

## PAPER

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## Tapwater exposures, residential risk, and mitigation in a PFAS-impacted-groundwater community†

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Tapwater (TW) safety and sustainability are priorities in the United States. Per/polyfluoroalkyl substance(s) (PFAS) contamination is a growing public-health concern due to prolific use, widespread TW exposures, and mounting human-health concerns. Historically-rural, actively-urbanizing communities that rely on surficial-aquifer private wells incur elevated risks of unrecognized TW exposures, including PFAS, due to limited private-well monitoring and contaminant-source proliferation in urbanizing landscapes. Here, a broad-analytical-scope TW-assessment was conducted in a hydrologically-vulnerable, Mississippi River alluvial-island community, where PFAS contamination of the shallow-alluvial drinking-water aquifer has been documented, but more comprehensive contaminant characterization to inform decision-making is currently lacking. In 2021, we analyzed 510 organics, 34 inorganics, and 3 microbial groups in 11 residential and community locations to assess (1) TW risks beyond recognized PFAS issues, (2) day-to-day and year-to-year risk variability, and (3) suitability of the underlying sandstone aquifer as an alternative source to mitigate TW-PFAS exposures. Seventy-six organics and 25 inorganics were detected. Potential human-health risks of detected TW exposures were explored based on cumulative benchmark-based toxicity quotients ( $\sum_{TQ}$ ). Elevated risks ( $\sum_{TQ} \geq 1$ ) from organic and inorganic contaminants were observed in all alluvial-aquifer-sourced synoptic samples but not in sandstone-aquifer-sourced samples. Repeated sampling at 3 sites over 52–55 h indicated limited variability in risk over the short-term. Comparable PFAS-specific  $\sum_{TQ}$  for spatial-synoptic, short-term (3 days) temporal, and long-term (3 years quarterly) temporal samples indicated that synoptic results provided useful insight into the risks of TW-PFAS exposures at French Island over the long-term. No PFAS detections in sandstone-aquifer-sourced samples over a 3 year period indicated no PFAS-associated risk and supported the sandstone aquifer as an alternative drinking-water source to mitigate community TW-PFAS exposures. This study illustrated the importance of expanded contaminant monitoring of private-well TW, beyond known concerns (in this case, PFAS), to reduce the risks of a range of unrecognized contaminant exposures.

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### Environmental significance

Historically-rural, actively-urbanizing communities that rely on surficial-aquifer private wells incur elevated risks of unrecognized tapwater exposures, including per/polyfluoroalkyl substance(s) (PFAS), due to contaminant-source proliferation in urbanizing landscapes and to owner-dependent and, thus, generally limited private-well monitoring. A broad-analytical-scope tapwater assessment was conducted in a hydrologically-vulnerable, Mississippi River alluvial-island community, where PFAS contamination of the shallow-alluvial drinking-water aquifer was previously documented, but more comprehensive contaminant characterization to realistically inform public-health decision-making was lacking. This study illustrated the importance of expanded contaminant monitoring of private-well tapwater, beyond known concerns (in this case, PFAS), to reduce the cumulative risk of a range of unrecognized contaminant exposures.

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## Introduction

Drinking water (DW) safety and sustainability are priorities in the United States (US) and globally due to the biological imperative for water and its resultant role as a critical and increasingly vulnerable route of potential human exposures to a wide range of environmental contaminants.<sup>6–8</sup> DW contamination by per and polyfluoroalkyl substance(s) (PFAS) is a growing public-health concern due to prolific industrial use and commercial product applications,<sup>9,10</sup> numerous potential surface sources<sup>11–16</sup> and routes to ground and surface DW resources,<sup>6–9</sup> widespread human DW exposures,<sup>17–20</sup> and pervasive occurrence in humans.<sup>18,21–23</sup> The growing list of recognized adverse human-health effects<sup>24–27</sup> includes cancer<sup>28–31</sup> and impacts on endocrine,<sup>32–34</sup> thyroid,<sup>29,35</sup> and immune<sup>36–40</sup> functions, and on birth outcomes.<sup>23,41–43</sup> PFAS DW contamination has been documented in private-well tapwater (TW),<sup>44–48</sup> public-supply TW,<sup>19,46</sup> and bottled water (BW).<sup>49–54</sup> A recent U.S. Geological Survey (USGS) national TW PFAS assessment of 716 locations (269 private-wells; 447 public supply) in all 50 US states, Puerto Rico, and the US Virgin Islands estimated exposure to at least one PFAS in about 45% of US DW.<sup>19</sup> Recent modeling indicates that 11–18 million (27–45%) private-well users in the conterminous US potentially rely on groundwater with detectable concentrations of PFAS.<sup>55</sup>

The risk of unrecognized exposures is notably higher for private-TW due to a comparative lack of information on associated contaminant exposures,<sup>44–48</sup> including PFAS.<sup>19</sup> PFAS have been monitored in public-supply by many US states for more than a decade,<sup>56</sup> by the United States Environmental Protection Agency (EPA) in large (>10 000 served) DW facilities since the third Unregulated Contaminant Monitoring Rule (UCMR3, 6 PFAS),<sup>57</sup> and more broadly by EPA (29 PFAS; small [<3300 served] to large [>10 000 served] facilities) under the ongoing fifth UCMR (UCMR5).<sup>58</sup> However, EPA is not authorized to regulate or monitor private-TW,<sup>59</sup> and about 14% of the US population relies on private wells for DW.<sup>60</sup> High analytical costs, lack of technical training and awareness, and conflation of aesthetic quality with safety severely limit homeowner monitoring of private-well TW. The TW-contaminant-exposure data gap in private-well-dependent remote and rural locations undermines individual and community DW risk-management decision making.<sup>46,48,61</sup>

The recent USGS national TW PFAS survey indicated similar overall probability of PFAS occurrence in private-TW and public-TW, with increasing probabilities of PFAS contamination for both in developed landscapes.<sup>19</sup> Thus, historically-rural, actively-urbanizing communities that depend on shallow, surficial aquifer sources incur elevated risks of unrecognized TW-contaminant-mixture exposures, including PFAS, due to combined vulnerabilities of limited private-well monitoring and proliferation of surface contaminant sources in urbanizing landscapes. For example, a recent study to inform community and end-user risk-management/mitigation decision-making at hydrologically-vulnerable Cape Cod, Massachusetts,<sup>46</sup> which depends on a shallow, surficial sole-source DW aquifer<sup>62–64</sup> with

documented PFAS concerns;<sup>65,66</sup> demonstrated broad exposures to a range of additional TW-contaminants of potential human-health concern, including metal, volatile organic chemical(s) (VOC), and wastewater-derived contaminants. Herein, the same broad-analytical-scope TW-assessment approach was applied to a hydrologically-vulnerable, alluvial-island, suburban community, where PFAS-contamination of the shallow DW aquifer has recently been documented but more comprehensive contaminant characterization to inform decision-making is currently lacking.

The Town of Campbell, Wisconsin (2020 population: 4284 (ref. 67)), is located on an alluvial island (French Island) in the Mississippi River, next to the city of La Crosse, Wisconsin (2020 population: 52 680 (ref. 67)), which owns and operates a regional airport and several municipal DW-supply wells on the northeastern corner of the island (Fig. 1). Persistent detection of perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) in excess of then existing Wisconsin Department of Health Services recommended enforcement standards and preventive action limits<sup>68</sup> in a municipal well during UCMR3 monitoring (2013–2015) prompted a 2020–2021 Wisconsin Department of Natural Resources (Wisconsin DNR) PFAS-

