Water Research 201 (2021) 117285

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Effectiveness of point-of-use and pitcher filters at removing lead phosphate nanoparticles from drinking water

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ARTICLE INFO

Article history:
Received 22 December 2020
Revised 11 May 2021
Accepted 19 May 2021
Available online 25 May 2021

Keywords:
Lead
Colloidal particles
Nanoparticles
Orthophosphate
Pitcher filter
Point-of-use filter
Drinking water

ABSTRACT

Orthophosphate (PO_4) addition is a common corrosion control treatment used to lower lead (Pb) concentrations at the consumer's tap by forming relatively insoluble Pb-phosphate (Pb-PO_4) minerals. However, some Pb-PO_4 particles that can form in drinking water are mobile nanoparticles (i.e., 0.001-0.1 μm) that have the potential to reach the tap. Point-of-use (POU) or pitcher filters are often used to manage risks during distribution system upsets, when corrosion control treatment is not optimized, or following Pb service line replacements. To abide by industry convention, POU and pitcher filters must be NSF/ANSI-certified for Pb reduction (NSF/ANSI-53) using a test water containing dissolved Pb and large Pb particles. Certification for particulates reduction (NSF/ANSI-42) is done using a test water that contains particles, but not leaded particles. To address the lack of testing for Pb nanoparticles, this study challenged six certified commercially available faucet-mounted POU (3) and pitcher (3) filters with aqueous suspensions of Pb-PO_4 nanoparticle. For the water quality investigated, the Pb particles formed ranged between 0.016 and 0.098 μm, based on scanning electron microscopy, transmission electron microscopy, and dynamic light scattering analysis. These particles represented 98.5% of total Pb in suspension. The total Pb removals were between 44.6 and 65.1% for the POU filters, and between 10.9 and 92.9% for the pitcher filters. The electron microscopy results confirm that Pb-PO_4 nanoparticles passed through the filters. The findings can inform future efforts to re-examine the test waters used in the certification challenge tests.

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1. Introduction

There is no safe level of exposure to lead (Pb) as it is a neurotoxin which can have detrimental human health effects, even at low levels (Centers for Disease Control and Prevention 2019). In drinking water distribution systems, Pb sources can include service lines, brasses and solders (Lytle et al. 2019, Sandvig et al. 2008). Appropriately certified point-of-use (POU) filters and/or pitcher filters have been recommended as a mitigation measure to decrease Pb exposure (Bosscher et al. 2019), particularly in short-term response to an emergency Pb release event. POU and pitcher filters are also distributed by many cities in the United States (US), including Cincinnati (Webb 2014), Denver (Denver Water 2020) and Milwaukee (Milwaukee Health Department 2020), following Pb service line replacement.

Relevant voluntary certifications associated with the reduction of Pb by POU and pitcher filters in drinking water are covered under standards NSF/ANSI-42 and NSF/ANSI-53, developed by the NSF/American National Standards Institute (NSF/ANSI 2019a, b). NSF/ANSI-42 is the standard aimed at reducing non-health related contaminants that cause aesthetic effects (e.g., chlorine, taste and odor), including Class I particulates (0.5 to <1 μm). To be certified under NSF/ANSI-42, a reduction ≥85% must be achieved from a 10,000 particles/mL solution, which does not contain Pb (NSF/ANSI 2019a). The relevance of this aesthetic effects' standard is that Pb has been associated with other particles (e.g., iron) in water (Trueman and Gagnon 2016). Therefore, this certification would conceivably ensure reduction of Pb-containing Class I par-

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https://doi.org/10.1016/j.watres.2021.117285
0043-1354/Published by Elsevier Ltd.

ticulates from water. NSF/ANSI-53 is a health effects' standard directly associated with Pb reduction for POU/pitcher filters. Certification is carried out by challenging filters with two test waters with a Pb concentration of 150 µg/L; one at pH 6.5 with dissolved Pb added as $Pb(NO_3)_2$ and the other at pH 8.5 with both dissolved and particulate Pb added. At pH 8.5, at least 20% of total Pb in the NSF/ANSI synthetic water should be fine particulate, defined as particle size between 0.1 and 1.2 µm (NSF/ANSI 2019b). As of 2019, the filter must reduce the concentration of Pb to 5 µg/L or lower to obtain the certification (NSF/ANSI 2019b).

Appropriately certified POU and pitcher filters have been shown to reduce Pb in drinking water and provide a Pb reduction option to homeowners and utilities under field settings. Certified POU filters and pitcher filters were provided to residents in cities such as Flint, MI, Newark, NJ, and University Park, IL, (Aqua Illinois 2019, Bosscher et al. 2019, CDM Smith 2019, Lytle et al. 2020b, (US Environmental Protection Agency 2019) to reduce Pb in drinking water following distribution system upsets. In Flint, MI, following the transition to water from the Flint River, federal agencies, including the US Environmental Protection Agency (USEPA) and the Department of Health and Human Services (HHS) recommended the use of NSF/ANSI-42/53 certified POU and pitcher filters or bottled water to lower exposure to Pb from drinking water (Bosscher et al. 2019). Field drinking water sampling at over 345 locations in Flint, MI showed that all POU filters evaluated reduced Pb levels below the certification target, and 97% of the filtered samples had Pb concentrations below 0.5 µg/L (Bosscher et al. 2019). Pitcher filters could remove 99.85% of Pb from an initial concentration of 13,200 µg/L (Pieper et al. 2019). Deshommes et al. (2010) tested certified POU and pitcher filters in the laboratory and field conditions, concluding that POU filters adequately lowered Pb concentrations below 10 µg/L and only occasionally exceeded this threshold. Most of the certified POU filters and pitcher filters tested by Purchase et al. (2021) successfully decreased soluble Pb concentrations below NSF/ANSI-53 standards for certification and 3 out of the 5 filters tested reduced particulate Pb to values lower than 10 µg/L. Not all studies on POU and pitcher filters systematically assessed the form of Pb (soluble, colloidal particulate), nor did they assess the nature (e.g., size, composition, mineralogy) of Pb colloids and particles when present.

System-wide corrosion control to decrease exposure to Pb from drinking water involves the application of corrosion control treatment to form protective relatively insoluble Pb minerals over leaded materials (Schock 1989). Orthophosphate (PO_4), for example, is added by many utilities to promote the formation, in pipe scales, of insoluble Pb-phosphate (Pb-PO_4) minerals such as hydroxypyromorphite [$Pb_5(PO_4)_3(OH)$], chloropyromorphite [$Pb_5(PO_4)_3(Cl)$] and tertiary Pb phosphate [$Pb_3(PO_4)_2$] (Schock 1989, Trueman et al. 2018). However, Pb-PO_4 compounds are also known to produce nanoparticles with high mobility tendencies if not immediately incorporated into the scale. This occurs under certain water qualities (e.g., low hardness) (Bae et al. 2020, Lytle et al. 2020b, Trueman et al. 2018). Furthermore, nanoparticulate Pb (0.001-0.1 µm) could present a challenge to certified POU and pitcher filters because they are certified, under NSF/ANSI-42/53 to reduce much larger particles (>0.1 µm) (NSF/ANSI 2019a, b).

Initial Pb sampling from POU and pitcher filters in Newark, NJ homes revealed that two of three sampled filters failed to reduce Pb below 10 µg/L, but a large follow-on POU and pitcher filter testing program initiated by the city found that 97.5% of the 198 filters evaluated reduced Pb $\leq$ 10 µg/L (CDM Smith 2019). Furthermore, flushing for 5 minutes increased the percentage to 99.5%. (CDM Smith 2019, Lopez 2019, Lytle et al. 2020b). Follow-up USEPA sampling at four of those homes found that Pb-PO_4 nanoparticles were present in the water before and after treatment by either a POU filter or a pitcher filter (Lytle et al. 2020b). The finding, albeit isolated, raised concerns over filter efficacy when leaded nanoparticles are present. This then raised questions about the representativeness of Pb particles used in the current certification protocol to challenge POU and pitcher filters.

