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An evaluation of properly operated NSF/ANSI-53 Pb certified drinking water filters in Benton Harbor, MI

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Abstract

Communities across the United States and particularly in the Midwest continue to grapple with the complications associated with aging infrastructure. This includes the presence of lead (Pb)-bearing plumbing components such as lead service lines, downstream galvanized iron pipes, and Pb/tin solder. The community of Benton Harbor, MI, experienced six Pb action level exceedances between 2018 and 2021, leading to increasing community concern and a request from the state of Michigan for the US Environmental Protection Agency involvement. Between 9 November and 17 December 2021, US EPA Region 5 and Office of Research and Development, along with the state of Michigan, conducted a water filter efficacy and Pb-nanoparticulate (<100 nm) study to evaluate the performance of NSF/ANSI-53 Pb-certified drinking water filters and the presence of nanoparticulate. In this study, a total of 199 properly installed and operated drinking water filters (combination of faucet mounted and pitcher) were tested in their residential locations. One hundred percent of the water filters were found to perform to the standard to which they were certified, with filtered drinking water Pb concentrations below 5 ppb (maximum observed was 2.5 ppb). In addition, Pb particulate was identified; however, discrete Pb-containing nanoparticles were not widely found or identified.

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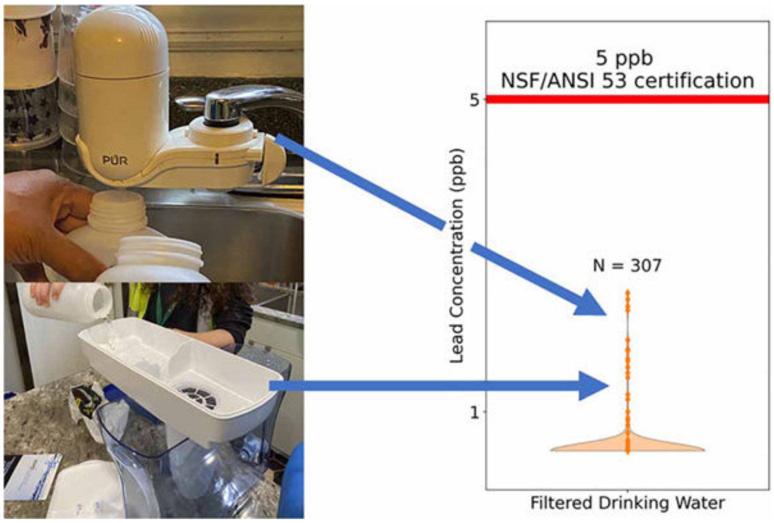
CONFLICT OF INTEREST
The authors declare there is no conflict.

Graphical Abstract



Keywords

certified water filters; community; lead in water; NSF/ANSI-42; NSF/ANSI-53; lead-nanoparticulate

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1. INTRODUCTION

The recent drinking water crises of Flint, Michigan, and Newark, New Jersey, have highlighted the failing drinking water infrastructure of the United States (US) and represent the challenges that many communities are still facing across the United States with minimizing the lead (Pb) content of their drinking water. In 2018, Benton Harbor, Michigan, became another example of a system that was having difficulty in minimizing Pb in their drinking water. From September 2018 to June 2021, Benton Harbor had six lead and copper rule (LCR) Pb action level exceedances (ALEs) (Supplemental Figures 1 and 2). As in other aging Midwestern communities, many homes in Benton Harbor were served by lead service lines (LSLs) and contained other potential sources of Pb such as galvanized iron pipes, Pb/tin (Sn) solder, and brass fixtures and fittings (EGLE 2022). Prior to the ALEs beginning in 2018, Benton Harbor had not established any corrosion control treatment (CCT). However, as a result of the ALEs, the city, with approval from the State of Michigan Department of Environment, Great Lakes and Energy (EGLE), began adding a blended phosphate corrosion control inhibitor in March 2019 (EGLE 2019; EGLE 2020).

As a temporary measure, Benton Harbor residents were able to pick up free drinking water filters (pitcher and faucet-mounted water filters) and replacement cartridges with NSF/ANSI-53 Pb reduction certifications from the Berrien County Health Department (BCHD) beginning in February 2019. All water filters distributed were certified in accordance with NSF/ANSI-53 for Pb removal, and faucet-mounted water filters had an additional NSF/ANSI-42 certification for class I particulate (0.5− < 1 μm) reduction (NSF/ANSI 2021a, 2021b). It should be noted that the NSF/ANSI-53 certification for Pb removal (at the time of this study) required the filtered water effluent concentration to be ≤5 ppb Pb, which is the same concentration that the US Food and Drug Administration requires for bottled water, 21 CFR 165.110(b)(4)(iii)(A) (NSF/ANSI 2021b; US FDA).

Residents were instructed to follow the individual manufacturer's instructions for the operation, maintenance, and use of their specific drinking water filter (BCHD 2024). Previous studies have detailed the certification requirements/laboratory testing along with the general structure/composition of drinking water filters (Bosscher *et al.* 2019; Doré *et al.* 2021; NSF/ANSI 2021b; Kutzing *et al.* 2022; Tang *et al.* 2023). The certification process for water filters via NSF/ANSI-53 requires that the certifying laboratory prepare and operate the filter according to manufacturer specifications during the chemical reduction capacity testing (NSF/ANSI 2021b). NSF/ANSI-53 certification then requires that manufacturers include detailed instructions to be provided with each filter system for installation, operation, and maintenance of the water filter (NSF/ANSI 2021b).