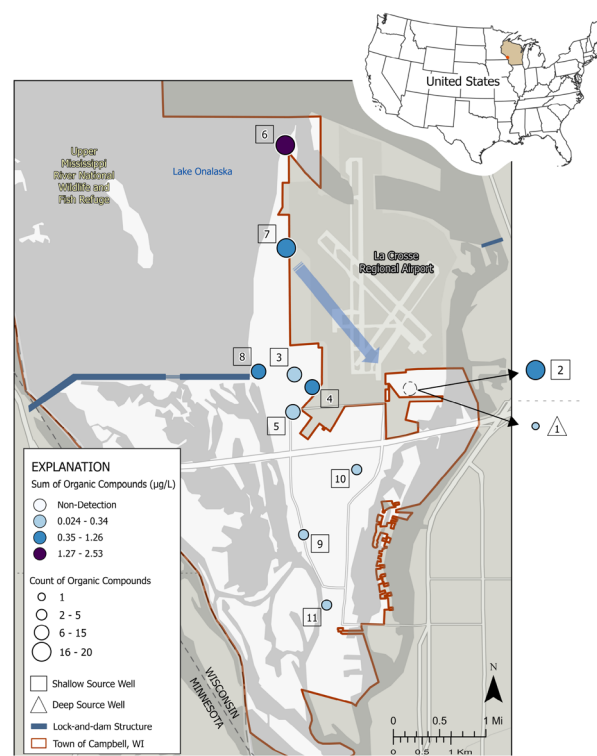


Fig. 1 Cumulative (sum of all detected) concentrations ( $\mu\text{g L}^{-1}$ ) and numbers of organics detected in spatial-synoptic tapwater samples collected in 2021 at Town of Campbell, Wisconsin. TW samples from Sites 2–11 are sourced from the shallow alluvial-aquifer, which served as the principal drinking-water supply for residences and public facilities. Site 1 tapwater is sourced from the underlying, Mount Simon, sandstone aquifer. Arrow indicates general northwest to southeast groundwater flow direction within the alluvial aquifer. Basemap,<sup>4</sup> Town boundary.<sup>5</sup>



contamination investigation on the island.<sup>69,70</sup> Identification of PFAS-contamination source areas and events at the La Crosse Airport<sup>71</sup> triggered a 2021 island-wide DW advisory due to the then unknown extent of PFAS contamination in the French Island surficial DW aquifer.<sup>69,70</sup> A subsequent 2021 spatial surveillance of 200 private and 20 public-supply wells documented widespread private-well PFAS contamination.<sup>72</sup> Efforts to mitigate DW PFAS exposures include ongoing delivery of bottled water to affected residential locations and assessment of alternative DW sourcing from the underlying, confined, Mount Simon sandstone aquifer,<sup>73</sup> as a long-term solution.

The USGS Drinking Water and Wastewater Infrastructure Research Team<sup>74,75</sup> collaborates with federal and state agencies, Tribal nations, universities, utilities, and communities to inform contaminant-mixture exposures at the DW point-of-use (POU) and associated distal (*e.g.*, ambient source water) and proximal (*e.g.*, premise plumbing) drivers in a range of socioeconomic and source-water vulnerability settings across the US.<sup>44–47,76–78</sup> In 2021, we assessed exposures to a broad suite of potential inorganic/organic/microbial TW contaminants in 11 locations (residential, public) on French Island within the Town of Campbell to (1) provide insight into cumulative contaminant risk to human health<sup>79–81</sup> of private-well TW, (2) assess day-to-day and year-to-year variability in TW exposures, (3) more broadly assess potential shallow DW-aquifer contaminant-exposure concerns beyond recognized PFAS issues, (4) comprehensively characterize water quality in the underlying, Mount Simon, confined, sandstone aquifer currently under consideration as an alternative DW source (*i.e.*, long-term DW-exposure mitigation option), and (5) continue to expand the national perspective on contaminant-mixture exposures in POU DW by maintaining the same general sampling protocol and analytical toolbox employed in previous studies.<sup>44–47,76–78</sup>

For this study, TW exposures were operationally represented as concentrations of 510 organics, 34 inorganics, and 3 microbial groups in residential and community TW samples. Potential human-health risks of individual and cumulative TW exposures were explored based on effects-weighted quotients, including cumulative benchmark-based toxicity quotients ( $\sum_{\text{TQ}}$ )<sup>46,82</sup> for detected inorganics and organics and on cumulative molecular-scale, *in vitro* exposure-activity ratio(s) ( $\sum_{\text{EAR}}$ )<sup>46,83</sup> for detected organics.

## Methodology

### Site selection and sample collection

Individual private wells tapping the unconfined, shallow, alluvial aquifer comprise the principal DW source for public facilities and private residences on French Island. Because this study was conducted under SARS-CoV-2 pandemic and associated social-distancing constraints, TW samples for spatial and temporal variability assessments were collected primarily from Town of Campbell public buildings/facilities and from the USGS Upper Midwest Environmental Sciences Center (UMESC), with samples from 3 residential locations collected at externals taps to avoid entering homes.

TW samples for broad-scope target analysis of spatial variability were collected from Town of Campbell public building (Sites 3, 5, and 10), public park (Sites 4 and 6), and fire-department pump-station (Site 9) locations, UMESC (Sites 1 and 2), and three (Sites 7, 8, and 11) residences (Fig. 1). Locations were chosen to provide broad spatial coverage of the Town of Campbell, with emphasis on sites bordering the La Crosse Regional Airport, a documented source area for PFAS contamination in the shallow alluvial aquifer.<sup>69,71,72</sup> All taps (cold water) were sampled at least once during October 2021 (Table S1†). Except as noted below for the 3 days short-term variability samples, taps/faucets were sampled as is (*i.e.*, without pre-cleaning, screen removal, *etc.*) throughout the day without Lead and Copper Rule stagnant-sample protocols,<sup>84,85</sup> with one exception. A non-potable-brass hose adapter was removed from the potable fixture at Site 2 immediately prior to TW-sample collection, potentially resulting in metal-particulate surface contamination as discussed further below.

All TW samples were sourced from individual wells drawing from the surficial, alluvial, sand and gravel aquifer, except for Site 1 TW samples, which were sourced from a well (well 972; Fig. S1†) drawing from the underlying, Mount Simon, confined, sandstone aquifer<sup>73</sup> that is currently under consideration as a potential alternative DW supply for the Town of Campbell. For Site 1, the source-well construction was steel casing to a depth of 52 m below land surface (bls), with a 24 m open interval (*i.e.*, withdrawal depth) approximately 52–76 m bls.<sup>86</sup> For Site 2, TW was sourced from three UMESC source-water wells (wells 122–124), each constructed of steel with a total depth of approximately 23 m bls and a bottom-positioned 6 m stainless-steel screened interval approximately 17–23 m bls.<sup>86</sup> For all other spatial sampling locations, source-well construction was black steel, with total depths ranging approximately 14–25 m bls and bottom-positioned, 1 m stainless-steel screened intervals.<sup>86</sup> See Table S1† for all estimated withdrawal depths.

The lock-and-dam structure (Lock and Dam 7), which separates Lake Onalaska (Mississippi River Pool 7) from downstream Mississippi River and Black River sections (Pool 8), extends from the northeast corner of the La Crosse Regional Airport to the Wisconsin eastern bank and from near Site 8 to the Minnesota western bank (Fig. 1 and S1†). This configuration creates a general northwest to southeast hydrologic gradient and associated groundwater-flow direction in the highly transmissive, unconfined, surficial aquifer, with locally curving downstream flow lines around the dam structures.<sup>71,73</sup> TW Site 2 and corresponding surficial source wells (122–124) are located along the presumptive groundwater flowpath, downgradient from confirmed and suspected PFAS source areas (*e.g.*, burn pits, terminal apron, aqueous film-forming foam [AFFF] nozzle test area, fire station) at the airport.<sup>71</sup>

To assess short-term variability in TW contaminant-mixture exposures, Sites 1–3 were sampled for broad-scope target-analysis 6 more times each (total of 7 samples per site) over a 3 days period (Table S1†). For 3 consecutive days, a first-flush, 6 h over-night stagnant sample (consistent with Lead and Copper Rule stagnant-sample protocols<sup>84,85</sup>) was collected at each location in the morning, followed by a second afternoon



sample collection approximately 6 h later. To assess potential premise-plumbing-derived contaminants, a one-time, immediate post-flush sample also was collected at each site on day 1, approximately 30 min after the first-flush sample.