Given the reliance on using POU and pitcher filters to reduce Pb under some circumstances, questions remain regarding their effectiveness to remove very small Pb particles. The objectives of this study were to: (1) Challenge commercially available NSF/ANSI-42/53 certified POU and pitcher filters with a stable Pb-PO_4 nanoparticle suspension; (2) Quantify the Pb fractions (total, particulate, colloidal and soluble) before and after filtration; (3) Identify other water quality changes that occur after water passes the filters. This information will help inform the drinking water industry, particularly with regard to efforts to develop more robust certification testing protocols for removing Pb from drinking water.

2. Material and methods

2.1. POU and pitcher filters tested

In this study, POU filters refer to devices which attach to the faucet—as opposed to pitcher filters which do not. Three certified (NSF/ANSI-42/53) POU filters and three certified pitcher filters were evaluated (Table 1). The three POU devices consisted of carbon block-based filters containing natural zeolite, with reported lifespan between 378 and 780 L. The reported filter lifespan of the three pitchers were generally lower (56.8-454 L), particularly for Pitcher-3. The pitcher filters all utilized activated carbon and/or ion exchange resin medias. All filters reported high Pb reduction efficiency (98.5-99.7%) and particulate Class I reduction efficiency (97-99.9%) for NSF/ANSI-53 and NSF/ANSI-42, respectively, except for Pitcher-3 which was not certified under NSF/ANSI-42.

2.2. Preparation of challenge water

Synthetic stable Pb-PO_4 nanoparticle challenge water was prepared daily in the laboratory based on previous work from Formal et al. (2021) and Lytle et al. (2020a) (Table 2), which is referred to as "challenge water" throughout this manuscript.

For the preparation of the challenge water, a Pb-PO_4 nanoparticle stock suspension (5 mg Pb/L, soluble Pb < 10 µg/L, pH 7.5, 7 mg C/L as total inorganic carbon [TIC], PO_4 in excess of 3.0 mg PO_4/L) was first prepared daily. The stock solution was prepared by adding sodium bicarbonate ($NaHCO_3$, Fisher Chemical Fairlawn, NJ), adjusting the pH to 7.5 $\pm$ 0.1 with sodium hydroxide (NaOH) and nitric acid (HNO_3) (0.6 N, Fisher Chemical, Fairlawn, NJ) and finally adding solutions of PO_4 ($NaPO_4{\cdot}H_2O$, Fisher Chemical, Fairlawn NJ, 2,263 mg PO_4/L) and lead chloride ($PbCl_2$, Acros Organics, Morris Plains, NJ, 1,000 mg Pb/L) to 1 L of de-ionized (DI) water. The pH of the Pb-PO_4 nanoparticle stock suspension was maintained at 7.5 $\pm$ 0.1 throughout. Immediately after particle generation, Pb particle hydrodynamic size and polydispersity index were measured using a Malvern Zetasizer Nano-ZS90 (Malvern, United Kingdom) based on dynamic light scattering (DLS) principles. For the first ten POU filters and pitcher filters tested, the 2,000 mg PO_4/L stock solution was made from NaH_2PO_4 (Fisher Chemical Fairlawn, NJ), resulting in a concentration of 3 mg PO_4/L, whereas the remaining of the tests were done at a concentration of 3.4 mg PO_4/L. Throughout the experiments, PO_4 levels were above the stochiometric ratio required to precipitate Pb-PO_4 particles (i.e., soluble PO_4 was available).

Challenge water was prepared daily: 20 L for pitcher filters and 58 L for the POU filters, based on the work of Lytle et al. (2020a). Challenge water was mixed using a stir plate and magnetic stir bar at room temperature in high-density polyethylene (HDPE) carboys.

Table 1
Properties of point-of-use filters and pitcher filters tested in the laboratory, including NSF/ANSI overall percent reduction, as provided by the vendors in user manuals. The percent capacity reached during the experiments was calculated compared to the vendor-reported filter capacity. NSF/ANSI-42 Particulate Class 1 is defined as particles 0.5 µm to < 1.0 µm. NA: Not applicable; POU: point-of-use.

POU or Pitcher filters	Filter Study #	Filter Composition	Service flow rate (L/min)	Pressure (psi)	Lifespan (L)	Capacity reached during testing (%)	NSF testing		
							NSF/ANSI-53 Health Effects - % reduction from 150 µg/L		**NSF/ANSI-42 Aesthetic Effects - % reduction from 10,000 particles/mL Particulate Class 1 fine dust**
							Lead pH 6.5	**Lead pH 8.5**	
POU	POU-1	Carbon block with external matrix	2.19	20 - 100	378	15.1	>99.3	>99.3	99.6
	POU-2	Carbon block with lime minerals	2.0	20 - 100	378	15.1	>99.7	99.9	98.8
	POU-3	Carbon block with external matrix	1.7	10 - 100	760	7.5	99	99	97
Pitcher	Pitcher-1	Ion exchange resin mixed with activated carbon and fibrous matrix to hold material	NA	NA	151	13.2	99.3	98.5	>99.9
	Pitcher-2	Activated carbon, fibrous matrix to hold material, absorbent in filter media	NA	NA	454	4.4	99.5	99.6	99.6
	Pitcher-3	Coarse filter screen, foam distributor, activated carbon, dual ion exchange resin, layer of ultra-fine screening and non-woven membrane	NA	NA	56.8	35.2	99.7	99.0	No

Table 2
Targeted water quality parameters for this study's challenge water relative to the NSF/ANSI-53 test water. TIC: Total inorganic carbon, NA: Not available.

Type of water	Total Pb (µg/L)	pH(-)	Alkalinity (mg $CaCO_3$/L)	Hardness(mg $CaCO_3$/L)	TIC(mg C/L)	Calcium(mg Ca/L)	Total PO_4 (mg PO_4/L)	Total chlorine(mg Cl_2/L)
Challenge water	100	7.5	28	NA	7	0	3	0
NSF test water at pH 8.5	150	8.5	100	100	23.7*	13.7*	0*	0.50

* Calculated based on alkalinity/hardness and NSF/ANSI-53 synthetic water protocol.

The carboys were filled with DI water, then sodium bicarbonate and PO_4 stock solution were added to obtain targeted water quality (Table 2). The pH of the challenge water was maintained at 7.5 ± 0.1 with NaOH (0.6 N) and HNO_3 (0.6 N). Once pH was stable, the Pb-PO_4 nanoparticle stock suspension was added to the challenge water. After 30 minutes of mixing, samples were drawn from the top and the bottom of the tanks and analyzed for total Pb concentration, to confirm suspension uniformity.

A HACH (Denver, CO) Hq440d multi meter with a pHC101 probe pH electrode was used to make pH measurements. HACH spectrophotometric method 8048 was followed for PO_4 measurements in the laboratory, using a HACH DR1900 spectrophotometer. Rapid screening of total Pb concentration was performed using an anodic stripping voltammetry (ASV) analyzer (Palintest SA1100 Scanning Analyzer, Golden, CO) following the user manual to ensure Pb concentration goals were achieved, and mixing was uniform.

3. Challenging the filters

3.1. POU filters

The laboratory POU challenge test apparatus consisted of a 60 L HDPE carboy with two ports located at the bottom (Fig. 1 and Supplementary information, SI, Figure S1); one was used for sampling during the experimental run and the other to supply challenge water to the POU filter. A variable speed pump, with a pressure gauge, fed the water from the tank to the POU filter, using 182 cm of ¼" Teflon and 28 cm of ½" Schedule 80 polyvinyl chloride (PVC) tubing. The faucet used for the experiment was non-metallic to avoid Pb contamination sources. Challenge water interactions with ambient air were minimized by placing a HDPE floating lid in the tank and the pH electrode was inserted into a bored hole in the lid. Sampling was performed at the beginning of the experiments to assess loss of Pb by adsorption to the tank or the tubing by allowing challenge water to stagnate over a 72 hour period in all the wetted parts of the experimental system. No significant changes in Pb characteristics or concentration of the challenge water were observed between the tank and the by-pass of the POU filters. A control test run was performed with the POU filter in by-pass mode (i.e., water was diverted around the filter) to assess whether the relatively short plumbing distance between the tank and POU device changed the suspension properties. Results showed that changes in Pb particle and suspension characteristics (particle size, shape, distribution), and total Pb concentration of the test water as it was pumped from the tank and through the by-pass of the POU filters were not observed (data provided in SI Figures S2 and S3). Also, during one test run, following collection of the samples from the tank and filtered by the POU, samples were collected by placing the filter in by-pass mode (data provided in Table S1).