Due to Benton Harbor's repeated Pb ALEs, citizen concerns mounted and culminated in a Safe Drinking Water Act petition sent to the US Environmental Protection Agency (EPA) on 9 September 2021 (Petitioners 2021). One of the actions requested by the petitioners was for EPA's Office of Research and Development (ORD) to conduct a filter study to verify that NSF/ANSI-53-certified filters are effective at reducing the Pb levels present at Benton Harbor's taps. Two main factors brought water filter efficacy into question for the petitioners, the first being some unfiltered water samples taken in Benton Harbor had >150 ppb Pb (including three first draw LCR samples collected in 2021, with 469, 605 and 889 ppb Pb). The third-party laboratory certification of NSF/ANSI-53 for Pb ensures certified treatment units are tested and pass the Pb reduction criteria, but the influent challenge waters used for the test do not contain Pb in excess of 150 ppb and are not representative of all drinking water chemistries that a unit may encounter (NSF/ANSI 2021b). This can lead to an erroneous conclusion that NSF/ANSI-53-certified filters will not perform as certified when challenged with water containing >150 ppb total Pb. However, the previous research has shown that certified water filters are effective at reducing Pb even at concentrations well above the influent NSF/ANSI-53 Pb challenge water of 150 ppb because in drinking water in which >150 ppb Pb is observed, Pb in excess of 150 ppb is generally in the particulate form, which is easily physically removed by NSF/ANSI-53-certified water filters (AWWARF-TZW 1996; Hayes 2010; Hayes 2012; Bosscher *et al.* 2019; Purchase *et al.* 2021; Kutzing *et al.* 2022). However, the ability for Pb nanoparticulate (<100 nm) to pass through certified water filters is not evaluated by the current NSF/ANSI-53 and 42 standards (Kutzing *et al.* 2022).

This led to the second petitioner concern for the potential formation of Pb-orthophosphate nanoparticles due to the implementation of the system's blended phosphate CCT in 2019, which would be so small that they would not be removed by filters (Zhao *et al.* 2018; Formal 2021; Locsin *et al.* 2023). The unique formation of Pb-orthophosphate nanoparticles and their potential to pass through NSF/ANSI-53- and NSF/ANSI-42-certified pitcher water filters and faucet-mounted water filters have been documented in the laboratory and the field (Lytle *et al.* 2020; Doré *et al.* 2021). The original fieldwork that identified this possibility occurred during the Newark, NJ lead in drinking water crisis.

There are distinct differences between the Pequannock service area in Newark, NJ, and Benton Harbor, MI, namely, water quality and Pb pipe scale composition. For example, Benton Harbor has higher total alkalinity and calcium concentrations than Newark (Table 1 and Supplemental Table 1). Then the pipe scales in the Pequannock service area were also dominated by decomposing PbO_2 (Pb(IV)), which will not react directly to phosphate CCT, compared to Pb (II) carbonates in Benton Harbor (similar to Flint, MI pipe scales), which are capable of reacting to phosphate CCT (DeSantis *et al.* 2020). Thus, certified water filters in Benton Harbor were expected to perform similarly to what had been observed years prior in Flint, MI (Bosscher *et al.* 2019).

However, out of an abundance of caution, a water filter efficacy study was designed and implemented to evaluate the effectiveness of distributed NSF/ANSI-53 certified water filters to remove Pb from Benton Harbor's drinking water and to characterize the nature of any leaded-particulate present. This article describes the EPA ORD-developed statistical design, framework, and sampling protocol that provides a template for implementation, if future community drinking water filter efficacy studies are deemed necessary.

Two critical components of the information collected to determine conditions necessary for effective Pb removal by household tap water filtration units include particulate analysis and documenting proper installation and operation of filter units tested. Specifically, speciation of Pb (soluble versus particulate) and characterization of Pb-containing particulates (size and elemental composition), where present, in the water was completed. These data were necessary to assess whether water filters in the community were removing Pb consistent with certification expectations, to understand Pb removal effectiveness, and to find whether Pb nanoparticles were persistent in the system. Proper installation and operation of the water filter, as specified in the manufacturer's instructions, was essential to drawing community-wide conclusions because of how the water filters are prepared and treated during the laboratory NSF/ANSI-53 certification process. It is imperative that any field evaluation of water filters follow those same manufacturer specifications to ensure systems are operating within the bounds in which they were certified.

2. METHODS

2.1. Statistical study design

The objective for the statistical sample size calculations was to determine the 95% lower confidence bound of a 95% effective rate (95% of water filters performing as certified). An initial estimate of the percentage of water filters performing as certified was needed to calculate the sample size. This effective performance rate was selected by evaluating previous water filter studies in Flint, MI, and Newark, NJ, where the proportion of water filters performing at or below the certification standard was 98–100%. Therefore, the statistical design for the study assumed a 98% effectiveness rate ($\hat{p} = 0.98$) for the water filters in the community, which resulted in the need to collect samples from 200 unique locations to have a statistically representative sample size to demonstrate that 95% of water filters are effective in this community at a 95% confidence level.

The study design also took into account the different types of water filters deployed and available to residents in Benton Harbor and was planned such that the total number of samples collected would be divided proportionally across the water filter types. Although Brita® faucet-mounted water filters and PUR® pitcher water filters were noted as having been available to Benton Harbor residents, while EPA was on the ground in the Fall of 2021, PUR® faucet-mounted water filters and ZeroWater® pitcher water filters were the most prevalent and readily available. Records provided by the BCHD indicated that of the water filters being provided to the residents of Benton Harbor, 89% were faucet mounted and 11% were pitcher water filters. Statistical counsel from Neptune and Company, Inc., suggested sampling the same percentage of water filters as BCHD had provided, which equated to 178 (out of 200) faucet-mounted water filters and 22 (out of 200) pitcher water filters at a minimum, and to collect additional samples from pitcher water filters if possible.