Multi-year variabilities in TW PFAS exposures were assessed by quarterly sampling at UMESC (1st quarter 2021–1st quarter 2024), including the underlying Mount Simon sandstone aquifer source well for Site 1 TW (well 972, Fig. S1†) and the three, shallow, alluvial-aquifer, source wells (wells 122–124) for Site 2 TW. Complete sampling details are provided elsewhere.<sup>87–89</sup>

### Analytical methods and quality assurance

Briefly, TW samples were analyzed by USGS for 510 unique organic analytes, 34 inorganic (ions/trace elements) analytes, 3 microbial indicators, and 3 field parameters (Table S2†), as discussed<sup>84,46,76,87</sup> and described in detail previously.<sup>90–109</sup> Organic analytes included cyanotoxin, disinfection byproduct(s) (DBP), pesticide, PFAS, pharmaceutical, and semi-volatile/volatile organic chemical (VOC collectively, herein) classes. Additional method details and all analytical results are in Tables S3, S4a and S5† and in Romanok *et al.*<sup>1–3</sup>

Quantitative ( $\geq$ limit of quantitation,  $\geq$ LOQ) and semi-quantitative (between LOQ and long-term method detection limit, MDL<sup>110,111</sup>) results were treated as detections.<sup>110,112,113</sup> Quality-assurance/quality-control included analyses of 3 field blanks (Table S6†), as well as laboratory blanks, spikes, and stable-isotope surrogates (Table S4b†). Only nitrate–nitrogen ( $\text{NO}_3\text{-N}$ ) was detected in inorganic blanks at concentrations in the range observed in TW samples; corresponding results were censored at the maximum blank concentration ( $0.01 \text{ mg L}^{-1}$ ), as footnoted (Tables S3 and S6†). Among the detected organics, only butyl benzyl phthalate ( $0.8 \text{ } \mu\text{g L}^{-1}$ ), diethyl phthalate ( $0.1 \text{ } \mu\text{g L}^{-1}$ ), and di-*n*-butyl phthalate ( $0.17 \text{ } \mu\text{g L}^{-1}$ ) were detected in any blank (once each) in the concentration range observed in TW samples; corresponding results were censored at 2 times the maximum blank concentration, as footnoted (Tables S4 and S6†). The median surrogate recovery (Table S4b†) was 102% (interquartile range [IQR]: 93.5–116%).

### Risk and molecular-effects screening

A human-health DW-benchmark-based screening assessment of cumulative inorganic and organic contaminant risk ( $\sum \text{TQ}$ ) was conducted, consistent with World Health Organization/International Programme on Chemical Safety [WHO/IPCS] framework Tier 1 Hazard Index risk screening,<sup>114</sup> European Food Safety Authority Tier 1 Reference Point Index (RPI) risk screening,<sup>115</sup> and EPA Tier 1–2 cumulative risk screening<sup>116–119</sup> guidance, as described previously (*e.g.*,<sup>45,78</sup>). Potential molecular-level effects of mixed-organic contaminant exposures also were explored, using an exposure-activity ratio (EAR) approach based on Toxicity ForeCaster (ToxCast<sup>TM</sup>)<sup>120</sup> high-throughput data,<sup>121</sup> as described previously (*e.g.*,<sup>45,78</sup>). ToxEval version 1.3.0 (ref. 122) of R<sup>123</sup> was used to sum (non-interactive concentration addition model<sup>124–126</sup>) individual benchmark-based TQ or ToxCast-based<sup>127,128</sup> EAR, respectively. For the former, the lowest

benchmark concentration (*i.e.*, most protective human-health benchmark) among National Primary Drinking Water Regulation (NPDWR) maximum contaminant limit goal(s) (MCLG),<sup>129,130</sup> EPA Drinking-Water Health Advisories (DWHA),<sup>131</sup> WHO guidelines,<sup>132</sup> state MCL or DWHA,<sup>133</sup> or USGS Health-Based Screening Level(s) (HBSL) or Human Health Benchmark(s) for Pesticides (HHBP)<sup>134</sup> was used. MCLG values of zero (*i.e.*, set when there is evidence that chemical may cause cancer and there is no dose below which the chemical is considered safe, emphasizing vulnerable sub-populations, including infants, children, the elderly, and those with compromised immune systems and chronic diseases<sup>130,135</sup>) were set to  $0.1 \text{ } \mu\text{g L}^{-1}$  for metals (arsenic [As], lead [Pb], uranium [U]) and VOC and to  $0.0001 \text{ } \mu\text{g L}^{-1}$  for PFOS and PFOA, as described in detail.<sup>136</sup>

Human-health risks of individual and cumulative contaminant exposures are screened herein based on MCLG and other human-health advisories, for the following reasons. (1) EPA MCL/AL are applicable to public supplies only.<sup>59,129,130</sup> (2) Although set as close as feasible, MCL/AL take into account technical and financial constraints of DW monitoring and treatment and, consequently, are often higher than corresponding human-health-only MCLG targets.<sup>135</sup> (3) MCLG and health-advisory values generally include a margin of exposure to provide a safety threshold, in the case of MCLG defined as “the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur, allowing an adequate margin of safety,” and are determined in consideration of risks to presumptive “most vulnerable” (*e.g.*, infants, children, the elderly, those with compromised immune systems and chronic diseases) sub-populations.<sup>135</sup> MCLG is set at “zero” if “there is evidence that a chemical may cause cancer” and “there is no dose below which the chemical is considered safe”.<sup>135</sup> Health-based benchmarks,  $\sum \text{TQ}$ , ToxCast exclusions, and  $\sum \text{EAR}$  are summarized in Tables S7a and S8c.†

## Results and discussion

Seventy-six (15% of analytes) organics (Fig. 1–3, S2–S3; Table S4a†) and 25 (76%) inorganics (Fig. 4 and Table S3†) were detected in French Island TW samples. The following sections address spatial and short-term (3 days) temporal variability in broad-scope TW-contaminant (*i.e.*, mixtures) exposures and respective potential human-health risks as well as longer-term (multi-year quarterly) variability in PFAS-specific exposures and potential human-health risks.

### TW mixtures spatial synoptic

Regulated and unregulated organic/inorganic contaminants, beyond previously-documented PFAS, were detected in TW samples across French Island (Fig. 1–4, S2–S3, Tables S3, S4a and S5†), including at concentrations of potential human-health concern (Tables S7a and b†). In the following subsections, only the results for the first collection (day 1, morning) were included in the spatial-synoptic assessment, for locations (Sites 1–3) with multiple TW-sample collections (Table S1†).



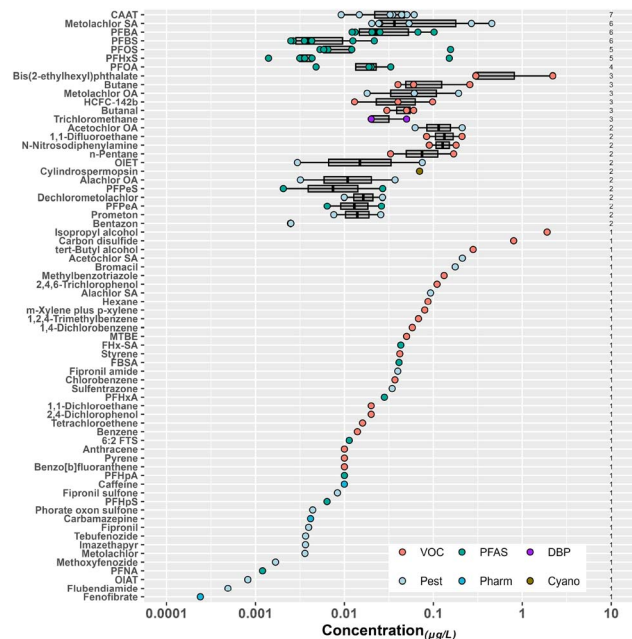


Fig. 2 Detected concentrations ( $\mu\text{g L}^{-1}$ ) and number of sites (right axes) for 76 organic analytes (left axis, in order of decreasing total detections) detected in tapwater samples collected in 2021 at Town of Campbell, Wisconsin. Circles are data for individual samples. Boxes, centerlines, and whiskers indicate interquartile range, median, and 5th and 95th percentiles, respectively.

### Organic exposures and individual benchmark comparisons

French Island TW samples were screened for 4 cyanotoxins, 22 DBP, 213 pesticide, 32 PFAS, 112 pharmaceutical, and 141 VOC analytes, of which 16 were included in 2 methods resulting in 510 unique organic analytes (Table S2†). Seventy-six unique organic analytes were detected at least once across all sites (Fig. 1, 2 and Table S4a†). Multiple organic analytes (median: 12; IQR: 6–19; range: 2–20) were detected in all spatial-synoptic samples at cumulative concentrations ranging  $0.06\text{--}2.53 \mu\text{g L}^{-1}$  (median:  $0.696 \mu\text{g L}^{-1}$ ; IQR:  $0.342\text{--}2.00 \mu\text{g L}^{-1}$ ).