POU filters were conditioned and operated according to specific vendor supplied instructions. For example, POU filter housings equipped with a light indicator or a flow totalizer were operated appropriately by following instructions provided by the vendor. Minimum operating pressure was 20 psi and pressure readings were recorded throughout the experiments to ensure the devices were operated within specifications (Table S2).

Once the challenge water was fully mixed (approximately 30 minutes), the Teflon and PVC tubing were flushed for at least 15 seconds in by-pass mode and then the POU filter was turned to filtering mode. Water samples were collected from the challenge water tank and from water that passed through the POU filter at

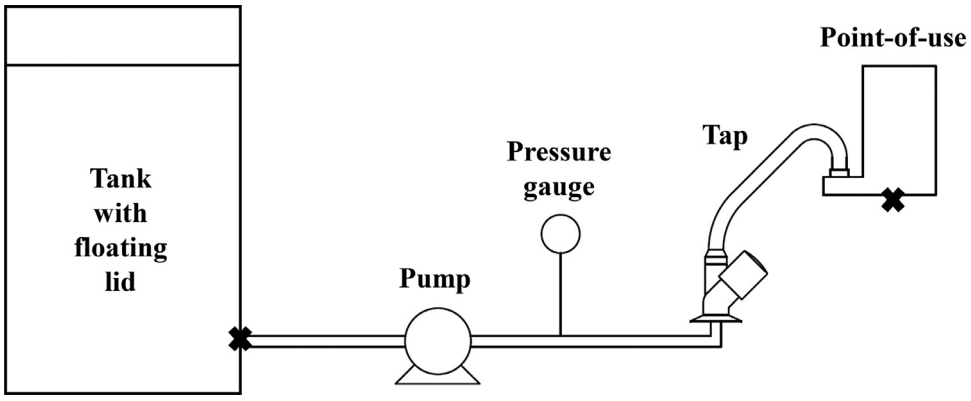


Fig. 1. Schematic of the setup for testing faucet-mounted POU filter. Sampling locations are represented by black Xs.

three time points: at the beginning of each experiment (1 L), after half of the challenge water volume (29 L) had passed through the filter and when the challenge water tank was nearly empty (55 L). Pressure and flow rate after the POU filter unit were recorded during each sampling event. Lastly, pH was monitored and adjusted to pH 7.5 ± 0.1 if required. Experiments were repeated in triplicate.

3.2. Pitcher filters

The pitcher filters were rinsed three times with DI water prior to testing, in order to remove dust from the packaging and ensure no outside contamination. They were conditioned according to manufacturer instructions. DI water was used in cases where water had to run through the filter and be discarded before the first use, or if the filter had to be soaked in water. As with the POU device evaluations, precautions were taken to minimize Pb losses to the tank, by letting challenge water stagnate during a 72 hours period in the tank. Once the challenge water was completely mixed in a 26.5 L HDPE carboy, it was added to the reservoir of the pitcher filters and filtered by gravity. Samples were collected from the challenge water and the effluent of the pitcher filter at the beginning of the experiment (1 L), after half the water was filtered by the pitcher filter (10 L), and when the solution was almost completely used (17 L). Experiments were repeated in triplicate.

3.3. Water quality and particles analysis

A series of water samples were collected during each sampling event from the challenge water and after the faucet-mounted POU filter or the pitcher filter as follows: 250 mL in HDPE wide-mouth bottle for total metals (i.e., Pb, Cu, Zn, others) analysis, 250 mL in HDPE wide-mouth bottle for ultrafiltration, 60 mL sample in polypropylene syringe for 0.2 µm filtration, 60 mL glass vial for immediate bench water quality analyses (pH, temperature, PO_4) (Fig. 2). Water samples collected in the middle of the challenge experiments also included 60 mL amber glass vial for total inorganic carbon (TIC) analysis and 250 mL in HDPE wide-mouth bottle for analysis of wet chemistry parameters (alkalinity, PO_4, chloride). Immediately upon collection, the water sample designated for ultrafiltration was filtered through a 400 mL Amicon® Stirred Cell with an Anodisc™ Ultracel® 30 kDA ultrafiltration disc, which was estimated to be approximately equivalent to 0.01 µm pore size (Erickson 2009, Guo and Santschi 2006). Previous internal investigations showed that the filtration apparatus can adsorb a significant amount of soluble Pb. To avoid this likelihood, the stirred cell was filled with 120 mL of sample and then allowed to mix for 5 minutes and then discarded before the actual sample was filtered. The remaining sample was placed in the pre-rinsed stir cell and pushed through the ultra-filter using pressurized nitrogen (10 psi). The ultrafiltrate was collected in a 60 mL HDPE bottle. This sample was defined as the soluble Pb fraction for the purposes of this work, operationally defined as Pb passing an ultrafilter (Fig. 3) which is consistent with the work of Tobiason et al. (2016).

Particulate and colloidal Pb fraction was calculated by subtracting soluble Pb from total Pb (Fig. 3). Samples collected in the 60 mL syringe were filtered through a 0.2 µm Whatman® Nuclepore™ Track-Etched 13 mm syringe filter membrane. The colloidal fraction <0.2 µm was calculated by subtracting the soluble fraction from the 0.2 µm filtrate (Fig. 3). This fraction includes nanoparticles (0.01 – 0.1 µm). Nanoparticles smaller than 0.01 µm can also be present in the soluble fraction, but only represents a small percentage of nanoparticles based on size definition. The particulate and colloidal Pb >0.2 µm was calculated by subtracting the 0.2 µm filtrate from the total Pb. Overall, the classification of total Pb into four Pb fractions in this work followed a different and more refined filtration approach, compared to the simpler operational distinction into soluble and particulate Pb as determined by a single 0.45 µm syringe filtration in Method 200.8 (US Environmental Protection Agency 1994b). It is also different from the NSF/ANSI-53 (2019b) definition of particulate Pb as it is the difference between total Pb and the 0.1 µm filtrate, with fine particulate further defined as the difference between 1.2 µm filtrate and 0.1 µm filtrate. As a research tool, particle size fractionation by filtration is limited by the filters commercially available and a trade-off between ease of use of the filters and results obtained. Filters chosen in this study were readily available in the laboratory. Ultrafilters of 30 kDa (~0.01 µm pore size) can retain most nanoparticles (defined as particles between 1-100 nm) present in samples, which was necessary to quantify the Pb soluble and nanoparticulate fractions. Filters of 0.2 µm were used to identify the colloidal Pb fraction <0.2 µm, as they capture small colloids and a broader range of particles than 0.45 µm filters

All samples for laboratory metal analysis were acidified to pH <2 for at least 16 hours and analyzed using ICP-AES and ICP-MS following USEPA methods 200.7 and 200.8 (US Environmental Protection Agency, 1994a, US Environmental Protection Agency, 1994b). PO_4 concentrations were analyzed using USEPA Method 365.1 (US Environmental Protection Agency 1993). Samples collected in glass vials without airspace were analyzed for total inorganic carbon using ASTM D513 Test Method B (ASTM International 2016). Samples collected in the 60 mL clear glass vial were analyzed, using bench analysis, for total Pb, PO_4, pH and temperature using methods described previously.

