Interim Recommendations for Designing Treatment for the Removal of 1,4-dioxane - Pilot Testing of Advanced Oxidation Processes (AOP)

This document is intended for use by local health departments (LHD) and New York State Department of Health (Department) engineering staff to provide guidelines for piloting treatment for the removal of organic compounds such as 1,4-Dioxane from a Public Water Supply (PWS).

Contents

I. Policy

Pilot testing of AOP is strongly recommended except when it can be demonstrated to the satisfaction of the Department that piloting is not necessary.

II. Background

Unlike air-stripping or filtration which physically move contaminants from one phase to another, advanced oxidation processes (AOPs) transform contaminants in a single phase (water). The processes are indirect, which means that the oxidizing species (hydroxyl radicals) must first be created. There are a number of ways that AOP treatment technologies may create hydroxyl radicals, including combining different oxidants; combining specific oxidants with ultraviolet (UV) light; combining specific oxidants with specific transition metals; and exposing photocatalysts such as titanium dioxide to UV light. Target contaminant reduction will be directly related to the concentration of hydroxyl radicals created.

III. Piloting for AOP

Piloting provides information useful for the design of a full-scale treatment system. In addition to demonstrating/confirming the capability of the selected treatment process to reduce target contaminants, piloting can also provide data that can be used to understand how fluctuations in water quality may impact system performance; to characterize chemical feed rates; to characterize process waste residuals; and to understand system control logics and critical operating parameters. Piloting can reveal unanticipated operational challenges and provide flexibility to troubleshoot such challenges before a full-scale system is constructed and operational. Lessons learned from piloting can help ensure consistent performance of the full-scale system.

Information collected from piloting should:

- Demonstrate that the proposed treatment process will continuously produce water that meets State and Federal drinking water standards.
- Assess the production of treatment byproducts.
- Establish operational and performance setpoints of the proposed processes through a range of raw water quality, flow rates, chemical feed rates, and operating conditions.
- Assist the water supplier in estimating overall capital and operation costs.

Pilots should be of sufficient duration to address the range of temperatures and water quality conditions anticipated for the full-scale system. In addition, the pilot should assess the range of operating conditions anticipated for the full-scale system, such as continuous or intermittent operation or extended shut-down periods. Pilots should be of an adequate size to provide scalable results, so that pilots can be used to project full-scale system dimensions and performance. As much as practical, water system operators should be involved in the actual pilot study to gain insights on system controls and operating logic.

IV. Pilot Test Report

A pilot test report should be submitted to the Department as part of the Engineering Report to support the proposed AOP design. The following sub sections describe the information that should be included in a pilot test report for AOP. This information will be useful to inform the proposed design and aid regulatory review. The Department should be consulted when deviations, additions or omissions to the following subsections are proposed.

Introduction and Objectives

This section should include the public water supply name, project location and consultant retained. There should be a brief description of the reason the pilot is being proposed and preliminary expectations based on knowledge of the technology to be piloted. In addition, the engineering consultant should provide a justification for the selection of the proposed technology, along with a list of other locations that this technology has been approved and used within New York State.

The pilot study objectives should be clearly described. Examples of a pilot study objective for AOP include:

- Demonstrate capability of the selected AOP technology.
- Reduce 1,4-Dioxane and other organic contaminants.
- Investigate formation of treatment by-products.
- Demonstrate that the proposed AOP process is capable of treating residuals, including residual oxidant concentrations or treatment by-products, if any.

The section should also include the following as appropriate:

- A description of each component of the pilot equipment including temporary chemical storage; secondary containment and leak detection; the location of the shower/eye wash station; and the name of chemicals, dose and safety feature.
- A drawing of the pilot unit with a detail that indicates the location of the pilot equipment within the plant.
- A pilot process diagram that shows the size and material of side stream piping; flow rate of side stream; and location of backflow prevention devices, flow meter, UVT monitor, UV, chemical injection point, sampling taps, static mixer, valve, GAC and wastewater disposal location.