As expected based on (1) previous PFAS assessment results at French Island,<sup>70–72</sup> (2) growing concerns for adverse effects of TW PFAS exposures,<sup>24–27</sup> and (3) corresponding promulgation of increasingly strict, federal/state-level, drinking-water PFAS regulations and health-advisories,<sup>56,137,138</sup> multiple co-occurring PFAS were the primary TW organic exposures of recognized human-health concern, with common-place co-occurring detections of a range of additional organics including pesticides and VOC (Fig. 2, 3, S2 and Table S4a†). Consistent with previous findings,<sup>70–72</sup> PFAS detections and individual/cumulative concentrations (Fig. 3) observed in alluvial-aquifer-sourced (Sites 2–11) TW samples were greatest near and south of the airport (Sites 2–5, 7), with no PFAS detections in this study north of the airport (Site 6) or south of Interstate 90 (Sites 9–11). Cumulative PFAS detections and concentrations in spatial-synoptic TW samples ranged 0–14 (median: 2) and not detected (nd) up to  $0.609 \mu\text{g L}^{-1}$  (median:  $0.023 \mu\text{g L}^{-1}$ ), respectively (Fig. 3). Likewise expected based on previous results,<sup>71,72</sup> the

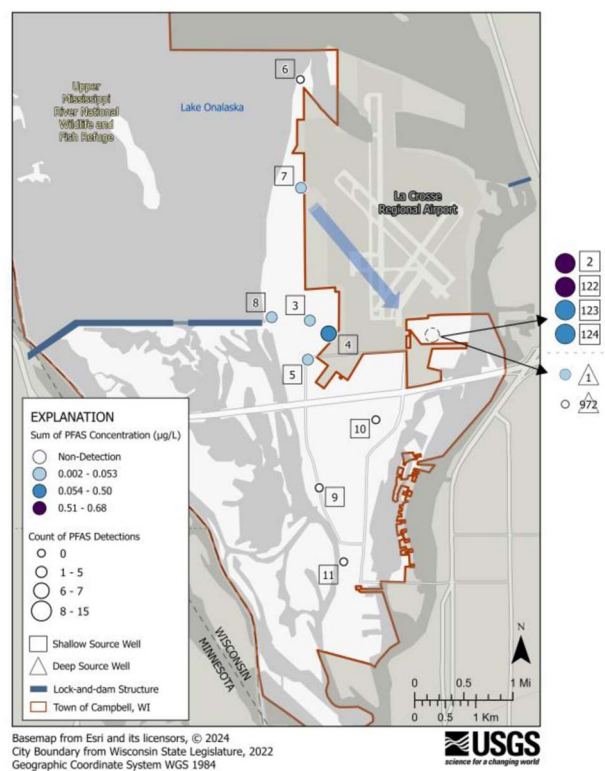


Fig. 3 Cumulative (sum of all detected) concentrations ( $\mu\text{g L}^{-1}$ ) and numbers of per/polyfluoroalkyl substance(s) detected in spatial-synoptic tapwater samples collected in 2021 at Town of Campbell, Wisconsin. Tapwater samples from Sites 2–11 are sourced from the shallow alluvial-aquifer, which serves as the principal drinking-water supply for residences and public facilities. Site 1 tapwater is sourced from the underlying, Mount Simon, sandstone aquifer. Arrow indicates general northwest to southeast groundwater flow direction within the alluvial aquifer.<sup>4</sup> Basemap:<sup>4</sup> Town boundary.<sup>5</sup>

highest PFAS cumulative (14) and percent (70% of all organic) detections and cumulative ( $0.609 \mu\text{g L}^{-1}$ ) and percent (56% of all organic) concentrations were observed in TW from Site 2, sourced from 3 shallow alluvial wells located along the presumptive flowpath downgradient of documented PFAS-use areas at the airport. In contrast, perfluorobutanoic acid (PFBA) was the only PFAS detected ( $0.025 \mu\text{g L}^{-1}$ ) in TW from Site 1, sourced from the deeper sandstone aquifer.

Notably, the TW location with co-maximum cumulative detections (20; same as Site 2) and maximum cumulative concentrations ( $2.526 \mu\text{g L}^{-1}$ ) was Site 6, a public water fountain (locked down during SARS-CoV-2 pandemic, except for sample collection) at the northern tip of French Island, up-gradient of the airport (Fig. 1). In contrast to Site 2, organic detections and cumulative concentrations at Site 6 were predominantly VOC (80% of organic detections; 99.5% of organic cumulative concentrations), consistent with proximal surface-water infiltration<sup>73</sup> and respective contamination of the shallow-alluvial-aquifer and with the location of Site 6 adjacent to and immediately down-gradient of a marina and public boat launch. Other notable contaminant profiles observed in alluvial-aquifer-sourced sample locations were the pesticide compositions of



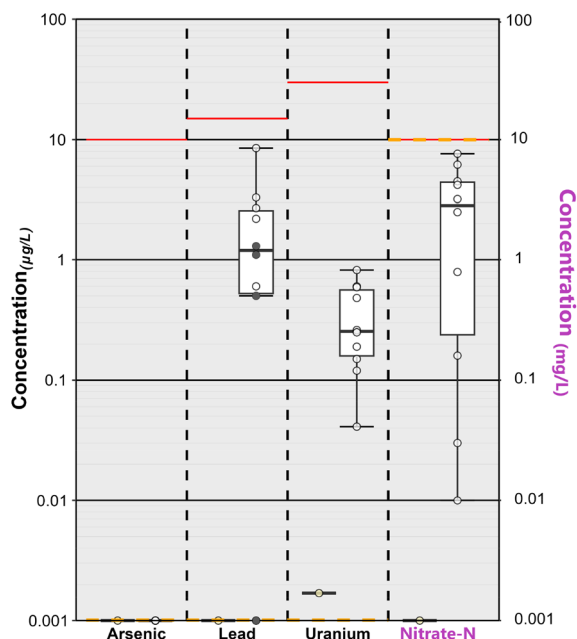


Fig. 4 Concentrations (circles, ●) of select inorganics (left Y-axis [ $\mu\text{g L}^{-1}$ ]: arsenic [As], lead [Pb], uranium [U]; right Y-axis [ $\text{mg L}^{-1}$ ]: nitrate–nitrogen [ $\text{NO}_3\text{--N}$ ]) detected in spatial-synoptic tapwater samples collected in 2021 at Town of Campbell, Wisconsin. Solid red lines indicate public-supply enforceable maximum contaminant level(s) (MCL) or technology treatment action level (Pb only). MCL goals (MCLG; dashed orange lines) are ‘zero’ for As, U, and Pb and  $10 \text{ mg L}^{-1}$  (same as MCL) for  $\text{NO}_3\text{--N}$ . For each analyte, single result on the left is for Site 1 and boxes, centerlines, and whiskers on the right indicate interquartile range, median, and 5th and 95th percentiles, respectively, for Sites 2–11. For Pb, shaded circles indicate non-potable samples not included in the tapwater exposure and risk assessment.

samples at the western side of French Island, comprising 53% of detections and 64% of cumulative concentrations of organics detected at Site 7, increasing to 92% of detections and >99% of cumulative concentrations at Site 8, immediately adjacent to and upstream of the western lock-and-dam structure (Fig. 1 and S1†). The high percentage detections and concentrations of pesticides (predominantly herbicides and herbicide degradates) at Sites 7 and 8 are consistent with proximal infiltration of Mississippi River water into the shallow-alluvial aquifer upstream of the western lock-and-dam structure;<sup>73</sup> agricultural pesticide use and corresponding surface-water contamination are well-documented in Corn Belt drainage basins,<sup>139</sup> including the Mississippi River.<sup>140–143</sup> In contrast to the alluvial-aquifer-sourced synoptic samples, only 3 organics were detected in the TW sample from the sandstone-aquifer-sourced Site 1 location, with more than 95% of the detected concentration attributable to a one-time (*i.e.*, not detected in any subsequent Site 1 samples, as discussed below) detection of isopropyl alcohol, a commonplace household and commercial solvent.

Among the 76 organics detected in this study, 14 (18%) have EPA MCL/MCLG promulgated for public supply. Three (PFOS, PFOA, perfluorohexanesulfonic acid [PFHxS]) exceeded concentrations equivalent to respective, newly-established MCL and corresponding MCLG<sup>137,138</sup> in samples from 5, 4, and 1

spatial-synoptic locations, respectively, all alluvial-aquifer sourced. In addition to the above, bis(2-ethylhexyl)phthalate [DEHP], benzene, and tetrachloroethene [PCE] have MCLG of “zero”, with DEHP detected in 3 spatial-synoptic locations and benzene and PCE detected once each (all *de facto* MCLG exceedances). Multiple MCLG exceedances per sample were common (7/10 or 70% of sites) in spatial-synoptic samples sourced from the shallow alluvial aquifer (Sites 2–10; median: 1.5; range: 0–3 per site); no MCLG exceedances were observed in the sandstone-aquifer-sourced Site 1 synoptic sample.