Presence of nanoparticles was systematically confirmed by transmission electron microscopy (TEM) and scanning electron mi-

Sample Collected from challenge water or filter	Sample Preparation: Filtration	Sample Preparation: Additional Preparation	Instrument used	Data Outputs
250 mL	No filtration	Acidify to pH <2 with nitric acid 16+ hours	ICP-MS/ICP-AES	Total Pb in water
		Air dry drops of samples on TEM grid	TEM/EDS	Particle size, elemental composition, morphology
250 mL	Ultrafiltration on 30 kDa membrane	Acidify to pH <2 with nitric acid 16+ hours	ICP-MS/ICP-AES	Soluble Pb in water
		Dab membrane with SEM stub	SEM/EDS	Particle size, elemental composition, morphology
60 mL	Filtration on 0.2 µm filter	Acidify filtrate to pH <2 with nitric acid 16+ hours	ICP-MS/ICP-AES	Colloidal Pb <0.2µm Particulate and colloidal Pb > 0.2 µm (by calculations)
60 mL	No filtration	No additional preparation	ASV analyzer	Total Pb in water

Fig. 2. Samples collected for Pb analysis during challenge studies from POU or pitcher filters at the beginning, middle and end of the experiments. TEM/EDS samples were not collected after filtration because of low particle presence. ASV samples were not acidified with nitric acid but were instead treated with the vendorprovided tablet according to vendor instructions. ICP-MS: Inductively coupled plasma mass spectrometry, ICP-AES: Inductively coupled plasma atomic emission spectrometry, TEM: Transmission electron microscopy, EDS: Energy dispersive spectroscopy, SEM: Scanning electron microscopy, ASV: Anodic stripping voltammetry.

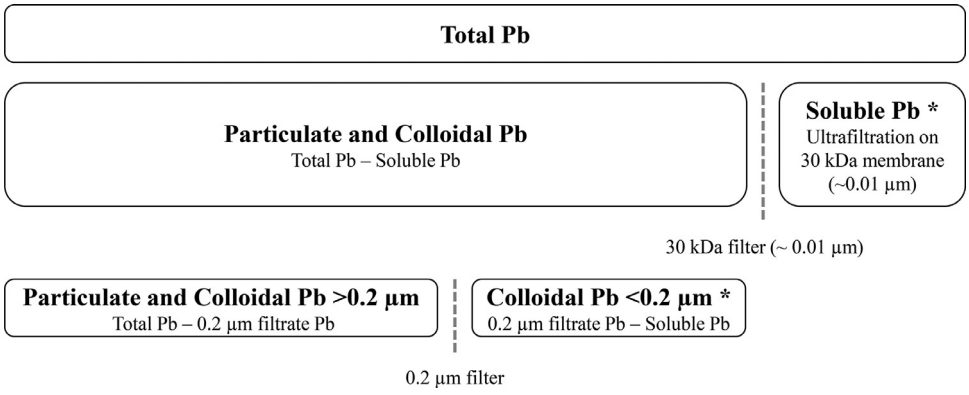


Fig. 3. Fractionation of total Pb in water samples in this work, based on size separation by filtration on 30 kDa membrane and 0.2 µm filter. The vertical dash lines represent the porosity of the filters used in this work. Nanoparticles can be present in the Soluble Pb and the Colloidal Pb <0.2 µm fractions. *Represents fractions in which nanoparticles can be present, presence can be confirmed by SEM and TEM analysis.

croscopy (SEM) for the challenge water and the filtered water, for each run. For solids analysis, the challenge and filtered waters were prepared per Lytle et al. (2020b) and Harmon et al. (2020) by placing a drop of sample water onto a TEM 3 mm sample holder copper grid. The TEM copper grids were held in place by self-closing forceps and allowed to air dry. A F200x high resolution-TEM imaging system was used to analyze the grids. The field emission gun was operating at 200 kV for all micrographs obtained and images were processed with ImageJ software program. Aluminum sample stub with double-sided carbon adhesive was dabbed on the wet ultrafilter discs to collect particles for SEM and energy-dispersive X-ray spectroscopy (EDS). Particles were examined using a JEM7600FE SEM (JEOL USA Inc., Peabody, MA) at 15 kV and a working distance of 8 mm. An Oxford X-max 50 EDS (Oxford Instruments America Inc., Concord, MA) and the low angle electron backscatter detector were used to identify elemental composition of the particles. The EDS spectra was analyzed using Aztec software (Oxford Instruments America Inc., Concord, MA). Size of particles was estimated, based on SEM and TEM images, using free Java^{TM}-based image processing software called ImageJ Fiji (Schindelin et al. 2012).

3.4. POU and pitcher filters material analysis

While some information was provided by the filter vendors (Table 1), the elemental composition of the POU filters and pitcher filters media was further determined by SEM/EDS before and after challenge water testing. The devices were dismantled, and SEM stubs were prepared for each internal component. Material was examined using the SEM/EDS mentioned in the previous section and JEOL JSM-6490 LV (JEOL USA Inc., Peabody, MA) coupled with Oxford X-max 50 mm^2 EDS (Oxford Instruments America Inc., Concord, MA) to determine composition.

To better understand the Pb removal mechanisms for Pitcher-3, a new filter was dismantled, and filter material was separated into 5 mL of resin and 5 mL of carbon-based material. Each of these separated materials was placed in a 20 mL, 12 cm x 15 mm polypropylene tube (Bio-Rad Laboratories, Hercules, CA) (Figure S4). Challenge water was gravity fed to each tube for 6 hours. A SEM stub was prepared for each filter material and allowed to air dry. SEM/EDS instruments detailed previously were used to analyze filtering material and determine Pb adsorption sites.

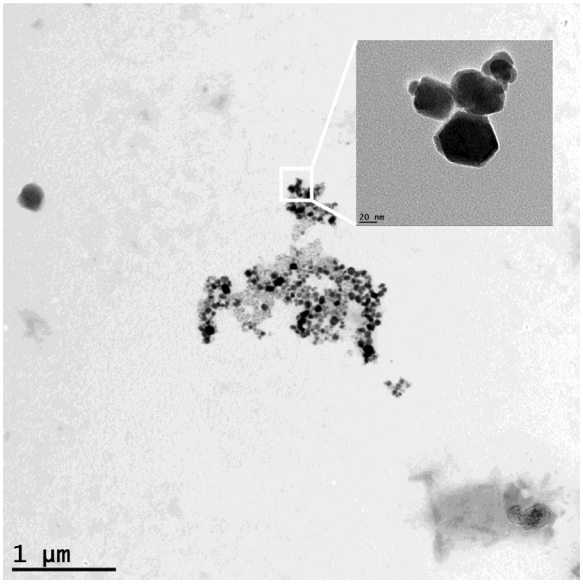


Fig. 4. TEM micrograph of Pb-PO4 nanoparticles in Pb-PO4 stock solution. TEM: Transmission electron microscopy.

3.5. Statistical analysis

Non-parametric statistical analyses (Kruskal-Wallis ANOVA) were performed in Statistica Version 13 (TIBCO Software, Palo Alto, CA). Differences were considered significant if $p < 0.05$, unless stated otherwise. Figures were generated in Sigmaplot Version 14.5 (Systat Software, San Jose, CA).

4. Results and Discussion

4.1. Pb-PO_4 stock solution

Pb-PO_4 stock solution was prepared daily, with an average (± standard deviation) pH of 7.49 ± 0.04, and total and soluble Pb concentrations of 5,283 ± 260 µg/L and 4.3 ± 10.4 µg/L, respectively, during all POU and pitcher filter tests (n = 12 stock solutions). The particulate and colloidal Pb fraction averaged 99.9% of the total Pb based on ultrafiltration (Fig. 3). Total and soluble PO_4 concentrations were 5.2 and 4.0 mg PO_4/L, respectively. Pb particle size based on dynamic light scattering (DLS) measurements averaged 0.083 ± 0.016 µm. From dynamic light scattering analysis, the average polydispersity index of the stock solution was 0.16 and ranged from 0.05 to 0.39, signifying low sample heterogeneity. SEM and TEM characterization revealed that the particles were hexagonal in shape (Fig. 4) and XRD analysis of the nanoparticles identified the particles as hydroxypyromorphite, $Pb_5(PO_4)_3OH$, which is consistent with previous work (Lytle et al. 2020a). TEM particle image analysis resulted in an average diameter of 0.038 ± 0.016 µm and sizes ranging between 0.017 and 0.095 µm. Based on the different size analysis methods, average size of the particles differed as there are intrinsic variations in how the measurements are carried out. For example, light scattering methodologies can be biased by particle clustering as dynamic light scattering measures Brownian motion and clustering is likely to prevent particles from following Brownian motion. Despite variability in particle size methods (dynamic light scattering, SEM, and TEM), all approaches concluded that Pb-PO_4 nanoparticles (i.e., <0.100 µm) were suspended in the stock solution. Comparison between particle sizes measured by dynamic light scattering, XRD, SEM and TEM is presented in Lytle et al. (2020a) for the same stock solution. Similarly, nanoparticles were larger when measured using dynamic light scattering than SEM/TEM, which is attributed to the agglomeration of nanoparticles.

