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November 19, 2016

watersupply@dep.nj.gov
New Jersey Department of Environmental Protection
Trenton, New Jersey

Re: Comment on the Proposed DWQI Addendum to Appendix C: Recommendation on Perfluorinated Compound Treatment Options for Drinking Water

Please find enclosed a technical analysis prepared by Fardin Oliaei, MPA, PhD, and Don Kriens, Sc.D., P.E. of Cambridge Environmental Consulting commissioned by Delaware Riverkeeper Network and submitted on behalf of the organization and its membership on the Drinking Water Quality Institute's document **Addendum to Appendix C: Recommendation on Perfluorinated Compound Treatment (PFC) Options for Drinking Water.**

Also attached is a PDF containing the Curriculum Vitae for Dr. Oliaei and for Don Kriens, Sc.D., P.E.

Delaware Riverkeeper Network submits these comments advocating that the public be protected from PFC contamination and that New Jersey's drinking water be required to be treated to a safe level based on the best available scientific evidence and the most effective treatment technologies.

We support the recommendations and findings made by Dr. Oliaei and Don Kriens of Cambridge Environmental Consulting in this technical analysis regarding the Addendum to the Treatment Options Report by the DWQI. We support the utilization of the most effective methods of removing PFCs considering the highly toxic properties of the compound.

Dr. Oliaei and Don Kriens recommend that reverse osmosis (RO) is needed to completely remove all PFCs from drinking water to the proposed safe drinking water standard. Dr. Oliaei and Don Kriens also find that RO alone or used after granular activated carbon (GAC) represents the best available technology for this purpose. Delaware Riverkeeper Network supports these findings and advocates for the use of the best available technology with a goal of providing safe drinking water to the public.

Thank you for the opportunity to comment on the Treatment Options to remove PFCs, including PFOA, PFNA, and PFOS.

Sincerely,

Maya K. van Rossum
Maya van Rossum
the Delaware Riverkeeper

Tracy Carluccio
Tracy Carluccio
Deputy Director

Attachments: <u>Technical Review of Proposed DWQI Recommendation on Perfluorinated Compound Treatment Options for Drinking Water</u>, Fardin Z. Oliaei, Don Kriens, Cambridge Environmental Consulting, Nov. 18, 2016

Technical Analyses of New Jersey Drinking Water Quality Institute

Recommendation on Perfluorinated Compound Treatment Options for Drinking Water

prepared by

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Cambridge Environmental Consulting

November 18, 2016

PREFACE

The opinions in this report are stated to a reasonable degree of scientific probability. The methods and principals used in forming these opinions are generally accepted within the scientific community and are consistent with their regular application within the scientific community. Qualifications of the authors, including publications where applicable, are summarized in the attached resumes. We reserve the right to modify or supplement opinions stated in this report.

** The views expressed in this report do not necessarily reflect those of the Harvard T.H. Chan School of Public Health, Harvard University, of which the author is affiliated as a Research Fellow.*

Technical Review of New Jersey Drinking Water Quality Institute's Recommendation on Perfluorinated Compound Treatment Options for Drinking Water

by

Cambridge Environmental Consulting

Executive Summary

We previously reviewed treatment technologies applicable to removal of PFCs at municipal drinking water supplies to remove PFOS, PFOA, and PFNA in our comments to NJDWQI proposed MCL for PFNA in 2015. This review updates our prior analysis of these technologies.

We found that reverse osmosis (RO) is needed to adequately remove all PFCs, including PFOA, PFNA, and PFOS, to proposed MCL standards. There are numerous installations across the U.S. where RO is economically applied to treat groundwater and, in some cases, surface water, as drinking water supplies. We believe that RO alone or RO after GAC (granular activated carbon) represents the best available treatment technology economically achievable to remove PFCs. Depending upon pilot studies and bench testing, nanofiltration (NF) may be a viable substitute for RO. RO preceded by conventional treatment (filtration) represents best technology at public water supplies using groundwater, and conventional treatment/coagulation-filtration followed by RO or a sequence of GAC followed by RO (or NF where applicable) represents best available technology for surface waters.