Water System Description

The description of the water system should include a site plan that shows the location of the wells and the topography and location of existing and proposed treatment. The engineering consultant should provide the Department with a description of:

- each source that will be treated, including permitted capacity, depth and historical water quality (1,4-dioxane, PFAS, POCs, IOCs, SOCs, UOCs);
- a description of existing water treatment systems, including chemicals used; and
- and a description of the ability to run the system to waste.

Bench Test Results

If bench scale tests were conducted, a description of the testing that was completed and the results should be included.

Technology Selection

A detailed description of the technology piloted should be provided. The manufacturer's information should be included.

Sampling Plan

This section of the pilot test report should include a description of the testing approach. At a minimum the sampling plan should include:

- The number and length of runs.
- Parameters to be adjusted.
- Analytes to be tested on each run.
- Name of ELAP certified laboratory to be used.
- Laboratory methods used for analysis.
- Manufacturer equipment methods of analysis.
- Sample collection locations and handling of water samples.

Water Quality Results

Results from samples collected both pre and post treatment should be included and focus on target contaminants and potential treatment byproducts[1], including:

- Aldehydes- acetaldehyde and formaldehyde
- Inorganic compounds- Chloride, chlorate, perchlorate, bromate, sulfate, nitrate and nitrite[2]
- Haloacetic acids[3]
- Chloropicrin[4]
- Organic acids- Acetic acid, oxalic acid[5]
- Trivalent and hexavalent chromium
- Hydrogen peroxide
- Hypochlorous acid

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[1] Residual oxidants should be quenched after samples for oxidation byproducts are collected. This will minimize the potential for oxidation byproducts to continue to form during sample holding time.

[2] Systems piloting medium pressure UV lamps must consider and assess the potential for nitrate reduction to nitrite across the AOP reactor.

[3] Systems piloting UV AOP technologies with trichloroethylene (TCE) in the raw water should monitor for haloacetic acids. Systems piloting UV and hypochlorous acid should monitor for haloacetic acids.

[4] Systems piloting medium pressure lamps and hypochlorous acid should monitor for chloropicrin.

[5] The Department may waive this monitoring for groundwater systems where supported with results from AOP treatment of other similar water quality.

V. Forgoing Pilot Testing

A PWS may be able to forego pilot testing if:

- The water quality of the raw water or pre-treated water (i.e., air stripper effluent, or other conventional treatment process) is similar with that of the water quality which was previously piloted in accordance with this document and the pilot testing used the same AOP reactor (make and model) and oxidant (e.g., hydrogen peroxide, hypochlorous acid) combination proposed.
- The project location can accommodate full-scale demonstration testing by sending water to waste.
- An applicant can otherwise demonstrate to the satisfaction of the Department that piloting is not necessary to project full-scale system dimensions and performance.[1]

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[1] The Department will approve, pending satisfactory monitoring results, the full-scale system for use at the demonstrated flow rate. Operation at higher flow rates without additional demonstration testing must be approved by the Department. When such approvals are sought, they should be supported with information which establishes that the target treatment goal can be met at higher flow rates. For systems combining UV and an oxidant, the information provided should demonstrate that the required UV dose can be delivered at the higher flow rates.

Table 1 – Technical Considerations

The following information should be considered when designing treatment for the removal of 1,4-Dioxane.