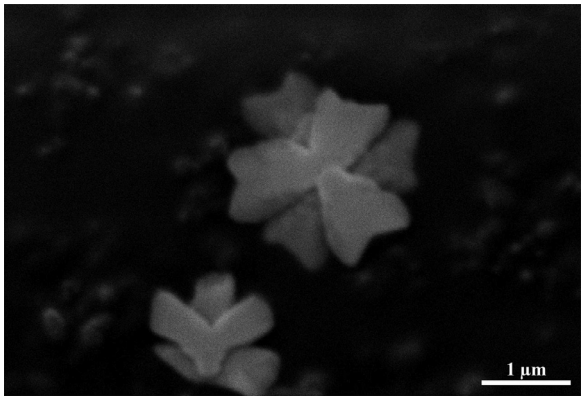


Fig. 5. SEM image of Pb particles formed according to NSF/ANSI-53 protocol at pH 8.5. SEM: Scanning electron microscopy.

In contrast, in the NSF/ANSI-53 test water at pH 8.5, particles were 5 orders of magnitude larger than the nanoparticles present in the Pb-PO_4 stock suspension (Fig. 5). Based on the chemistry of the NSF/ANSI-53 prepared challenge water, Pb carbonates were most likely to be formed. Pb carbonate particles formed in water have been reported to be much larger than the Pb-PO_4 nanoparticles particles reported here (Korshin et al. 2005, Noel et al. 2014).

4.2. POU filters

4.2.1. Challenge water characteristics

Pb size fractionation concentrations based on filtrations (total, particulate and colloidal > 0.2µm, colloidal <0.2 µm and soluble Pb) for the challenge water prior to filtration by POU filters are presented in Fig. 6. The average total and soluble Pb concentration of all POU filter challenge waters was 100.1 ± 3.6 and 1.1 ± 0.3 µg/L, respectively and was statistically similar across all experiments. The average particulate and colloidal Pb concentration of the challenge waters was 99.2 ± 3.8 µg/L (98.9% of total Pb). Of the particulate and colloidal Pb fraction, 53.7 ± 20.4 µg/L (53.5%) was colloidal <0.2 µm and the remaining was particulate and colloidal >0.2 µm in size based on filtrations. The Pb present in the challenge water was therefore primarily in the particulate and colloidal forms and specifically colloidal <0.2 µm form, which was consistent with the properties of the stock Pb-PO_4 solution (Fig. 4). The presence of nanoparticles in the challenge water was confirmed by SEM and TEM analysis (Fig. 7). Challenge water samples were collected throughout the experiment and showed that the suspension remained stable over the course of the experiment (Table S3). Lytle et al. (2020a) demonstrated that this challenge water remained stable over a 24-hour period. A control test run was performed to demonstrate that pumping challenge water through plumbing between the tank and POU filter did not change the characteristics of the challenge water suspension. Specifically, no Pb concentration losses were observed between the tank and the POU filter (Figure S2). Visual agreement of size and shape of Pb particles obtained using the SEM, combined with EDS for elemental composition determination (Figure S3) between tank and bypass water further confirmed that the test apparatus leading to the POU filters did not alter the properties of the nanoparticles (Figure S3).

Pb variability in the challenge water particulate and colloidal Pb >0.2 µm as well as colloidal Pb <0.2 µm was greater than it was for the particulate fraction. More variations in the Pb concentrations were observed for the samples filtered on 0.2 µm (49.2 ± 21.4 µg/L), than for the samples which were ultra-filtered (1.6

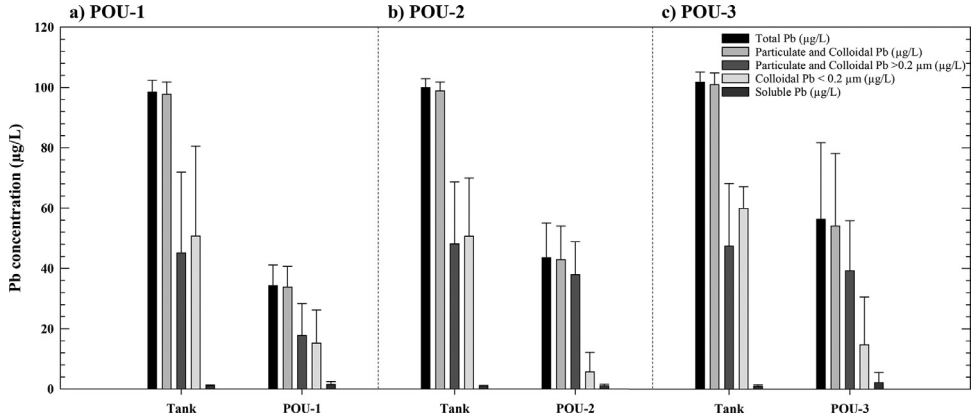


Fig. 6. Mean total, particulate and colloidal, particulate and colloidal >0.2 µm, colloidal <0.2 µm and soluble Pb concentration for challenge water (Tank) and water after filtration by faucet-mounted POU filters (POU). Whisker represents standard deviation. N=9 (triplicate experiments, 3 measurements during experiment).

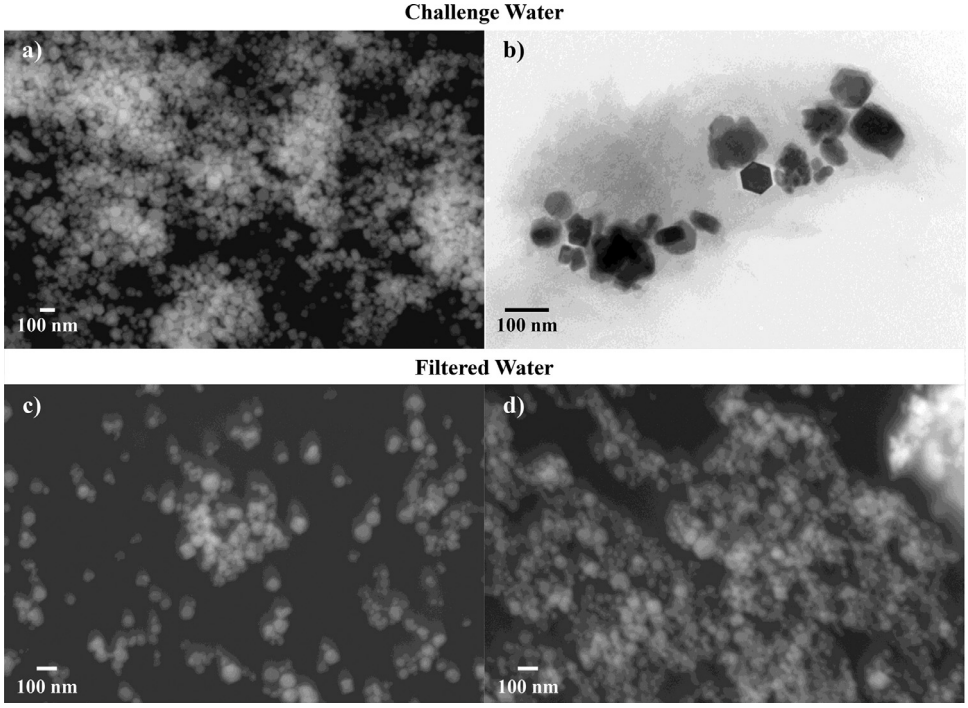


Fig. 7. SEM (a, c and d) and TEM (b) images from the challenge water prior to filtration (a and b) and after filtration by POU-2 (c) and by Pitcher-2 (d).