### Inorganic exposures and individual benchmark comparisons

TW inorganic results of potential human-health concern included detections of uranium (U), lead (Pb), nitrate–nitrogen ( $\text{NO}_3\text{--N}$ ), manganese (Mn), and fluoride (F), all at less than MCL-equivalent (90th percentile AL-equivalent<sup>84,85,130</sup> or WHO guideline<sup>132</sup> value of  $10 \mu\text{g L}^{-1}$  for Pb) concentrations (Fig. 4 and Table S3†). Although detected U and Pb concentrations were well-below MCL-equivalent  $30 \mu\text{g L}^{-1}$  and AL-equivalent  $10 \mu\text{g L}^{-1}$  concentrations, respectively, both have MCLG of ‘zero’ (“chemical may cause cancer” and “there is no dose below which the chemical is considered safe”<sup>135</sup>) and, thus, corresponding detections (*de facto* MCLG exceedances) warrant discussion.

The redox-reactive geogenic radionuclide U was detected at low concentrations (median:  $0.26 \mu\text{g L}^{-1}$ ; IQR:  $0.14\text{--}0.59 \mu\text{g L}^{-1}$ ; range:  $0.04\text{--}0.82 \mu\text{g L}^{-1}$ ) in every shallow alluvial-aquifer-sourced sample (Sites 2–11) in this study (Fig. 4). The concentration of U detected in TW sourced from the deeper sandstone aquifer (Site 1) was 1–2 orders of magnitude less ( $0.002 \mu\text{g L}^{-1}$ ). Drinking-water U exposure is associated with human nephrotoxicity<sup>144–148</sup> and osteotoxicity,<sup>146,147,149</sup> thyroid cancer,<sup>150</sup> inhibition of DNA-repair mechanisms in human embryonic kidney 293 (HEK293) cells,<sup>151</sup> estrogen-receptor effects in mice,<sup>152</sup> a range of reproductive endpoints in humans,<sup>146,147,153</sup> and elevated odds of type 2 diabetes.<sup>154</sup>

Including only samples from the 6 alluvial-aquifer-sourced sites with potable-tap collection points (Sites 2–6, 10), Pb was detected in 5 (83%) at concentrations ranging nd– $8.5 \mu\text{g L}^{-1}$  (median:  $2.7 \mu\text{g L}^{-1}$ ; IQR:  $1.4\text{--}5.9 \mu\text{g L}^{-1}$ ) but was not detected in the Site 1 sandstone-aquifer-sourced TW sample (Fig. 4). Drinking-water Pb is attributed primarily to premise-plumbing and distribution-infrastructure materials<sup>155</sup> that predate 1986 SDWA amendments.<sup>156</sup> Accordingly, Pb detections in samples collected from non-potable (*i.e.*, outdoor spigots, fire-department pump station) tap locations (Sites 7–9, 11) were not included, due to unknown residential-exposure relevance. Based on associations with neurocognitive impairment in infants and children,<sup>155,157,158</sup> the American Academy of Pediatrics<sup>157</sup> recommends that drinking-water Pb not exceed  $1 \mu\text{g L}^{-1}$ , a routine method detection limit for US public-supply compliance monitoring;<sup>84,85</sup> 66% (4/6) of potable-tap, shallow-aquifer-sourced samples exceeded  $1 \mu\text{g L}^{-1}$ .

$\text{NO}_3\text{--N}$  concentrations in alluvial-aquifer-sourced TW samples (median:  $2.8 \text{ mg L}^{-1}$ ; IQR:  $0.14\text{--}4.9 \text{ mg L}^{-1}$ ; range: nd– $7.6 \text{ mg L}^{-1}$ ) also were below the respective MCL-equivalent (also



MCLG) 10 mg L<sup>-1</sup> level (Fig. 4). The NO<sub>3</sub>-N MCL was established to protect against bottle-fed infant (<6 months) methemoglobinemia.<sup>130</sup> However, growing evidence, which links <MCL NO<sub>3</sub>-N concentrations with other adverse health outcomes,<sup>159,160</sup> including cancer,<sup>161–166</sup> thyroid disease,<sup>167,168</sup> and neural tube defects,<sup>169</sup> raises concerns for the human-health effects of long-term consumption of alluvial-aquifer-sourced TW at French Island. NO<sub>3</sub>-N was not detected (MDL = 0.01 mg L<sup>-1</sup>) in the Site 1 sandstone-aquifer-sourced sample.

No EPA MCL or MCLG<sup>131</sup> (or WHO guideline value<sup>132</sup>) presently exist for Mn. Instead, EPA maintains a federally non-enforceable, aesthetic-based National Secondary Drinking Water Standard secondary maximum contaminant level (SMCL) of 50 µg L<sup>-1</sup> Mn,<sup>170</sup> a concentration determined, during the Contaminant Candidate List 1 (CCL1) process, to be below expected health-concern levels for the general population.<sup>171</sup> EPA established a 300 µg L<sup>-1</sup> Mn life-time DW health advisory (assumes 100% exposure from drinking water),<sup>131</sup> and Wisconsin has set 300 µg L<sup>-1</sup> as its public-welfare groundwater quality Enforcement Standard.<sup>172</sup> However, growing concerns for cognitive, neurodevelopmental, and behavioral effects of long-term Mn exposures in children have prompted calls for regulatory reevaluation,<sup>173,174</sup> and DW Mn is again undergoing regulatory determination under Contaminant Candidate List 5 (CCL5).<sup>175</sup> To protect against neurological effects in bottle-fed infants, WHO<sup>176</sup> has established a provisional guideline value of 80 µg L<sup>-1</sup> Mn, a value exceeded in TW samples from 30% (3/10) of alluvial-aquifer-sourced locations (median: 22 µg L<sup>-1</sup>; IQR: 1.75–88.2 µg L<sup>-1</sup>; range: nd–203 µg L<sup>-1</sup>), in the current study (Table S3†).

In addition to the above TW inorganic exposures of potential concern, all TW F concentrations observed in the spatial-synoptic assessment (median: 0.1 mg L<sup>-1</sup>; range: nd–0.1 mg L<sup>-1</sup>), including for the sandstone-aquifer-sourced sample (Site 1), were below the US Public Health Service<sup>177</sup> optimum of 0.7 mg L<sup>-1</sup> to prevent dental caries (Table S3†), consistent with national groundwater results<sup>178,179</sup> and dental-health concerns for children on private-wells across the US.<sup>180</sup> The American Academy of Pediatrics<sup>181</sup> and Centers for Disease Control [CDC]<sup>182</sup> recommend F supplementation for children with drinking-water concentrations <0.6 mg L<sup>-1</sup> F.

### Microbial exposures and benchmark comparisons

French Island TW samples also were screened in triplicate using heterotrophic plate (HPC), total coliform, and *Escherichia coli* (*E. coli*) counts as indicators of microbial exposures (Table S5†). General heterotrophs (HPC) were detected in all synoptic TW samples (median: 13.4 colony forming units per mL [CFU mL<sup>-1</sup>]; IQR: 6–52 CFU mL<sup>-1</sup>; range: 1.8–>200 CFU mL<sup>-1</sup>), exceeding the quantitation limit (“too numerous to count” >200 CFU mL<sup>-1</sup>) in one sample. HPC bacteria are ubiquitous, common in DW, and not intrinsic health concerns but are useful indicators of system maintenance,<sup>130,131</sup> which would include routine disinfection in private wells.<sup>59</sup> Total coliform bacteria were detected only in 2 shallow-alluvial-aquifer locations (Site 4: park water fountain; Site 9 fire department water-

filling station), both outdoor fixtures for which some level of fixture-surface contamination (and corresponding initial sample contamination) is expected. Although the MCLG for total coliforms in TW is zero,<sup>130,131</sup> the lack of total coliform detections in any other alluvial-aquifer TW samples contradicts systematic microbial contamination of the shallow-groundwater system. No spatial-synoptic TW samples were positive for *E. coli* (fecal indicator bacteria).