Concept	Background	Technical Considerations
Kinetics	Reaction rate constants define how well hydroxyl radicals will react with target contaminants. The second order rate constant for hydroxyl radical oxidation of 1,4-dioxane is approximately 1.0×10^9 M^{-1} $s^{-1.}$ Given the relatively low concentration of target contaminants, as well as the short hydraulic residence times of typical AOP treatment processes, target organic contaminants with second order rate constants less than 1.0×10^7 M^{-1} s^{-1} may not be good candidates for this treatment process.	AOP may not be the best available technology for all organic contaminants Treatability should be supported with technical reference and/or results from pilot testing.
Oxidant Concentration and Delivery	The level of 1,4-dioxane reduction will depend on the sustained concentration of hydroxyl radicals achieved during AOP treatment. The sustained hydroxyl radical concentration will depend on the applied UV dose and concentration of applied oxidant (i.e., hydrogen peroxide or hypochlorous acid), or the relative concentration of multiple oxidants (i.e., hydrogen peroxide and ozone). For example, and with respect to UV/peroxide AOPs, the same sustained hydroxyl radical concentration can be achieved at high UV dose and low hydrogen peroxide concentration and low UV dose and a high oxidant concentration.	There may be a delay between system startup and when target oxidant concentrations are achieved (steady state). This will be dependent on system hydraulics. Tracer studies can be used to evaluate how long it takes to establish steady state after chemical addition. Pilot studies or demonstration testing, when completed, should also test a range of oxidant concentrations.
Treatment Byproducts (also see Table 2)	As with any oxidation process, there is potential for intermediate compounds to form as a result of the reaction between hydroxyl radicals and target contaminants. These intermediate compounds are also susceptible to oxidation by hydroxyl radicals.	Byproducts may be formed during AOP treatment. Available resources should be reviewed to identify any specific compounds that may be produced at significant concentrations as a result of AOP treatment of the proposed source water.

Concept	Background	Technical Considerations
UV Dose (For Systems Pilot Testing UV Light)	Direct UV photolysis of 1,4-dioxane is not significant, so its treatment will depend largely on the UV dose applied to hydrogen peroxide or hypochlorous acid, and the scavenging demand of the source water. In simplest terms the UV dose (mJ cm^{-2}) is a function of UV intensity (mW cm^{-2}) and time.	Applied UV doses are dependent on system flows and UV reactor hydraulics (hydraulic efficiency). Pilot studies when conducted using UV light to create hydroxyl radicals, should test various combinations of flow rate and UV ballast power level (BPL) that will result in UV doses comparable to those anticipated at full-scale. AOP system manufacturers should be consulted when developing BPL and flow combination that will be piloted. The electrical energy per order (EEo) for small-scale UV reactors are not representative of full-scale reactors because they are less efficient.

Table 2 – Treatment Byproducts

The following compounds should be considered when designing treatment for the removal of 1,4-Dioxane.

Potential Byproducts	Background
Acetaldehyde Formaldehyde	In general, organic compounds will be oxidized to aldehydes, which are further oxidized to organic acids, which are finally oxidized to carbon dioxide and mineral salts. The aldehydes of most interest are acetaldehyde and formaldehyde.
Acetic acid Formic acid Oxalic acid	Similar to the use of ozone, AOP treatment has the potential to increase the biologically available organics content (assimilable organic carbon) of the treated water. This is the result of oxidation transforming complex organic structures into simple organic structures. High concentrations of assimilable organic carbon (AOC) may impact the biological stability of the distribution system, promoting biological growth and impacting the stability of disinfectant residuals. Elevated AOC may also lead to increased chlorinated byproduct levels, if the water is not stabilized and free chlorine is used for protection.

Potential Byproducts	Background
Acetic acid, formic acid and oxalic acid, cont.	Water research literature reports that the threshold for minimizing biological instability in the distribution system is approximately 120 µg/L and 180 µg/L AOC with free chlorine and chloramine, respectively. Literature also reports that the sum of acetic, formic and oxalic acid concentrations can be considered a surrogate for AOC, and the organic acid analyses are a less expensive alternative.
Chlorite Chlorate Perchlorate Chromium (trivalent and hexavalent) Bromate Sulfate Nitrite and nitrate	The potential exists for AOP treatment systems to oxidize inorganics present, including chlorides, sulfur, bromide, trivalent chromium and nitrites.
Haloacetic acids Chloropicrin	TCE is susceptible to direct UV photolysis which may produce chlorinated acetic acids, particularly dichloroacetic acid. There is potential for UV/chlorine systems to produce chlorine radicals, which may interact with simple organic acids forming chlorinated acetic acids. Medium pressure UV/chlorine systems may reduce nitrate to nitrite and produce chlorine radicals leading to the formation of chloropicrin.

VI. References

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