± 1.9 µg/L). The variability does not necessarily suggest that Pb particle suspensions are difficult to consistently produce. Indeed, SEM and TEM imaging confirmed the similarity in shape and size of nanoparticles generated in this study. Rather, it more likely illustrates the inherent limitations of using filters to fractionate particles. For instance, voids in the 0.2 µm filters are not homogenous in size/distribution nor do they have a nominal pore size of 0.2 µm but instead are constructed of etched pores (Figure S5). As Pb particles are pushed through the filter using a syringe, they can agglomerate (particle-particle interaction) and/or attach to the filter, which can prevent them from passing, despite a particle size smaller than 0.2 µm. Filtration results can also be influenced by the operator of the syringe filter with varying pressure applied on the syringe and rate of filtration.

The size of Pb particles in the challenge water in the tank could not be reliably measured with dynamic light scattering because the concentration was too low (target concentration of 100 µg/L) for an accurate determination. Determination of particle size by dynamic light scattering method could only be performed on the Pb-PO4 stock solution (target concentration of 5,000 µg/L). Challenge water suspensions of 100 µg/L were too dilute to reliably determine lead particle sizes by dynamic light scattering. For small particles, concentration must be sufficient to scatter the light, as the scattering intensity is proportional to the radius of the particles (Hassan et al. 2015, Shaw 2014, Stetefeld et al. 2016). However, SEM and TEM images (and EDS analyses) of particles suspended in the challenge water showed that the size and shape of Pb-PO_4 nanoparticles were consistent and uniform with the stock suspensions (Figs. 4 and 7). Specifically, the particles were hexagonal in shape and, individually, very small with most considered to be nanoparticles falling between 0.05-0.1 µm in size, and all appeared to be smaller than 0.2 µm. There were larger clusters of Pb particle agglomerations that, if present in the water (i.e., not formed as an artifact of sample preparation), could be removed through a 0.2 µm filter. These observations were consistent across all runs supporting the conclusion that variability in fractionation results can be attributed to filtration artifacts. The SEM/TEM findings were an important confirmation that consistent

water quality and Pb suspension properties were achieved in all tests.

Pb nanoparticle filter challenge water suspensions were generated in the laboratory according to previously reported procedures (Formal et al. 2021, Lytle et al. 2020a) and greatly differed from Pb particles formed according to NSF/ANSI-53 used to certify POU filters for Pb reduction (NSF/ANSI 2019a, b). Specifically, the challenge water contained Pb-PO_4 nanoparticles, as compared to relatively large Pb-carbonate particles generated under the NSF/ANSI 53 protocol (Figs. 4 and 5). Although laboratory-generated, the Pb nanoparticles in this study closely resembled particles previously identified in one community's drinking water (Lytle et al. 2020b) and those mineralogically predicted for a PO_4 treated system (Schock 1989, Trueman et al. 2018).

ASV analyzer Pb measurements performed at the time of sample collection were compared to corresponding results determined by ICP-MS/AES (Figure S6). ASV analyzer Pb results agreed well with ICP-MS/AES measurements (slope of 1.08 and an R^2 of 0.918). Discrepancies between the methods tended to increase as Pb concentration increased. Pb in the challenge water was well characterized by the ASV analyzer, in agreement with some previous studies (Doré et al. 2020).

4.3. Performance of POU filters for Pb-PO_4 particles reduction

None of the tested POU filters reduced total Pb concentration below 10 µg/L. Results were compared to a concentration of 10 µg/L, the NSF/ANSI-53 Pb certification threshold at the time of this study. Since completion of the study, the NSF/ANSI-53 certification threshold has been lowered to 5 µg/L (NSF/ANSI 2019b).

After filtration by the POU filters, mean total Pb concentrations ranged between 34.3-56.4 µg/L, with a maximum concentration of 88.4 µg/L for POU-3 and are not statistically different (Fig. 6). These concentrations are much greater than the previous and current Pb certification thresholds under NSF/ANSI-53 for reference although a different test water than the current study that includes a 50% higher Pb concentration was used. The Pb reductions achieved by the filters when using the Pb-PO_4 challenge water were strikingly lower (44.6-65.1%) than the reported >99% Pb particle reduction under the NSF/ANSI-53 certification protocol (Table 1).

The removal of Pb fractions differed among the POU filters, despite variability in the 0.2 µm filtrate, as previously noted. POU-1 filtered out most of the particulate and colloidal fraction (66.4%), followed by POU-2 (56.5% particulate and colloidal Pb reduction) and POU-3 (46.4% particulate and colloidal Pb reduction). The POU filters did not decrease the already low concentration of soluble Pb present in the challenge water.

In general, although the filters were not operated until recommended lifespan, the concentration of Pb passing the POU filters did not substantially change with increasing volume of water volume treated (Table S3), especially when considering filtration variabilities. Removal efficiency did not improve over the course of the experiments (Table S3), as might be observed if retained particles blocked filter pore voids with time. Since a fraction of the Pb nanoparticles was trapped in the filters, there was possibility that with time or longer testing, Pb nanoparticle reduction efficiency would have improved as void spaces decreased. It is likely due to the filters were not run to their rated capacities after filtering 58 L of challenge water. Specifically, the three POU filters were only operated to 7.5-15.1% of their reported filter capacities (Table 1). However, a rather notable change was observed for POU-3 between the beginning of the experiment (1L filtered) where, on average, 64.9 µg/L remained in the filtered water versus 51.1-53 µg/L at the middle/end (29-55 L filtered) of the experiment (Table S3). Colloidal Pb <0.2 µm concentrations were the lowest at the end of the experiment for this filter. The primary nanoparticle removal mechanism by porous activated carbon block filters, the main component of all but one of the devices evaluated in this work, is to physically retain Pb-containing particles in the low void volumes between the carbon particles (Kuennen et al. 1992, Reed and Arunachalam 1994). The pore size of solid carbon block filters ranges between 0.5-1 µm (500-1000 nm) (US Environmental Protection Agency 2006). Although being porous, the pores are small enough to restrict relatively large Pb particles (e.g., NSF/ANSI-53 generated Pb particles) from passing. However, dispersed Pb nanoparticles can pass through as demonstrated in this work. Specifically, a large fraction of Pb-PO_4 nanoparticles ranging between 17- 95 nm passed through certified POU filters. SEM images confirmed that nanoparticles passed through all of the POU filters (Figs. 7, 8). The nanoparticles were identical to those of the challenge water for all POU filters tested. Flow rates were generally slightly lower at the beginning of each experiment, presumably as voids within the filters were cleared of additional fines from filter production or trapped air (Table S2). There was variability in the flow rates between test runs. Pressure remained stable within and between triplicate experimental runs, except for the second replicate run of POU-3 which experienced more variable pressure for an unexplained reason (Table S2). The experimental apparatus was not designed to simultaneously fine tune flow rates and pressure. The apparatus was able to maintain flow and pressure within manufacturers' specifications, which was the goal.

The differences in removal of the different Pb fractions could be attributed to the different composition and construction of the POU filters. All POU filters tested were dominantly composed of carbon-blocks, but analysis by SEM/TEM revealed that the composition of the POU filter media differed (Table S4). Differences in results could also be explained by different flow rates (Table S2) and pressures during operation, as well as different structure of the filter media and the housing (Table 1). Faucet-mounted filters were made of solid block activated carbon which contains small activated carbon particles fused with ion exchange or sorption media which is responsible for metals removal (Deshommes et al. 2010).

4.4. Pitcher filters

4.4.1. Challenge water characteristics

Characteristics of the water used to challenge pitcher filters were consistent with waters used to challenge POU filters. The total Pb concentration in challenge water prepared to test the POU filters averaged 101.9 ± 7.8 µg/L, and was statistically similar (Fig. 9). Soluble Pb concentration (only available for Pitcher-1 and Pitcher-2) averaged 2.1 ± 2.5 µg/L (1.9% of total Pb), total particulate and colloidal Pb concentration averaged 99.9 ± 6.2 µg/L (98.1% of total Pb), and colloidal Pb <0.2 µm concentration was 43.3 ± 22.3 µg/L (43.4% of total Pb). Average size of particles measured by dynamic light scattering was 0.083 ± 0.016 µm, as measured in the Pb-PO_4 stock solution. Over the course of the experiment, the characteristics of the challenge water remained stable. Notable Pb fraction differences in challenge water were not observed after up to 8 hours. Stability of the challenge water was in agreement with the work of Lytle et al. (2020a).