### Cumulative organic and inorganic chemical risk screening

Widespread co-occurring exposures to organic and inorganic contaminants of human-health concern in alluvial-aquifer-sourced samples suggest potential cumulative risk, at a minimum to the health of the island's most vulnerable populations. Accordingly, we screened for TW risk employing a  $\sum_{TQ}$  approach that provides insight into potential effects of simultaneous inorganic and organic exposures, is targeted at apical human-health effects, but is notably limited to available human-health benchmarks. Of the 101 total chemical analytes (25 inorganic; 76 organic) detected in the study, 56% (13 inorganic; 44 organic) have available human-health benchmarks focused on risks to presumptive most-vulnerable populations (Fig. S4 and Table S7a†). Every alluvial-aquifer-sourced (Sites 2–11) synoptic sample exceeded  $\sum_{TQ} = 1$  (Fig. 5, S5 and Table S7b†), indicating high probabilities of aggregated risks in French Island private-supply TW samples when considering exposures to both organic and inorganic chemicals. All but 2 alluvial-aquifer-sourced sites (Sites 9 and 11: U only) had

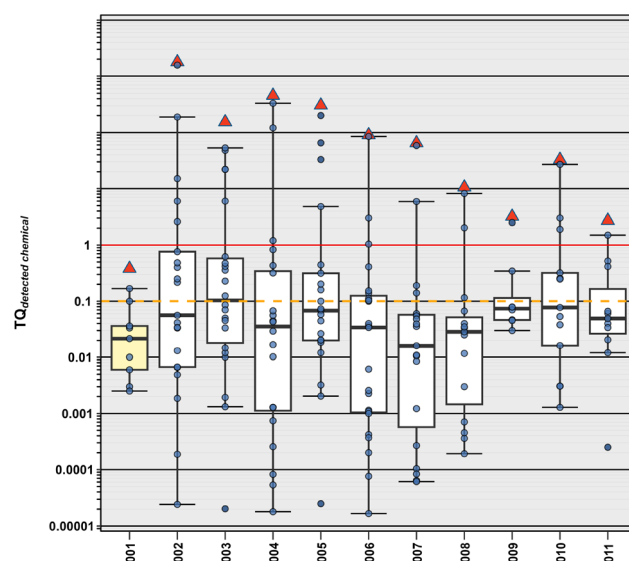


Fig. 5 Human-health benchmark-based individual toxicity quotient (TQ) values (circles, ●) and cumulative TQ ( $\sum_{TQ}$ , sum of all detected; red triangles, ▲) for inorganic and organic analytes with benchmarks in Table S7a† and detected in spatial-synoptic tapwater samples collected in 2021 at Town of Campbell, Wisconsin. Solid-red and orange-dashed lines indicate benchmark-equivalent level (TQ = 1) and effects-screening-level threshold of concern (TQ = 0.1), respectively. Boxes, centerlines, and whiskers indicate interquartile range, median, and 5th and 95th percentiles, respectively, for both plots.



multiple individual  $TQ \geq 1$  (median: 3; IQR: 1.75–4.25; range: 1–5), comprising, in decreasing detection frequency, U (9/10 sites), Pb (5/6 potable-tap sites only), PFOS (5/10), PFOA (4/10), DEHP (3/10), and Mn (2/10). Frequent exceedances of  $\sum TQ = 1$  in unregulated and generally unmonitored private-supply TW in this and previous studies<sup>44–48</sup> emphasize the intrinsic human-health challenge of unrecognized contaminant exposures in unmonitored TW.<sup>61,179,183–185</sup> Growing documentation of co-occurring inorganic and organic exposures and corresponding cumulative human-health-effects potentials support previous recommendations for systematic private-supply monitoring,<sup>61</sup> incorporating a broad analytical scope that more realistically reflects the range of inorganic and organic environmental contamination.<sup>186,187</sup>

In contrast, the  $\sum TQ$  for the sandstone-aquifer-sourced Site 1 synoptic sample was 0.38 and primarily attributable to one-time detections of the cyanotoxin cylindrospermopsin and elevated (4 times higher than all other detections) boron (B) concentrations (Fig. 5, S5 and Table S7b†). Compared to alluvial-aquifer-sourced TW, the Site 1 results indicate substantially lower cumulative risk and support consideration of the sandstone aquifer as an alternative DW source to mitigate human exposures to a wide range of TW-contaminant exposures of human-health concern, including PFAS.

### Cumulative organic EAR screening

To explore possible additional (beyond those with available benchmarks) TW-organic exposures of potential human-health interest at French Island, an EAR approach based on ToxCast<sup>120</sup> high-throughput data<sup>121</sup> was employed to screen for potential molecular-level effects of mixed-organic-contaminant exposures. The  $\sum EAR$  approach<sup>46,83</sup> leverages high-throughput exposure-effects data for 10 000+ organics and approximately 1000 vertebrate-cell-line molecular endpoints<sup>120,188</sup> in the invitroDBv3.2 release<sup>189</sup> of the ToxCast database to estimate potential cumulative activity at sensitive and perhaps more protective sublethal molecular endpoints but has limited to no coverage of inorganic contaminants and unknown transferability to organ/organism scales.<sup>190</sup> Notably, herein we aggregated contaminant bioactivity ratios across all endpoints without restriction to recognized modes of action as a precautionary screening for further investigation, but not as a direct indicator of health risk, due to uncertainties extrapolating from *in vitro* to *in vivo* (apical) effects<sup>83,190–192</sup> and the fact that not all bioactivities captured in ToxCast are necessarily adverse and may, in some instances (e.g., xenobiotic-metabolism activation<sup>193</sup>), reflect adaptive responses.

Forty-seven of the 76 organics detected in TW in this study had exact Chemical Abstract Services (CAS) number matches in the ToxCast invitroDBv3.2 database; among these, 38 had at least one individual  $EAR \geq 0.00001$  and were included in the  $\sum EAR$  assessment (Fig. S6 and Table S8b†). The EAR ( $\sum EAR$ ) results aligned with the cumulative-risk ( $\sum TQ$ ) assessment discussed above, with exceedances of  $\sum EAR = 0.001$  (precautionary screening-level threshold of interest) observed in all synoptic TW samples. The results indicate further investigation of the

cumulative biological activity from TW exposures is warranted, even when considering only the organic contaminants detected in this study. No exceedance of an *in vitro* effects level (*i.e.*, solid red  $\sum EAR = 1$  line) was observed. Individual EAR (and  $\sum EAR$ ) above 0.1 in TW samples collected from DW fountains in 2 parks (Sites 4 and 6) indicated elevated probability of molecular-effects and were attributable to *N*-nitrosodiphenylamine.

### TW-mixtures exposure: 3 days temporal assessment

To inform the short-term (few days) representativeness of the one-time synoptic TW samples and potentially provide insight into contaminant sourcing (e.g., groundwater system, premise-plumbing, TW-fixture surface), short-term variability in TW contaminant-mixture exposures was assessed in a total of 7 samples each collected from Sites 1–3 over a 3 days period using the same broad-scope target-analysis approach employed in the spatial synoptic. This discussion focuses on those detections of potential human-health concern discussed above and on summary metrics for inorganic and organic TW detections; however, all results are provided in Tables S3, S4 and S7b.† Short-term (53 h–55 h total) temporal variability in individual and cumulative TW-mixture exposures and associated risks ( $TQ$ ,  $\sum TQ$ ) was limited in this study (Fig. S7 and Table S7b†), with two exceptions comprising (1) elevated individual concentrations detected in an initial sample but not sustained in subsequent site-specific samples and (2) substantially lower concentrations in immediate post-flush (2nd sample day 1) TW samples than observed in any other site-specific TW samples.

Elevated initial-sample exposures and risks included organics (Site 1: isopropyl alcohol, cylindrospermopsins; Site 3: DEHP) and inorganics (Site 2: Pb), detected in the first sample but not thereafter, and boron (B), detected in the first sample collected at Site 1 at a concentration ( $84 \mu\text{g L}^{-1}$ ) greater than 4 times that observed in any other sample (range:  $13\text{--}20 \mu\text{g L}^{-1}$ ) from this location (Table S7b†). These one-time anomalous detections were ascribed to probable contamination at the collection point (TW fixture) and not to source-water contaminants. Because the focus of this and previous studies is better understanding of TW-contaminant exposures to humans regardless of where/when the contaminant is introduced, taps are sampled as is (*i.e.*, without any alteration/cleaning of the fixtures) and some potential for fixture-surface-derived contamination (e.g., isopropyl alcohol from SARS-CoV-2 disinfection activities; B from borate-containing cleaning products) exists during sample collection, as it also does during residential TW use. Metal-particulate contamination resulting from the removal of a non-potable-brass hose adapter immediately prior to TW-sample collection is a plausible explanation for the one-time detection of Pb ( $0.6 \mu\text{g L}^{-1}$ ) in the initial Site 2 TW-sample.