An evaluation of water filter performance in the community and adherence to the sample design was assessed via the Clopper-Pearson ‘exact’ binomial equation (Clopper & Pearson 1934). Unfiltered and filtered metal concentrations resulting from the water filter effectiveness study were analyzed via the $1-\alpha$ (probability) confidence interval for μ (mean of the population) based on the Student’s t distribution (Student 1908; Casella & Berger 2001). Confidence intervals provided the range in which there is 95% confidence level that the true mean of the sample concentration was captured.

2.2. Sampling protocol

The study was designed to evaluate whether properly certified and operated faucet-mounted water filters and pitcher water filters reduced Pb to at or below 5 ppb in a community setting. As Pb is a variable contaminant in drinking water, due to the variety of potential sources along a plumbing path, it is impossible to collect true ‘paired’ samples (Riblet *et al.* 2019; Triantafyllidou *et al.* 2021). As the parcel of water collected by-passing the filter is not the same as the parcel of water that is passed through the filter. A statistically representative sample pool was integral in ensuring the resulting data were representative of a variety of field Pb concentrations. Additional detail regarding the inability to collect true paired samples in a community drinking water filter study is presented in Section 3.

Single-family residences served by the Benton Harbor Water Plant, with BCHD-provided NSF/ANSI-53 and 42 certified PUR® or Brita® faucet-mounted water filters and NSF/ ANSI-53 certified ZeroWater® pitcher water filters, were targeted for this sampling effort (Table 2). Residences that voluntarily allowed sampling for the water filter study were confirmed to not have whole-house filters, water softeners, or reverse osmosis units on the kitchen faucet. Schedulers contacted residents with known/assumed LSLs or those with previously high Pb levels (based on LCR compliance and Michigan Department of Health and Human Services (MDHHS) sampling). Samples were collected in accordance with EPA’s Quality Assurance Project Plan and sampling protocol from 9 November 2021 to 17 December 2021 (USEPA 2021). Only cold water samples were collected, and aerators when present were unaltered.

Initial sample collection occurred with random stagnation times as reported by the residents. After a review of preliminary data, it was noted that most of the stagnation times reported were 1 h or less. Beginning with samples collected on 29 November 2021, schedulers encouraged residents to stagnate their water prior to the sampling visit, and all residences who received a scheduled appointment time on or after 29 November 2021 were requested to stagnate their water for 6+ h before the sampling visit. For this study, properly operated water filters included those that had a green or yellow indicator light when the samples were taken (or ≤006 mg/L total dissolved solids (TDS) for ZeroWater® filters) and only had cold water run through them. The color of the device's light is a manufacturer-created indicator that gives the consumer an idea of filter lifespan. A green light/indicator means the filter is within its functional lifespan; yellow means the filter will need to be changed soon; and finally, red means the filter must be replaced. In this study, PUR faucet filters displayed red lights after the filter reached 100 gallons (379 L) filtering or 90 days of use, whereas Brita faucet filters displayed red lights after the filter reached 100 gallons (379 L) filtering.

While properly operated water filters were the main focus of this study, the sampling team tracked inadequately maintained water filters (i.e., red or malfunctioning light, hot water was used through the water filter, or TDS reading for ZeroWater® water filters >006 mg/L), and the water was still sampled through these water filters. Pb data of filtered water from inade-quately maintained water filters is not included in this article; however, the number of excluded samples was tallied and categorized (Supplemental Table 2). When compromised water filters were used by residents, the sampling team provided water filter education and replaced the water filter (following manufacturer's instructions).

2.3. Faucet-mounted water filter sampling procedure

First, with the water filter in the on position, the cold water tap was turned on and the first 5 s of filtered water was collected in a 500 or 250 mL wide-mouth High Density Polyethylene (HDPE) bottle. This water sample is not considered proper filter use because according to the faucet-mounted water filter operation instructions, the water obtained at first 5 s should be discarded; however, this water sample was analyzed for metals (results not included in this article). Immediately following the 5 s flush sample, without turning the water off and taking care not to spill, a 1 L sample of filtered water was collected in a widemouth HDPE bottle. Next, the water filter was switched to the bypass mode without turning the water off, and a 1 L sample of unfiltered water was collected.

2.4. Pitcher water filter sampling procedure

Any water that was found to be in the pitcher water filter on sampler arrival was transferred to another container so that the pitcher was completely empty to start. The cold water tap was turned on, and the first-drawn 1 L sample was collected in a 1 L wide-mouth HDPE bottle. Then without turning off the water, a second 1 L sample was collected without allowing any water to spill. The first liter of water that was collected was turned 'end over end' five times to mix and then poured into the empty pitcher water filter. Once the sample passed completely through the water filter, the filtered water was poured into a new sample bottle for laboratory analysis.

2.5. Service line water filter study samples

After a review of preliminary data, beginning with samples collected on 2 December 2021, an additional two 1 L samples were collected during the water filter sampling visits. These additional samples aimed to collect water that had stagnated in contact with the service line. Based on the review of past MDHHS sequential profile Pb data collected from homes in Benton Harbor, water in contact with the service line was approximated to be at the seventh liter. The intent was to find higher Pb concentrations to challenge the water filters by targeting water that had a greater chance to capture the Pb contribution directly from known or assumed LSLs. After the first unfiltered water sample was collected, instead of turning the water off, the cold water was allowed to run (if a faucet-mounted water filter, the filter was in a bypass mode) while filling and wasting 1 L sample bottles until 4 L of water had been flushed. Then filtered service line and unfiltered service line water samples were collected.

