway 138 to North Hampton Road, is listed as impaired due to fecal coliform and will not supporting designated uses such as fishing. The figure below shows the reach of the Flint River that is designated as not supporting its designated use. Based on the non-support of the designated use of fishing, the assumption that three 6-ounce meals per month would be consumed from the Flint River in the immediate vicinity of the Site is very conservative.



In addition, the receiving stream where the in stream WQS will be applied is characterized as a highly urbanized, low quality stream. In the upper reaches of the system (immediately west of the Site), the surface water is contained within culverts and pipes discharging to an open channel at SS-1. Evidence of high sediment loadings, waste and debris are evident in the stream bed consistent with the highly urbanized nature of the area (EHS Support 2011). On the basis of the stream characteristics, this ecological setting can be considered low quality. The GADEP Rule 391-3-6-.03: Water Use Classifications and Water Quality Standards does allow for a mixing zone that is reasonable and limited, and that will not create a situation that prevents compliance with the applicable WQS. Based on the low quality within the unnamed tributary to Flint River (Stations SS-1 through T-1), there is a very low likelihood of a recreational fisheries that would be subject to human consumption based on quality of habitat and non-support designated use. Therefore, a mixing zone would be applicable that

includes the groundwater and stormwater discharges to the unnamed tributary, and would not result in non-compliance with the PCE in stream WQS.

Summary

The objective of this white paper was to evaluate the applicability of the PCE WQS, and suggest alternatives for compliance with GADEP requirements.

- The current WQS is based on the EPA AWQC that was developed in 2002 for the protection of human health from the ingestion of aquatic organisms based on a carcinogenic endpoint.
- Since 2002, a new cancer potency factor was developed for PCE that would result in an updated in stream WQS of 62.2 µg/l
- The reach of Flint River that contains the Site watershed, Highway 138 to North Hampton Road, is listed as impaired due to fecal coliform and not supporting designated uses of fishing
- The drainage ditch and unnamed tributary receiving surface water from the Site is characterized as a highly urbanized, low quality aquatic ecosystem
- A mixing zone would be applicable to the drainage ditch because of the lack of a viable fisheries habitat , and would not result in non-compliance with the PCE in stream WQS

On the basis of the above conclusions it is recommended that the point of compliance for the promulgated standards should be at the T-1 monitoring point where the storm-water drainage ditch intersects the unnamed tributary that ultimately discharges to the Flint River. Application of the revised WQS (62.2 µg/l) could be implemented between locations SS-1 and SS-2 as a performance criteria for the remedy and intent of both the Clean Water Act and the framework of the Georgia WQS.

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