Contaminants which exhibited lower concentrations in immediate post-flush (*i.e.*, 2nd sample) TW samples (Table S7b†), notably at Site 3 and to lesser extents at Sites 1 and 2, than in other site-specific TW samples, were attributed as premise-plumbing derived. The order of magnitude lower copper (Cu) concentration ( $30 \mu\text{g L}^{-1}$ ) observed post-flush, compared with other TW samples (median:  $460 \mu\text{g L}^{-1}$ ; range:



332–617  $\mu\text{g L}^{-1}$ ) at Site 3, is consistent with plumbing-derived contamination, as, to a lesser extent, are post-flush non-detect and 10  $\mu\text{g L}^{-1}$  Cu results compared to median concentrations of 9  $\mu\text{g L}^{-1}$  (range: 5–17  $\mu\text{g L}^{-1}$ ) and 45  $\mu\text{g L}^{-1}$  (range: 29–74  $\mu\text{g L}^{-1}$ ) at Sites 2 and 1, respectively. As noted above, detections of Pb in TW (*i.e.*, concentrations greater than 1  $\mu\text{g L}^{-1}$  MDL common to public-supply regulatory monitoring) are generally attributed to legacy use in distribution-system and premise-plumbing infrastructure.<sup>155</sup> In light of the Cu results, the 50% lower Pb concentration (1.4  $\mu\text{g L}^{-1}$ ) in the Site 3 post-flush sample, compared with the other TW samples (median: 3.2  $\mu\text{g L}^{-1}$ ; range: 2.2–4.3  $\mu\text{g L}^{-1}$ ) collected at the site, combined with sporadic detection of Pb in alluvial-aquifer synoptic TW samples collected from potable taps, are consistent with premise-plumbing as the probable source of TW Pb detection, rather than an alluvial-aquifer source.

Source attribution of the elevated TW zinc (Zn) exposures observed in the French Island alluvial-aquifer TW samples, however, is less clear (Table S7b†). TW Zn exposures (median: 177  $\mu\text{g L}^{-1}$ ; IQR: 63–726  $\mu\text{g L}^{-1}$ ; range: 21–968  $\mu\text{g L}^{-1}$ ) and associated risk (TQ) estimates (median: 0.088; IQR: 0.031–0.363; range: 0.010–0.484) varied substantially in alluvial-aquifer spatial-synoptic samples. The 48% lower Zn concentration in the Site 2 post-flush sample (557  $\mu\text{g L}^{-1}$ ), compared with the other TW samples (median: 1080  $\mu\text{g L}^{-1}$ ; range: 968–1280  $\mu\text{g L}^{-1}$ ) collected at the site, indicate that premise-plumbing may contribute in part to TW Zn exposures at Site 2. However, continued detection of substantial Zn concentrations post-flush at Site 2, the lack of a post-flush depression in Zn concentrations at Site 3, and the notable spatial variability in TW Zn exposures in spatial-synoptic samples raise the possibility of elevated groundwater Zn concentrations of potential human-health interest in the shallow-alluvial aquifer at French Island.

Remarkably, little variability was observed for individual or cumulative PFAS concentrations and associated risks in TW samples from Site 2 (Fig. S7; Tables S4 and S7b†), where concentrations were well above method detection limit(s) (MDL). In contrast, detected (*de facto* MCLG ‘zero’ exceedances) concentrations of the high-risk contaminants, PFOA and PFOS, in Site 3 TW samples were near the MDL; thus, while little variability in detected concentrations of PFOA and PFOS was observed at Site 3, intermittent non-detection of these compounds resulted in substantial variability in cumulative risk ( $\sum\text{TQ}$ ). Notably, concentrations of PFBA, the only PFAS detected at Site 1, decreased over time in the sandstone-aquifer-sourced samples, and PFBA was not detected in the last three samples. This finding raised the possibility that early-sample detections at Site 1 may have originated from fixture-surface or proximal premise-plumbing contamination and not from source-water contamination. As discussed in the following section, PFBA was not detected in 2021–2024 quarterly PFAS samples collected from the Site 1 source well (well 972), supporting the hypothesized fixture/premise-plumbing origin for PFBA contamination detected in the early short-term-variability samples at Site 1.

Consistent with the limited short-term variability in individual and cumulative TW exposures, little variability in cumulative risk ( $\sum\text{TQ}$ ) was observed in TW samples from Sites

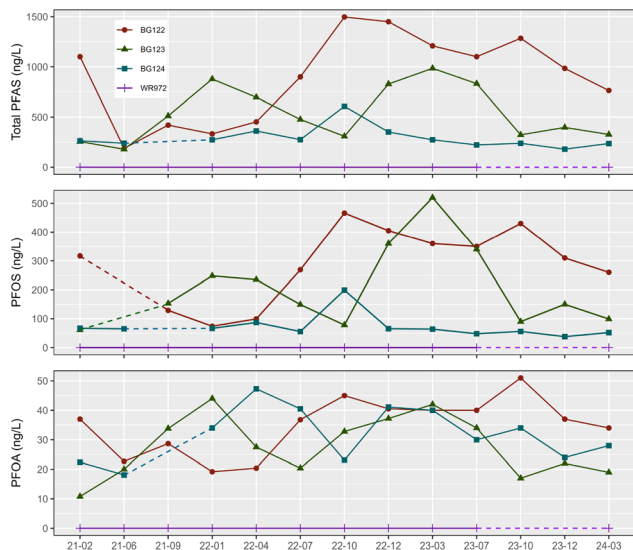
1–3 (Fig. S7 and Table S7b†). A median-absolute-difference-based, nonparametric, robust coefficient of variation ( $\text{RCV}_{\text{MAD}}^{194}$ ) was calculated to evaluate short-term  $\sum\text{TQ}$  variability. The  $\sum\text{TQ}$  short-term variability ( $\text{RCV}_{\text{MAD}}$ ) was approximately 42% for TW samples collected at Site 1 ( $\sum\text{TQ}$  median: 0.133; IQR: 0.119–0.276; range: 0.096–0.380), due primarily to the unrepeated, initial-sample detection of cylindrospermopsin (Table S4a†) and elevated B (Table S3†), as discussed.  $\text{RCV}_{\text{MAD}}$  at Site 3 was approximately 28% ( $\sum\text{TQ}$  median: 112; IQR: 73–131; range: 36–153) and largely attributed to circa-MDL detections and corresponding intermittent non-detections of PFOA and PFOS at the Site, as discussed. At Site 2, where PFAS concentrations were well-above MDL,  $\text{RCV}_{\text{MAD}}$  was substantially lower at approximately 12% ( $\sum\text{TQ}$  median: 1775; IQR: 1629–1935; range: 1607–1976).

The results indicate that the spatial-synoptic assessment provided reasonable insight into the risk of TW-mixture exposures at French Island over the short-term, and that corresponding cumulative TW-contaminant risks ( $\sum\text{TQ}$ ) were relatively stable. Further, the results illustrated the additional interpretive insight into TW-contaminant sourcing afforded by temporal sampling. Importantly, consistently lower  $\sum\text{TQ}$  for Site 1 short-term variability samples corroborated substantially lower cumulative risk in sandstone-aquifer-sourced TW samples compared to alluvial-aquifer-sourced samples and supported the use of the sandstone aquifer as an alternative DW source to mitigate human exposures to a wide range of TW-contaminant exposures of human-health concern, including PFAS.