2.6. Particulate analysis

As part of a concurrent sequential profile sampling study in Benton Harbor, targeted 1 L water samples were collected (wide-mouth HDPE bottles) within the profiles for the purpose of characterizing Pb particulate. All homes in the sequential sampling study had previously been sampled at least once by MDHHS. The historical profiles from each home were used to determine which liter from the residence should be targeted within the sequential profile for particulate analysis (previous volume(s) with the highest Pb concentration). Sequentially profiled homes stagnated their water for at least 6 h prior to sample collection. The targeted 1 L sample then underwent multiple filtrations: 0.45 μm syringe, 0.20 μm syringe, and a 30 kDa ultrafiltration step to determine the soluble fraction of Pb.

Pb particle analysis for size, morphology, and elemental composition was conducted using transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). TEM samples were prepared back at the field laboratory by collecting water from the targeted 1 L sample bottle in a disposable pipette and placing a drop of water on a formvar/carbon-coated copper TEM grid. The water drop was allowed to evaporate under ambient conditions so that any particles in the water were left behind on the grid. The samples were then examined using a JEOL JEM 2100 TEM with accelerating voltage of 200 kV coupled with an Oxford X-max® 80 mm^2 silicon drift detector (SDD) EDS system running AZtec® software (Oxford Instruments America Inc., Concord, MA).

In the field once the ultrafiltration process was complete, samples for SEM analysis were prepared by affixing a carbon adhesive tab to an SEM stub specimen mount. The carbon adhesive was used to collect particles from the ultrafiltration discs by lightly dabbing the adhesive on the surface of the disc. Then the solids were directly analyzed with a JEOL JEM 7600 Field Emission SEM at a working distance of 8 mm and accelerating voltage of 15 kV (JEOL USA Inc., Peabody MA). The elemental composition of particles was identified using an Oxford X-max® 50 mm^2 SDD EDS system, and spectra were analyzed using AZtec® software (Oxford Instruments America Inc., Concord, MA).

2.7. Water analysis

Water samples collected for metals analysis were field preserved with nitric acid to pH < 2. Water samples collected for assessing water quality parameters and total organic carbon (TOC) were placed in a cooler with ice at a temperature of <6 °C (Supplemental Table 3 for a table of methods and preservation requirements). TOC samples were also field preserved at pH < 2 using sulfuric acid. All water samples were taken by courier to EPA Region 5's Chicago Regional Laboratory (CRL) in Chicago, Illinois, within 48 h for analysis. CRL analyzed samples by EPA Methods 200.8 (Pb, Cu, Zn) and 200.7 (Al, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, Ni, P, Si, and Sn). The reporting limit for Pb was 0.5 ppb, and other analyte reporting limits are presented in Supplemental Table 3. A pooled analysis of variance based on replicate analyses of field samples suggests a standard deviation of 0.26 ppb Pb for samples that fall above the reporting limit of 0.5 ppb to 30 ppb Pb. Background water quality samples were not collected at each water filter study site; however, this type of sample was collected on fully flushed water during the concurrent sequential sampling study. Data presented in Table 1 and Supplemental Table 1 on the background water quality are derived from those samples.

Field blanks were collected and analyzed in this study. In accordance with the target minimum of 1 per 20 water samples, over 100 field blanks were collected, associated with the approximately 1,800 field water samples for metals analysis. Field blanks were filled with Milli-Q$^{®}$ water at the field laboratory and taken out to sampling sites. No field blanks were found to contain Pb above the reporting limit of 0.5 ppb.

All water analysis results were shared with the resident in a letter that presented an explanation of the results, available community resources, and contact numbers for assistance (USEPA 2022).

3. RESULTS AND DISCUSSION

3.1. Service line materials included in the study

Like many older US cities, Benton Harbor is aware that LSLs were present within the system; however, the exact residences with an LSL were unknown at the time of this study. While EPA prioritized residences with known or assumed LSLs based on available documentation as of late 2021, subsequently updated materials inventory has indicated that some assumed LSL sites ended up being non-Pb. Since the study, Benton Harbor has been working diligently to examine all the service line materials in their system and as of December 2023 has removed all their lead and galvanized service lines (WNDU 2023). EPA samplers, if permitted by the resident, also recorded customer-side service line information based on what they could observe coming into the home. In reviewing Benton Harbor's December 2022 service line data for the 199 valid filter study sampling sites, at the time of sampling, 133 sites had confirmed LSLs (18 Pb-copper, 110 Pb-galvanized, and 5 full LSLs), 34 had copper-galvanized service lines, 1 full galvanized service line, and 31 sites sampled ended up having a non-Pb and a non-galvanized service line (Figure 1).

3.2. 'Paired' samples

At least two sequential 1-L water samples were taken from each residence (filtered and unfiltered); however, the samples cannot be misconstrued as actual pairs. Pb in drinking water is a variable contaminant and is closely related to the individual sections of plumbing and Pb sources the water is in contact with (1 L samples representing ~20 ft of ½″ copper type M) (Triantafyllidou *et al.* 2021; Kutzing *et al.* 2022). Therefore, the actual Pb concentrations loaded onto the water filter in this study are unknown, and it cannot be assumed that if the unfiltered water sample associated with a location was below the reporting level (BRL) that the water which was filtered also had an initial Pb concentration BRL. The same applies for the detection of Pb in the unfiltered water sample, meaning Pb-laden water of the same concentration may or may not have passed through the water filter. Pb concentrations going onto the water filter could be higher or lower than what was observed in the unfiltered water sample.

There is no simple way to get a paired field sample where the concentration of Pb going onto the water filter is known. It is conceivably possible when sampling pitcher water filters, as a portion of the water collected to be filtered could be preserved and analyzed. However, even then, the chances of the presence of unevenly distributed particulate Pb (between the water to be filtered and the water to be analyzed as unfiltered) would remain an uncertainty. This discrepancy highlights the necessity of ensuring a statistically representative sample is collected, so that the sample size is large enough to capture the variability in multiple plumbing configurations and water Pb concentrations that may be present within a community.