4.4.2. Performance of pitcher filters for Pb particles reduction

Pitcher-3 was the only filter to consistently decrease concentrations below 10 µg/L but it was not able to meet the new 5 µg/L certification target. The total mean Pb concentration in the challenge water of 105.3 ± 9.6 µg/L (Fig. 9c) was reduced to 7.5 ± 1.5 µg/L, which is significantly lower than filtered water from Pitcher-1 and Pitcher-2. The percentage reduction in total Pb obtained using the challenge water was slightly lower than the vendor reduction claims based on NSF/ANSI-53 test conditions (Table 1). Nearly all

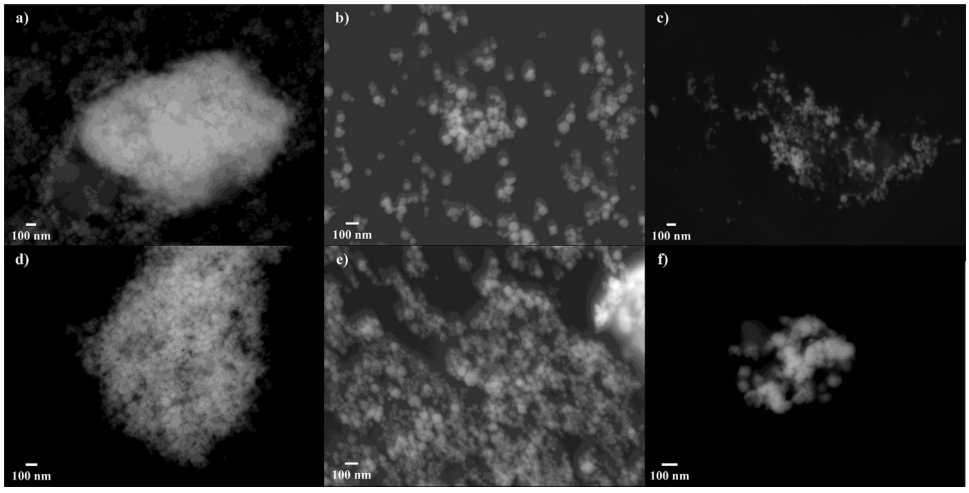


Fig. 8. SEM images of particles after filtration by faucet-mounted POU filters (a, b and c) and pitcher filters (d, e and f); a: POU-1, b: POU-2, c: POU-3, d: Pitcher-1, e: Pitcher-2, f: Pitcher-3. SEM: Scanning electron microscopy.

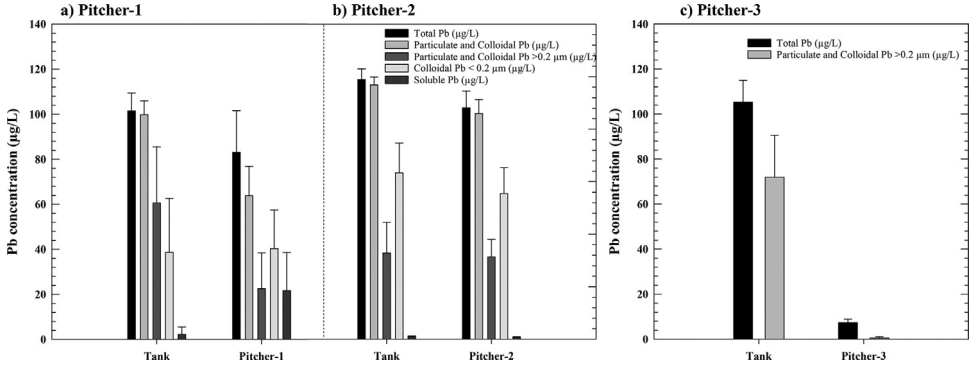


Fig. 9. Mean total, particulate and colloidal, particulate and colloidal >0.2 µm, colloidal , colloidal <0.2 µm and soluble Pb concentration for challenge water (tank) water and water after filtration by Pitcher-1 and Pitcher-2 (a) Mean total and particulate and colloidal >0.2 µm Pb concentration for Pitcher-3 (b), soluble Pb data was not available. Whisker represents standard deviation. Pitcher-1: N=12 (quadruplicates, 3 measurements during testing), Pitcher-2 and -3: N=9 (triplicates, 3 measurements during testing).

of the Pb that passed the pitcher filter (7.0 ± 1.3 µg/L) was retained on a 0.2 µm filter. In contrast, 31.6% of total Pb in the challenge water was retained on a 0.2 µm filter, and this fraction increased by over 3-fold (to 94.4%) after filtration by the pitcher filter. Pitcher-3 removed a consistent amount of Pb through the entire challenge test (Table S3) as the reduction efficiency of the filter to remove Pb remained consistent with volume of water treated. The pitcher reached 35.2% of the reported treated water volume capacity, whereas Pitcher-1 and Pitcher-2 only treated 13.2% and 4.4% of its reported capacity, respectively.

Similar to the POU filters, Pitcher-1 and Pitcher-2 failed to decrease Pb concentrations of the challenge water to levels even close to 10 µg/L, allowing Pb nanoparticles to easily pass (Fig. 8). After filtration by the pitcher filters, mean total Pb concentration was 83.1 ± 18.5 (19.3% reduction) and 88.2 ± 6.4 µg/L (10.9% reduction) for Pitcher-1 and Pitcher-2, respectively. Results obtained by Pitcher-1 and Pitcher-2 are statistically similar for total Pb. A perplexing increase in soluble Pb was observed in water filtered by Pitcher-1, which cannot conceptually be explained by the slight pH increase through that filter

Differences in the make-up materials and structure of the pitcher filters likely explain Pb reduction efficiency differences and the changes observed in the Pb fractions following filtration (Tables 1 and S4). Pitcher-1 was made of an ion exchange resin mixed with activated carbon, whereas Pitcher-2 was largely made of activated carbon and a fibrous matrix to hold the media in place. Pitcher-3 was the most complex, made of a layer of granular activated carbon followed by dual ion exchange resin. The materials present in the tested pitcher filters were more diverse than in the faucet POUs, with organic resin present in 2 of the 3 units. Different forms and amounts of activated carbon were present in the units, either as loose material in the casing of the filter or embedded in a membrane.

To understand Pb removal mechanisms associated with Pitcher-3, a new filter unit was dissected. The two different media (carbon-based material and dual cation/anion exchange resin) were then separated to perform additional capacity challenge testing on each media component independently. This simple experiment was not intended to replicate the earlier pitcher filter experiments, but rather to understand where Pb was retained by the Pitcher-3 filter in a preliminary way. Because the filter's two media were separated, Pb reduction efficiency was expected to be different than when testing an intact filter. Also, a small amount of media (5 mL) was used in this test, compared to an intact filter. As only 35% of the capacity of the filter was reached at the end of a normal experiment in the laboratory, the goal here was to exhaust the filtering material, to understand the role of each media in removing Pb from the challenge water. Specifically, filtered total Pb concentration increased from 56.1 µg/L at the beginning of the experiment to 99.7 µg/L at the end, from a challenge water with a Pb concentration of 106.0 µg/L. Water was filtered until no Pb reduction could be observed based on bench analysis (ASV analyzer) of Pb concentrations. The carbon fraction of the filter media removed 17.3 µg/L of Pb at the beginning of the experiment, compared to 49.9 µg/L

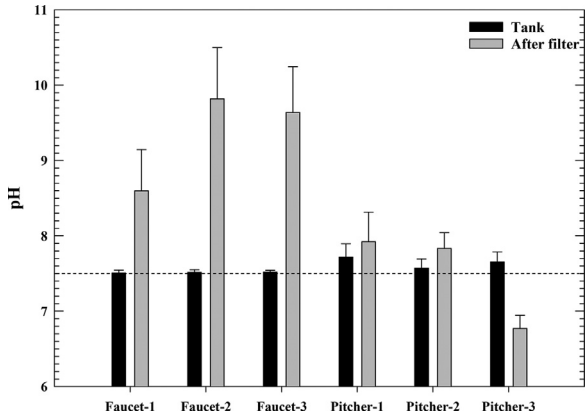


Fig. 10. Mean pH before and after filtration by faucet-mounted POU filters and pitcher filters. Whiskers represent standard deviation. N=103.

by the resin, suggesting that Pb reduction by Pitcher-3 was mostly achieved by the resin portion of the media. Additionally, SEM images coupled with EDS demonstrated that Pb was removed from the water by the dual-resin and that Pb was bound mostly to one of the resins (Figure S7). Indeed, Pb was observed on one type of resin beads, whereas on the other type, Pb could not be observed. This investigation was preliminary in nature and the results suggest a more detailed study is warranted.