Introduction

In the U.S. the majority of municipal drinking water treatment systems use conventional water treatment technologies, which typically include flocculation and coagulation, filtration, and disinfection using chlorine or chlorine derivatives. Alternative disinfectants such as ozone are occasionally used which also provide for organics removal, and occasionally municipal systems use advanced technologies such as activated carbon. Conventional drinking water treatment technologies have little effect on PFC removal, including PFOS, PFOA, and PFNA. More advanced technologies are used to remove selective organic compounds and include, but are not limited to, advanced microfiltration technologies, such as ultrafiltration and nanofiltration, advanced oxidation processes, such as ozonation, peroxide, and UV peroxide, and reverse osmosis and activated carbon technologies. A combination of technologies may be applied where superior removals are needed, such as in water reclamation processes. A number of advanced water treatment systems using combinations of advanced technologies are in operation worldwide where recycled domestic wastewater is reclaimed and treated to very high quality (Queensland, Australia; Los Angeles; Singapore; Windhoek). These advanced systems, however, are used at locations where water scarcity is the primary constraint.

PFC compounds have relatively high molecular weight, at least for higher carbon number PFCs, that leaves them amenable to adsorptive removal technologies such as activated carbon. They are both hydrophobic and hydrophilic, although aqueous solubility varies greatly between PFCs. This duality can reduce carbon adsorption capacity for the carboxylic PFCs to some extent, although the hydrophilic portion of the molecule increases potential removal by membrane (reverse osmosis) and ion exchange technologies.

Cost is a consideration in addition to treatability of PFCs at municipal systems using various advanced technologies. Analysis of the economic benefits of reduction in health costs versus the cost of treatment (benefit-cost analysis) would be useful to assess overall social benefit of treatment for PFC at locations containing these contaminants in their water supplies. Cost-effective analysis would help to determine the most suitable removal technology. However, economic considerations are beyond the scope of this review.

Granular Activated Carbon

Granular activated carbon (GAC) has been shown to be very effective to remove most PFCs. GAC systems typically employ pre-filtration via sand or mixed-media filtration.

Some studies indicate that powdered activated carbon (PAC) versus granular activated carbon provides better PFC removal. One study found that powdered activated carbon generally showed better adsorption than granulated activated carbon, sulfonates were more strongly adsorbed than carboxylic acids, and PFC adsorption increased with increasing PFC chain length (Hansen et al., 2010). A study by Ochoa-Herrera found that PFOS is strongly adsorbed by GAC. PFOA and PFBS were also removed by GAC but to a lesser extent (Ochoa-Herrera and Sierra-Alvarez 2008). Results in this study indicate stronger adsorption to perfluorosulfonates as compared to perfluorocarboxylates at equivalent chain lengths. In a study by Arvaniti, PFOS, PFOA and PFNA were removed by nearly 100% using PAC, but at considerably lesser percent removals using GAC (Arvaniti 2013).

There are some municipal drinking water treatment systems in operation in the U.S. designed for removal of PFCs. In Oakdale, Minnesota a GAC system treats water for about 30,000 residents, meeting the current Minnesota drinking water standard for PFOA and PFOA of 300 ng/L (to be updated to the revised EPA standard of 70 ng/L). These limits are much higher than New Jersey's proposed limit of 14 ng/L. The quantitative analytical reporting limit for PFOA in Minnesota is 14 ng/L. Although Oakdale's GAC water is produced at levels below this limit it is unknown whether that GAC facility would meet a limit lower than 14 ng/L. The NJWQI report notes that PFNA is removed to less than detectable with a RL of 5 ng/L at the New Jersey American Water-Logan System, although no data is provided for PFOA.

The Minnesota Mining and Manufacturing (3M) Cottage Grove, Minnesota plant also uses a GAC system to remove PFCs from its wastewater discharge effluent to the Mississippi River. A 2006 study found a 79% reduction in PFOA and a 95% reduction in PFOS at the 3M GAC treatment system (Oliaei and Kriens 2006).

In summary, GAC has been shown to very effectively remove PFCs, in practice or via research studies, although the form of AC (GAC or PAC) could affect performance in some instances and individual PFCs are removed at different rates.