As noted in Section 2, steps were taken to target higher Pb concentration waters for challenging the water filters, including increasing stagnation times and targeting water more likely to have been in contact with the service line materials in addition to the first 2 L out of the faucet. Neither of these efforts intended to capture higher Pb concentrations in the unfiltered water increased the Pb levels observed in the unfiltered water. The maximum Pb concentration observed in the unfiltered water was 77 ppb with an average of 3.6 ppb (Table 3 and Figure 2). However, a trend was observed that the eighth liter targeted (unfiltered) service line samples did have a higher average than the second liter unfiltered samples, 4.7 ppb and 3.1 ppb, respectively (BRLs included in the calculation as 0.5 ppb). Due to the violation of normality assumptions with a high proportion of results BRL in this sampling effort, when these variables are assessed in a log-transformed two-variable regression model, there is no evidence of an effect on Pb levels from stagnation time or from the difference between nonservice line and service line samples.

3.3. Performance of properly operated water filters for Pb

EPA collected a total of 307 properly operated filtered water samples (216 PUR® faucet-mounted water filters, 85 ZeroWater® pitcher water filters, and 6 Brita® faucet-mounted water filters) from 199 unique locations (Table 2). One hundred percent of the filtered water samples were below the NSF/ANSI-53 certification standard of 5 ppb Pb, with no filtered water concentrations exceeding 2.5 ppb Pb (Figure 3). The majority of filtered water samples (95%) were below 1 ppb Pb, with 90% of the results (277 filtered water samples) reporting concentrations below the 0.5 ppb reporting limit for Pb (Table 3). Sixteen pitcher-filtered water samples (5%) had Pb concentrations between 1 and 2.5 ppb Pb. The samples collected surpassed the minimum statistical study design parameters given 100% of samples were found to meet the NSF/ANSI-53 Pb certification standard. As all properly operated filtered water samples (first and seventh liter, $n = 307$) were <5 ppb, at 95% confidence level, at least 98% of locations with properly operated water filters will have filtered water Pb concentrations <5 ppb.

However, despite the proficient performance of the water filters, during sampling, EPA did note that many residents expressed not knowing how to properly install or use their water filter, when the filter requires replacement, or that hot water can damage the filter media and should never be run through a water filter (Durno 2022). In the 238 homes that EPA visited while in the community, 28 homes reported running hot water through the filter, 9 homes had damaged filter assemblies or no cartridge installed in the filter assemblage, and 27 homes had filters with red or malfunctioning indicator lights (Durno 2022). Approximately 13% of the samples collected for the purpose of the filter study (excluding 5 s flush samples) were not representative of proper filter operation and were excluded from the results analysis (Supplemental Table 2). As NSF/ANSI-53 water filters are being increasingly used as a temporary layer of protection in communities experiencing Pb ALEs, these devices require substantial public outreach and supplemental education to be effective and to properly protect residents.

3.4. Characterization of particulate

As Pb nanoparticulate has been found to be a cause for Pb breakthrough in properly operated, certified, and maintained water filters (Lytle *et al.* 2020; Doré *et al.* 2021), the concurrent Pb particulate study conducted alongside the filter efficacy study was meant to characterize particulate in Benton Harbor's system.

A variety of particles (non-Pb and Pb-containing) were observed in the electron microscopy analysis. When Pb was detected, it was a minor to trace component of the EDS analysis, with other elements such as O, Ca, P, and Al being predominant. In the 32 samples analyzed and over 200 images collected, Pb-containing particles could be classified into six categories based on visual features observed (Figure 4).

The most observed categories for Pb-containing particles were mats of semi-rounded hexagonal clustered particles and mats of matrix material with embedded clusters of particles (Figures 4(a) and 4(e), respectively). Although the ultrafiltration process likely contributed to the observation of this particle feature in the SEM imaging, particles imaged in the TEM were collected before ultrafiltration and show that mats (agglomerations) of particles are present. Both categories of particles were found to be mainly composed of O, Ca, P, and Al. In Figure 4(e), the matrix material (darker) also contained Fe, Si, Mg, Zn, Mn, Cl, and a minor amount of Pb, and the brighter particles included Fe, Si, Mg, Mn, Zn, Cl, Cu, and Pb. The embedded clusters of particles were found to vary as semi-rounded hexagonal particles, irregularly shaped particles, needle-like particles, and were occasionally indistinctive (mass of bright material with no definite structure visible). Another commonly observed category was conglomerates (Figure 4(f)). These were irregularly shaped particles containing both angular and rounded embedded grains. Some conglomerates were found to have a mainly Fe-rich matrix, while others were more Si rich.

Less-observed categories were needle-like particles and single chains of semi-rounded hexagonal particles (Figures 4(d) and 4(b), respectively). For the needle-like particles, the main elements observed were still O, Al, Ca, and P, but Fe was also frequently detected. One residence (Location 3446) had the highest water Pb concentration by inductively coupled plasma-mass spectrometry (ICP-MS) analysis of the particle characterization samples at a Pb concentration of 133 ppb. While many Pb-containing particles were found in this sample by both SEM and TEM, no discrete <100 nm Pb-containing particles were identified. Instead, all Pb-containing particulate was associated with a matrix or agglomerated particles. In one agglomeration, multiple particle categories were visible including chains/agglomerations of semi-rounded hexagonal particles, along with needle-like particles (Supplemental Figure 3).

Single, discrete Pb-containing nanoparticles (<100 nm) were not widely found or common. When single particles were identified, they differed greatly from those characterized in Newark, NJ's Pequannock drinking water system, having irregular edges and shapes (Figure 4(c)) when the particles characterized in Newark (which caused some water filter units to fail) were euhedral (Lytle *et al.* 2020). Pb was also not the main element comprising these single particles in Benton Harbor, some appear to be rich in O, Fe, Al, and P, while others contain mainly O, Ca, Si, and P. The lack of microscopic evidence of Pb-containing nanoparticles coupled with all properly operated filters performing as they were certified to do provided data to support that Pb nanoparticulate was not a cause for concern in Benton Harbor.