4.5. Other water quality parameters

The pH of challenge waters increased after passing through all POU filters, from mean pH values of 7.5 ± 0.03 (Fig. 10) to between 8.6 and 9.8, with the highest pH measured for POU-2 at the beginning of the experiment, but differences are not statistically significant (Table S3, Fig. 10). For POU filters, initial pH was also higher than measurements conducted in the middle or end of the experiment, since pH was decreasing as increasing volumes of water were filtered. For the pitcher filters, mean pH varied between 6.8 and 7.9, which is significantly lower than for the POU filters, with the lowest value measured in Pitcher-3. The different changes in pH observed between water filtered by the POU and pitcher filters is attributed to the different filtering media (Table 1). The filtering media of the pitcher filters consisted of activated carbon and/or ion exchange resin, whereas the point-of-use filters mainly consisted of solid block activated carbon impregnated with natural zeolite resin. The decrease in pH observed through Pitcher-3 was attributed to bicarbonate ions being removed through the anion exchange resin in the mixed ion exchange resin bed (Crone et al. 2019, Carrière et al. 2011, Bauman and Eichhorn 1947). However, caution should be exercised when evaluating pH measurements in low conductivity samples, which would be the case for challenge water filtered by Pitcher-3.

For Pitcher-3, soluble Pb concentrations could not be obtained due to contamination of the samples from the stir cell of the ultrafilter. Filtering the challenge water by Pitcher-3 dropped the pH to between 6.6 and 7.1 (mean = 6.8) in the filtrate. Investigations showed that presumably adsorbed Pb was released from the stir cell at pH below 7. Preliminary testing showed a release of the Pb adsorbed in the stir cell of the ultrafilter when pH is below 7. Of the devices tested, Pitcher-3 was the only one that decreased the pH of the challenge water, whereas the other POUs increased the pH of the filtered water (Fig. 10).

Initially, the drop in pH to 6.8 was thought to be associated with the pitcher's ability to remove Pb by dissolving Pb-PO_4 particle (Schock et al. 1996) within the filter and subsequent removal of dissolved Pb. One of the Pb removal mechanisms of Pb in granular activated carbon is by adsorption of free metal ions (Kuennen et al. 1992), which would increase as the pH of the solution decreases. A follow-up test with POU-1 at pH 6.5 did not affect the performance of POU-1 with similar Pb concentrations of 34.3 µg/L and 33.7 µg/L, respectively. Thus, the reduction of Pb by Pitcher-3 cannot solely be explained by the drop in pH of the bulk water.

Passing challenge water through the POU and pitcher filters increased the concentration of several inorganic elements—most notably Fe, Mg, S and Zn—which were observed in the virgin filter media (Table S4). All filters increased the effluent water Fe concentration, with Pitcher-1 yielding the highest mean concentration (0.129 ± 0.243 mg/L vs. 0.015 ± 0.020 mg/L for the challenge water). Mg and S concentrations were only increased by the faucet-mounted POUs, with the highest mean concentrations for POU-3 (0.065 ± 0.059 mg Mg/L vs. 0.007 ± 0.003 mg Mg/L for the challenge water). Increases in Fe, Mg, S and Zn are explained by the presence of trace contaminants on the filter media, presumably associated with the product manufacturing process. Concentrations of P remained stable, with slight increases/decreases for the POU filters tested, except for Pitcher-3.

4.6. Implications

Although this work demonstrated a limitation of certified POU and pitcher filters to effectively reduce Pb nanoparticles, the conditions under which such particles may be present likely represent an extreme case. The effectiveness of faucet-mounted POU filters and pitcher filters to reduce Pb in drinking water and provide protection until Pb sources are removed has been demonstrated by others (Bosscher et al. 2019, Pieper et al. 2019, Purchase et al. 2021, Deshommes et al. 2010). This work demonstrated Pb nanoparticles can pass through POU and pitcher filters certified to remove particulate Pb, but the findings were not necessarily unexpected. Certification test water Pb particles are much less challenging to remove due to their relatively large size and their behavior does not reflect that of much smaller Pb nanoparticles, which are fine enough to pass through the pores of carbon-based filter blocks. Secondly, the Pb particulate challenge condition in this work likely represents an extreme case where very small homogenously dispersed Pb nanoparticles were present in a relatively simple aqueous background chemistry. Despite being an extreme challenge, the filters still managed to reduce Pb by 10.9-92.9%.

The outcome of this work was consistent with filter effectiveness concerns initially raised in Newark where similar appearing Pb-PO_4 nanoparticles were reported to have passed POU and pitcher filters (CDM Smith 2019, Lytle et al. 2020b), and together clearly raises the need to perform future work in two areas. First, POU and pitcher filter certifiers should consider exploring alternative Pb particle test suspensions that are more representative of the greater challenging particles. Pb particles come in many shapes and sizes, the latter clearly being important to filter performance. Lytle et al. (2020a) detailed a "recipe" for producing stable Pb-PO_4 nanoparticles as a potential starting point for identifying a more challenging case. An outcome may be that filter manufacturers consider reevaluating filter designs. Secondly, there needs to be a broader and regular examination of the nature of Pb particles formed in drinking water systems and isolated from consumer's tap water. There is very little information available on the subject. The nature of the Pb particles should be related to Pb source, scale properties, water quality, corrosion control practices and other considerations to establish a better understanding of conditions that might produce Pb nanoparticles. Improvements in sampling strategies, protocols and analysis techniques should also be considered.

5. Conclusion

In this study, appropriately certified POU and pitcher filters for Pb reduction in water reduced Pb in Pb-PO_4 particle challenge suspensions containing 98.5% particulate and colloidal Pb but to nowhere near the NSF/ANSI certification target of 10 µg/L at the time of the study with the exception of one pitcher filter. On average, 45% of the total Pb (approximately 100 µg/L) passed through the POU and pitcher filters, and the passing Pb was in the particulate and colloidal form (dominantly nanoparticles). The findings are not necessarily surprising, given that Pb particles produced under the NSF/ANSI protocol are relatively large (700-1800 nm) Pb-carbonate particles that would not pose the same filterability challenge. Although this work was not performed under NSF/ANSI certification protocols, all filters were operated within manufacture provided specifications and baseline water quality fell within the bounds of drinking water supplies. Of the pitcher filters tested, only Pitcher-3 decreased total Pb concentrations below 10 µg/L but not below 5 µg/L (average of 7.5 µg/L), which appeared to be tied to attraction between the ion exchange resin and Pb-PO_4 nanoparticles. Given the results of this study showing that small Pb-PO_4 particles similar to those reported to be present in some community water distribution systems (Lytle et al. 2020b) passed filters, there is an obvious need to better understand what drinking water quality conditions and mechanisms promote the formation and mobility of such particles in drinking water systems. Such an understanding will help target locations where additional Pb sampling may be considered and filter device effectiveness explored. Lastly, the results of this work should be considered by POU and pitcher filter certifiers and serve as the basis to consider alternative particle challenge conditions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors acknowledge Michael R. Schock, Michael K. DeSantis, Eugenia Riddick and David Wahman for advice while carrying laboratory work and for sample analysis. The authors would also like to acknowledge Tom Speth (ORD) and Nathan Delano (USEPA Region 8) for their technical reviews of the manuscript. This project was supported in part by an appointment to the Research Participation Program at the Office of Research and Development, USEPA, administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the US Department of Energy and USEPA. This article has been reviewed in accordance with the EPA's policy and approved for publication. Any opinions expressed in this article are those of the author(s) and do not, necessarily, reflect the official positions and policies of the USEPA. Any mention of products or trade names does not constitute endorsement or recommendation for use by the USEPA.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2021.117285.

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