Reverse Osmosis

Reverse osmosis and nanofiltration are very effective to remove PFCs. Reverse osmosis resulted in greater than 99% rejection of PFOS, and nanofiltration resulted in 90-99% PFOS removal in a study by Tang et. al. (Tang 2007). The effectiveness of reverse osmosis treatment is shown by Quinones and Snyder (2009), where a utility using microfiltration and reverse osmosis in wastewater treatment for indirect potable reuse reduced total PFC influent of 80 ng/L and influent PFOS of 41 ± 18 ng/L to no reportable levels (Quinones and Snyder 2009).

In Point of Use (POU) studies in Minnesota GAC and GAC in combination with reverse osmosis were evaluated to determine their effectiveness to remove PFCs. These POU devices are typically under-sink for drinking water, but may also be designed for whole-house treatment, and are primarily used in residential settings treating domestic well water (groundwater). This comprehensive study found that GAC and GAC combined with reverse osmosis were effective to remove PFCs at manufacturer recommendations for water flow rate and volume throughput, although lower chain PFCs were removed at reduced rates using GAC alone (Olson and Paulson 2008). In cases where GAC was shown less effective, reverse osmosis enhanced PFC removal performance. In this study, GAC systems alone (without reverse osmosis) showed a loss of performance towards end of the carbon useful life, while combined GAC/reverse osmosis systems did not show a loss of performance at total throughput volumes. We expect that enhanced removal by reverse osmosis is likely due to added capability of reverse osmosis to remove charged ionic species, (inorganic and organic), such as the carboxylic PFCs, through both adsorption and electrostatic repulsion.

Advanced Oxidative Processes

Advanced oxidative processes such as chlorination, ozonation and UV peroxide, have been found effective to breakdown of organic compounds, including complex organics, but are not expected to provide significant removal of PFCs due to the strength of the C-F bond. No significant removal of PFCs was observed using UV and UV peroxide in a study by Arvaniti et al., 2013. One study showed only relatively modest PFOS removals between 10-50%, dependent on the oxidative process used (Ribeiro 2015).

Resin Adsoprtion/Ion Echange

Zeolites are widely used to purify water. One study found that PFOS adsorbs strongly to a NaY80 (Si/Al 80) zeolite, but other zeolites demonstrated poor adsorption (Ochoa-Herrera and Sierra-Alvarez 2008). This study also found that this zeolite adsorbed to PFOS at the same order of magnitude as GAC, although overall GAC provided better PFOS removal. Anion exchange resins were also found effective for PFOS removal in wastewater in a study by Deng et. al., which also noted that sorption rates for PFOS were dependent on their polymer matrix and porosity (Deng et al., 2010). Ion exchange would not provide an equivalent level of PFC removal compared to GAC at equivalent cost.

Further Evaluation of RO versus GAC

Although both GAC and RO remove PFOA, PFOS, and other long chain PFCs to greater than 90%, RO has been shown in full scale and lab studies to remove PFOA to 99%. RO and NF also remove lower molecular weight short chained PFCs like PFBA and PFBS, found in water supplies. The recent Water Research Foundation (WRF) report of 2016 notes that "all PFASs were below the MRLs (maximum reporting limits) in the collected samples immediately following the RO systems, making this the most effective form of treatment evaluated in this study." The study included evaluation of GAC, anion exchange, oxidation, nanofiltration, and conventional water treatment methods (WRF 2016). The WRF study also notes that GAC and anion exchange "were less effective at removing shorter chain PFASs, whereas NF and RO were effective at removing even the smallest PFAS studied". RO and/or NF will assure removal of shorter chain PFBA and PFBS present.

Similar rejection of PFOS (>99%) was shown in a bench testing study of RO efficiency (Tang et al. 2006). WRF also notes in its 2016 report that nanofiltration membrane systems can be less costly and could prove to be just as capable of rejecting PFASs as RO in full-scale plants, as NF has been deemed potentially effective (> 95%) in bench-scale experiments using NF270 membranes (WRF 2016; Steinle-Darling and Reinhard 2008)."