4. CONCLUSION

All properly operating filtered water samples were found to be below the NSF/ANSI-53 certification requirement and the Food and Drug Administration standard for bottled water of 5 ppb Pb (US FDA). Despite EPA's effort to challenge water filters by targeting LSL homes and efforts in the latter portion of the study to increase stagnation time and target water from the service line, Pb concentrations in associated unfiltered water samples were often found to be low in the homes sampled, with 80% of unfiltered water samples containing <5 ppb Pb. The concurrent study indicated that Pb phosphate nanoparticulate was not present within Benton Harbor's system even with the addition of a phosphate CCT since 2019. Pb-containing particles were identified in the electron microscopy, but when identified, tended to show up embedded in a matrix or mat of other materials rather than showing up as discrete Pb-laden nanoparticles. This visual evidence coupled with 100% of properly operating water filters performing as certified lends confidence to Pb nanoparticles not adversely impacting water filter performance in Benton Harbor.

Although NSF/ANSI-53 certified filters are effective at reducing Pb in drinking water to 5 ppb or less, that effectiveness hinges on the resident properly operating and maintaining their water filter. With additional implementation support, the body of detailed filter performance studies in various water qualities, combined with analytical evidence from dissolved and particulate Pb present in multiple water systems, strongly support that NSF/ANSI-53 certified filtration is a comparable intervention to bottled water.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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HIGHLIGHTS

- Water filter effectiveness study results show that all properly operating filter samples were below the 5 ppb Pb standards for certification under NSF/ ANSI-53 and bottled water.
- All properly operating filtered Pb samples were below 2.5 ppb.
- Some resident confusion about proper installation and use of the filters was noted.
- Pb phosphate nanoparticles <100 nm were not identified in the community.

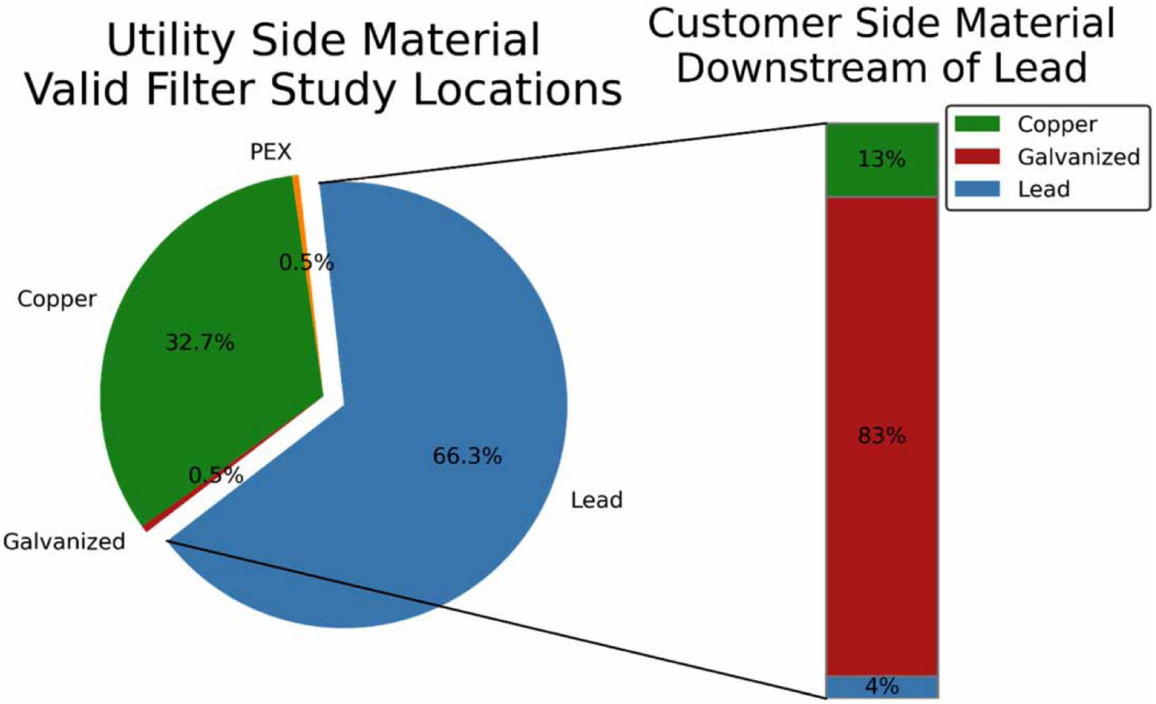

Figure 1 |.

Valid water filter study location utility side service line types at the time of sampling ($N =$ 199). Customer-side detail included for the utility side lead sites.