### TW-PFAS exposure: multi-year temporal assessment

Multi-year variabilities and trends in TW PFAS exposures were assessed by quarterly sampling at UMESC during February 2021 to March 2024, including from the underlying Mount Simon sandstone aquifer source well for Site 1 TW (well 972) and the three, shallow-alluvial-aquifer, source wells (wells 122–124) for Site 2 TW (Fig. 1; Tables S9a and b†). During this 3 year period, PFAS were continuously detected in samples from wells 122–124 (Fig. 6), documenting persistent PFAS contamination of the shallow-alluvial-aquifer DW source and corresponding persistent TW-exposure risks (*i.e.*,  $\sum\text{TQ} \gg 1$ ; Fig. S8†) to human-health. Kendall Tau rank correlation indicated no statistical ( $\alpha = 0.05$ ) trend in total PFAS ( $p$ -value range: 0.153–0.590) or PFOA ( $p$ -value range: 0.178–0.945) concentrations in any samples from wells 122–124 or in PFOS ( $p$ -value range: 0.459–0.841) concentrations in samples from wells 122–123. A statistical (Kendall's Tau  $p$ -value = 0.021) decrease in PFOS concentrations of approximately 22% was observed in samples from well 124 during the 3 year period. In contrast to the shallow alluvial well results, no PFAS were detected in well 972 samples over the 3 year period (Fig. 6 and Table S9a†), apart from a single, unrepeated detection of perfluorobutanesulfonic acid (PFBS) below the method detection limit (MDL), indicating no PFAS-associated human-health risk (*i.e.*,  $\sum\text{TQ} < 0.01$ ; Fig. S8†) from corresponding TW consumption and supporting managed utilization of the sandstone aquifer as an alternative DW source





**Fig. 6** Concentrations ( $\mu\text{g L}^{-1}$ ) of total per/polyfluoroalkyl substances (total PFAS, top), perfluorooctane sulfonate (PFOS, middle), and perfluorooctanoic acid (PFOA, bottom) detected during quarterly monitoring of Site 1 (972) and Site 2 (122–124) source wells, during 2021–2022. Dashed lines indicate samples not collected or missing.

to mitigate TW-PFAS exposures to French Island residents. Comparable PFAS-specific cumulative risk ( $\sum_{\text{TQ}}$ ) estimates for synoptic (*i.e.*, 1st sample), short-term (3 days) temporal, and long-term (3 years) assessment samples (Fig. S8†) indicated that the spatial-synoptic assessment also provided reasonable insight into the risks of TW-PFAS exposures at French Island over the long-term, and that corresponding cumulative TW-contaminant risks ( $\sum_{\text{TQ}}$ ) were relatively stable.

### Study limitations

Several limitations deserve consideration when interpreting the results of this study. First, the extensive and environmentally-informative target-analytical scope employed in this and previous studies by the research group is only a fractional indicator of the estimated 350 000 commercially produced chemicals (not including environmental transformation products and degradates) potentially present in the environment;<sup>195</sup> thus, the cumulative TW exposure and associated risk assessments presented herein are potential orders-of-magnitude underestimates. Second, the  $\sum_{\text{TQ}}$  and  $\sum_{\text{EAR}}$  approaches employed herein are constrained by available weighting-factors; human-health benchmarks and ToxCast ACC were available for 55% of detected inorganic/organic TW constituents and 50% of detected organics, respectively. Third, for both approaches, approximate concentration addition was assumed (*e.g.*, (ref. 124, 126, 196 and 197), potentially underestimating or overestimating cumulative effects in the event of synergism/potential or antagonism, respectively;<sup>198</sup> while documented,<sup>199–202</sup> departures from approximate concentration addition are considered comparatively rare, increasingly unlikely with increasing number of mixture components, and typically within one order of magnitude.<sup>197,203,204</sup> Fourth, EAR

estimates were aggregated across all ToxCast endpoints without restriction to recognized modes of action to provide a precautionary lower-bound estimate of *in vivo* adverse-effect level,<sup>205</sup> a useful approach for bioactivity screening but not necessarily indicative of adverse apical effects.<sup>83,190</sup> Fifth, the PFAS results reflect then-available methods, with reporting limits generally above current PFAS human-health concern levels (*e.g.*, 2024 PFAS MCLG and associated benchmarks<sup>137,138</sup>), and, thus, should be considered underestimates of TW PFAS exposures and risks; methods with reporting limits  $\leq 1 \text{ ng L}^{-1}$  are available now (*e.g.*,<sup>206</sup>). Sixth, MCLG values of 'zero' were set to  $0.1 \mu\text{g L}^{-1}$  for metals and VOC and to  $0.0001 \mu\text{g L}^{-1}$  for PFOS and PFOA to avoid overinflating TQ estimates, but this approach may not be sufficiently precautionary for toxicities like endocrine disruption and carcinogenicity. Lastly, the extensive analytical scope employed in this study provided critical and actionable insight into potential residential and public-facility TW-contaminant exposures to inform exposure-mitigation decision-making at individual-household and community levels, but the limited number of samples and sample locations may not represent the full range of source-water- and premise-plumbing-derived TW-exposures on French Island.

## Conclusions

The broad-analytical-scope spatial synoptic results indicated that simultaneous exposures to contaminants of human-health interest are common in alluvial-aquifer-sourced TW locations across the study area. The human-health-benchmark-based  $\sum_{\text{TQ}}$  results indicated that exposures to PFAS, including above MCL concentrations, are the primary drivers of human-health risks from shallow alluvial-aquifer-sourced TW exposures for locations adjacent to and downgradient of the municipal airport. However, comparable  $\sum_{\text{TQ}}$  results attributable to inorganic and VOC exposures in several TW samples without detectable PFAS (collected upgradient of the airport and south of Interstate 90), illustrated that human-health risks from shallow alluvial-aquifer-sourced TW-contaminant exposures are widespread and not solely attributable to PFAS (Fig. S5†).

Common co-occurrences of multiple analytes with human-health implications in private-well TW samples, including co-occurring exceedances of MCLG and  $\sum_{\text{TQ}} > 1$ , have raised community concerns<sup>6,7</sup> and corresponding interest in exposure-mitigation, including POE-/POU-treatment options<sup>207–211</sup> and DW-source alternatives. The median health-benchmark exceedances per sample in TW sourced from the shallow alluvial aquifer (current primary DW source for Town of Campbell residences, businesses, and public facilities) was 2 (range: 1–5), illustrating the importance of identifying stand-alone POE/POU treatment options for unregulated private-well TW, which are effective against multiple contaminants<sup>207,212</sup> or identifying a more suitable DW aquifer for new private wells or a public-supply system. Regarding the former, broadly effective single-stage treatment technologies (*e.g.*, reverse osmosis [RO]) or multi-stage/multi-filtration (sediment filter, redox media, activated carbon, ion exchange, RO, UV disinfection) systems are generally considered more appropriate for organic-/inorganic-



contaminant-mixtures,<sup>207</sup> like those observed in alluvial-aquifer-sourced TW at Town of Campbell. Regarding the latter, notably lower organic-/inorganic-contaminant exposures and associated cumulative risks, including PFAS exposures and risks, in sandstone-aquifer-sourced TW samples over a 3 year period support consideration of the sandstone aquifer as an alternative DW source to mitigate alluvial-aquifer TW-PFAS exposures to French Island residents.

Assessment and communication of TW contaminant exposures is essential to DW-risk management and public-health decision-making at household and community scales. Analytically extensive datasets like this study, which are intended to inform scientific and public-health understanding of DW as a vector for human contaminant exposures and associated human-health outcomes, remain limited because broad assessments of regulated and unregulated contaminants are not generally conducted at the TW point-of-use in the US or worldwide. These results emphasize the importance of continued broad characterization of POU-DW exposures, especially in unregulated and unmonitored private-supplies, using an analytical coverage that serves as a realistic indicator of the breadth and complexity of inorganic and organic contaminant mixtures known to occur in ambient source waters<sup>186,187</sup> to improve models of TW contaminant exposures and related risks. Increased availability of such health-based monitoring data, including results below current, technically- or economically-constrained public-supply enforceable standards (e.g., MCL), is important to support engagement in source-water protection and DW treatment and to inform community- and consumer-level DW decision-making throughout the US.

## Data availability

Data discussed in this paper are summarized in ESI† (Tables S1–S9b†) and in the USGS data releases.<sup>1–3</sup>

## Author contributions

Conceptualization: PMB, KMR, KLS, LD, MPG. Data curation: PMB, KMR, SMM. Formal analysis: PMB, KMR, KLS. Investigation: PMB, KMR, KLS, KAL, RBM, SMM. Methodology: PMB. Project administration: PMB, KLS. Resources: MPG, RKH. Visualization: PMB, KMR, SEG. Writing – original draft: PMB. Writing – review & editing: PMB, KMR, KLS, LD, MPG, RKH, SEB, SEG, KAL, RBM, SMM, MLS.

## Conflicts of interest

There are no conflicts to declare.

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trademark of the American Chemical Society. CAS recommends the verification of the CASRNs through CAS Client Services<sup>SM</sup>.

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