Although GAC has been shown effective to remove PFOA, PFNA, and PFOS, often to > 90%, there are inconsistencies in GAC removal efficiency. In a study using GAC in Amsterdam, PFOA was not effectively removed, with a final mean GAC concentration of 5.3 ng/L (range 0.8 ng/L - 9.4 ng/L) versus a mean influent PFOA concentration of 4.4 ng/L (range 3.8 ng/L– 5.2 ng/L). In that study greater removal of PFOS and PFNA were achieved with a mean final water level of <0.23 ng/L and <0.24 ng/L, respectively, versus influent levels of 6.7 to 10 ng/L for PFOS and 0.5 to 0.8 ng/L for PFNA (Eschauzier et al., 2012). In a study of removal of PFOS and PFOA at a water treatment plant in Spain, treating about 100 million gallons per day of Llobregat surface river water to supply over 1 million inhabitants, RO removed PFOA to a mean of 2.1 ng/L in final water with influent raw water at a mean 6.9 ng/L. GAC removal resulted in a mean of 4.7 ng/L for PFOA in final water. This study found that PFOS was removed to a mean of 0.7 ng/L in final water, whereas GAC removed PFOS to a mean of 22 ng/L in final water, with raw water at 86 ng/L PFOS. Overall, this study found an efficiency of removal of 99% ± 1 for RO and 63% for GAC (Flores 2013).

In testing of 5 RO membranes and 3 NF membranes researchers found that rejection efficiencies (efficiency of removal) for RO membranes were **>**99% and for NF membranes ranged from 90-99% (Tang et al., 2007).

PFC removal was studied at two water reclamation plants (treating domestic effluents as influent) in Southeast Queensland, Australia. One plant (plant A), treating about 2 million gallons per day, utilizes de-nitrification, ozonation, coagulation/flocculation, dissolved air flotation and sand filtration and biologically activated carbon filtration processes. The other plant (plant B), treating about 17 million gallons per day, utilizes coagulation/flocculation and sedimentation, ultra-filtration (UF), reverse osmosis (RO), advanced oxidation (peroxide with ultraviolet) and final stabilization and disinfection. In plant A using activated carbon PFCs were detected at all sampling points across the treatment train. In plant B using RO, PFCs were below reporting limits in samples taken from points after RO treatment (Thompson et al., 2010). Reporting limits (RL) ranged from 0.4 to 1.5 ng/L. At PFOA influent levels ranging from 15 to 27 ng/L, PFOA was removed to < RL to 1.4 ng/L in the RO effluent stage of plant B. PFOS was removed to <RL in the RO effluent stage with influent levels ranging from 23 to 39 ng/L. In this study activated carbon (biological) was ineffective to remove PFCs. However, this may have been due to the age of the carbon beds or short contact times.

Summary of Technology Effectiveness to Remove PFOS, PFOA, and PFNA

We conclude that the best available technology economically achievable to remove PFOS, PFOA, and PFNA from dilute aqueous streams at public water supplies is reverse osmosis (RO). In some cases GAC may be sequenced ahead of RO, and NF may potentially offer a substitute for RO. GAC followed by RO may be economically applied at Point-of-Use (POU) systems treating well water at residences or, in some cases, at residences receiving municipal drinking water with PFC contaminants. POU systems, in particular those using both GAC and RO, have been successful in Minnesota to remove PFCs, and allow redundancy in assuring continuous removal. Use of RO or GAC/RO is advantageous since additional health benefits may be derived by removal of disinfection byproducts (DBPs) produced during chlorination/disinfection of water supplies. RO is necessary to remove the haloacetic fraction of DBPs in these water supplies.

Given the nature of PFOA to cause long lasting adverse impacts on humans and the uncertainty inherent in toxicological studies to determine a protective MCL, best available technology should be used to assure health protection, irrespective of whether an MCL is 1 ng/L, 6 ng/L, or 14 ng/L.

** The views expressed in this report do not necessarily reflect those of the Harvard T.H. Chan School of Public Health, Harvard University, of which one the author is affiliated as a Research Fellow.*

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