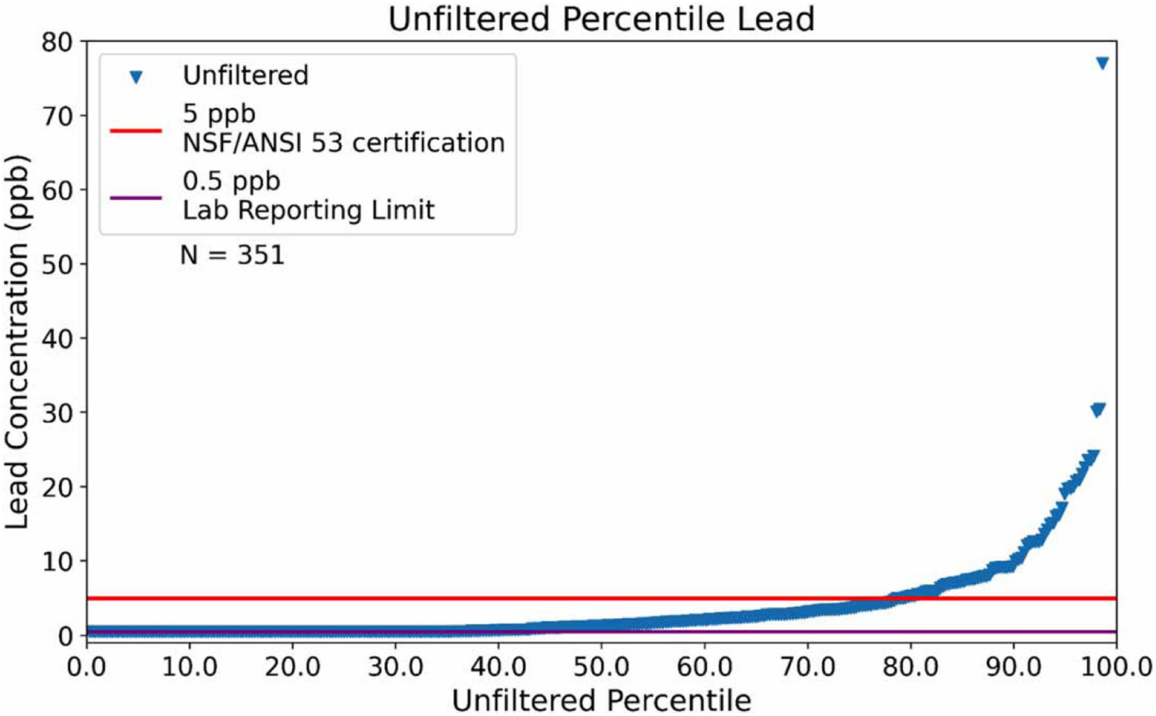

Figure 2 |.

Unfiltered (second and eighth liter) water sample lead concentrations.

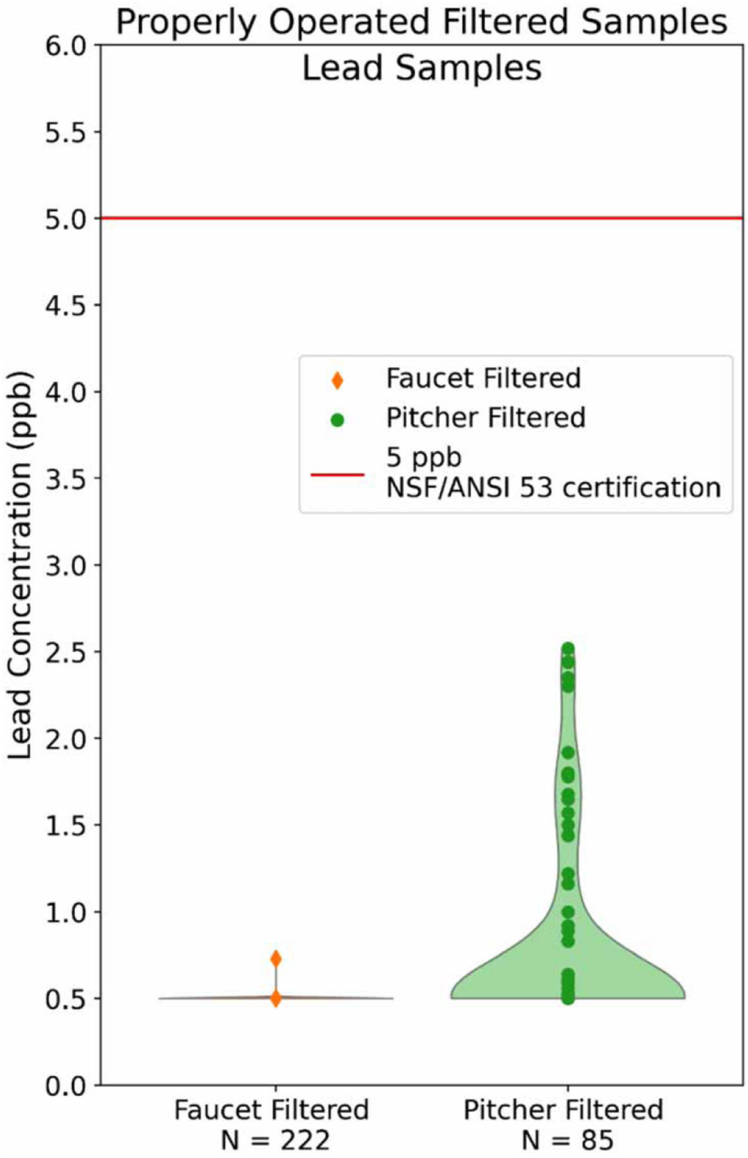

Figure 3 |.

Violin plots of the faucet-mounted water filter and pitcher water filter samples with the *y*-axis restricted to 6 ppb (maximum sample Pb concentration in filtered water is 2.5 ppb). Distribution of sample concentrations is shown by spread across the *x*-axis. Samples BRL are plotted at the Pb reporting limit of 0.5 ppb.

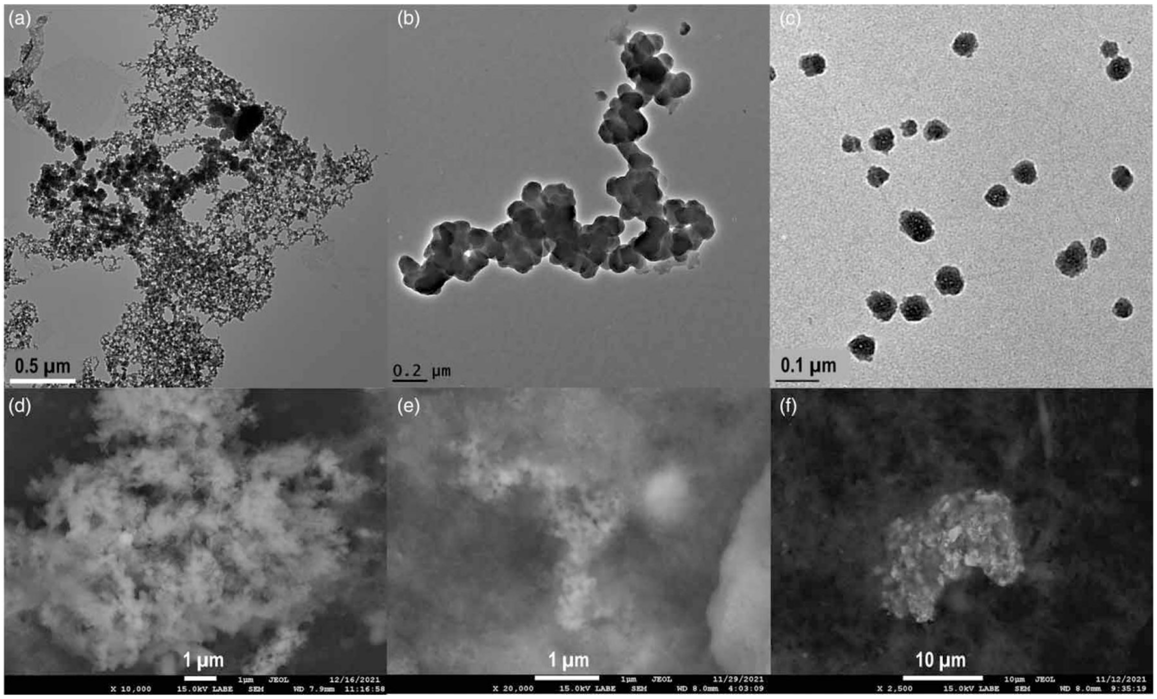

Figure 4 |.

Pb-containing particle categories observed in the electron microscopy. (a-c) Collected on the TEM at 200 kV. (d-f) Collected on the SEM at 15 kV and a working distance of 8 mm. (a) Semi-rounded hexagonal clustered particles, (b) single chains of semi-rounded hexagonal particles, (c) single, irregularly shaped particles, (d) needle-like particles, (e) mats of matrix material with embedded clusters of Pb-containing particles, and (f) conglomerates.

Table 1 |

Water quality comparison between Flint, MI; Newark, NJ; and Benton Harbor, MI

Parameters	**Flint, MI, water quality 18 April 2016–18 July 2017 from Williams *et al.* (2018)[a] (average ± standard deviation)**	**Newark, NJ, Pequannock system water quality 21 August 2019–22 August 2019 from Lytle *et al.* (2020)[b,c]**	**Benton Harbor, MI, water quality 9 November 2021–16 Dcember 2021 (n = 26)[c]**
Aluminum (mg/L)	0.003 ± 0.010	0.04–0.05	<0.5
Calcium (mg/L)	25.96 ± 0.81	11.9–12.3	37–43
Magnesium (mg/L)	7.6 ± 0.3	3.31–3.36	12–14
Potassium (mg/L)	-	0.5–0.6	1.6–1.9
Sodium (mg/L)	5.3 ± 0.3	23.3–24	13–16
Zinc (μg/L)	2.0 ± 1.0	28–81	<10–86
Fluoride (mg/L)	0.8 ± 0.1	-	0.15–0.35
Chloride (mg/L)	10.1 ± 0.6	38.3–39.2	19–22
Sulfate (mg SO_4/L)	19.8 ± 1.4	9.8–10.4	32–35
Total alkalinity (mg $CaCO_3$/L)	73.3 ± 3.1	29.6–31.5	120
Total phosphorus (mg/L)	-	-	1–2
Phosphate (mg PO_4/L)	3.6 ± 0.2	1.38–1.57	-
pH	7.32 ± 0.10	7.6	7.69
Scale composition (type)	Amorphous upper layers, lower layer mainly Pb(II), and Pb(II) phosphates	Presence of destabilized PbO_2 (Pb(IV)) in surficial layer	Amorphous upper layer, lower layer Pb(II) carbonate
Particle characterization	Not evaluated	Discrete Pb phosphate nanoparticles	No Pb phosphate nanoparticles
Secondary disinfectant	Free chlorine	Free chlorine	Free chlorine

Note: ‘<‘ indicates values below the reporting limit for an analyte.

[a] Influent pipe rig background water quality.

[b] Ranges across four residential homes sampled.

[c] Background water quality in fully flushed samples, collected from residential taps.

Table 2 |

A total of 307 properly operated water filter samples were included in the study

	# Samples/filter status		# Samples/type of sample		# Samples/type of filter	
Unique locations	**Green**	**Yellow**	**First liter**	**Service line**	**Faucet mount**	**Pitcher**
199	297	10	201	106	222	85

Table 3 |

Summary statistics for Pb concentrations in filtered and unfiltered water

Sample type	Percentage of samples BRL	Maximum Pb concentration (ppb)	Average Pb concentration (ppb)[a]	Standard deviation[a]	95% confidence interval	
					Low[a]	**High[a]**
Faucet-mounted water filter $N = 222$	99% (221)	0.73	221 samples BRL			
Pitcher water filter $N = 85$	66% (56)	2.52	0.76	0.53	0.65	0.87
Unfiltered water $N = 351$	35% (124)	77	3.59	6.39	2.92	4.26

[a] Samples BRL are represented with the analyte reporting limit (0.5 ppb) in these calculations.