# Addressing the Contribution of Indirect Potable Reuse to Inland Freshwater Salinization

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**Abstract**

Inland freshwater salinity is rising worldwide, a phenomenon called the freshwater salinization syndrome (FSS). We investigate a potential conflict between managing the FSS and indirect potable reuse, the practice of augmenting water supplies through the addition of reclaimed wastewater to surface waters and groundwaters. From time-series data collected over 25 years, we quantify the contributions of three salinity sources—a wastewater reclamation facility and two rapidly urbanizing watersheds—to the rising concentration of sodium (a major ion associated with the FSS) in a regionally important drinking water reservoir in the Mid-Atlantic United States. Sodium mass loading to the reservoir is primarily from watershed runoff during wet weather and reclaimed wastewater during dry weather. Across all timescales evaluated, sodium concentration in the reclaimed wastewater is higher than in outflow from the two watersheds. Sodium in reclaimed wastewater originates from chemicals added during wastewater treatment, industrial and commercial discharges, human excretion, and down-drain disposal of drinking water and sodium-rich household products. Thus, numerous opportunities exist to reduce the contribution of indirect potable reuse to sodium pollution at this site, and the FSS more generally. These efforts will require deliberative engagement with a diverse community of watershed stakeholders and careful consideration of the local political, social, and environmental context.

## Introduction

While historically a problem only in areas with arid and semi-arid climates, poor agricultural drainage practices, sodic soils and saline shallow groundwater [1-3], inland freshwater salinization is on the rise across many cold and temperate regions of the United States (US) [4-8]. The trend is particularly notable in the densely populated Northeast and Mid-Atlantic [9-12] and agricultural Midwest regions [8,13,14] of the country. Globally, inland freshwater salinization has been reported in Canada, Finland, France, Greece, Italy, Iran, and Russia [15]. The ions driving inland freshwater salinization vary by location and source, but generally include a subset of the so-called major ions (defined here as $Na^{+}$, $Ca^{2+}$, $Mg^{2+}$, $K^{+}$, $Cl^{-}$, $SO_4^{-2}$) [5]. Freshwater salinization is part of a broader change in the chemistry of many of earth's inland freshwaters—including rising pH, alkalinity and base cation concentration—known as the "Freshwater Salinization Syndrome" (FSS) [8]. Human drivers include the use of deicers on roads and parking lots [9,16-20], water softener use [12], wastewater and industrial discharges [21], fertilizers and pesticides [22], the weathering of concrete [9,23-26], and the accelerated weathering of geologic materials from the release of strong acids and human excavation of rock, which currently exceeds natural denudation processes by an order of magnitude [27,28]. In a recent modeling study, Olson [13] predicts that specific conductance (one measure of salinity) will increase >50% in more than half of U.S. streams by 2100.

The FSS threatens freshwater ecosystem health and human water security. Chloride enrichment of streams is associated with declines in pollution-intolerant benthic invertebrates and loss of critical freshwater habitat [29]. Stream borne salts can mobilize, through biogeochemical processes, previously sequestered contaminants (e.g., nutrients and heavy metals) into sensitive ecosystems and drinking water supplies [15,17,30,31], potentially reversing hard won pollution reductions. Salinization of drinking water supplies can mobilize lead, copper and other heavy metals from aging drinking water infrastructure through cation exchange and corrosion [32-35]. It can also alter the perception of potability—at high enough concentrations, sodium and other salts degrade the taste of drinking water [36]. The World Health Organization and the U.S. Environmental Protection Agency (EPA) have set taste thresholds for the concentration of sodium in drinking water of 200 (NaCl mg)/L (about 78.6 Na mg/L) and between 30 to 60 Na mg/L, respectively [37,38]. An EPA drinking water health advisory of 20 Na mg/L applies to individuals on sodium restricted diets [36,38].

In this paper, we explore a potential conflict between two important sustainability goals: (1) minimizing or reversing the FSS and (2) augmenting water supplies through the addition of highly treated wastewater to reservoirs and groundwaters, a practice referred to as "indirect potable reuse" (IPR) [39]. While the number of IPR facilities is modest at present [40-42], the EPA recently released a draft national Water Reuse Action Plan [43,44] that promotes IPR and other forms of wastewater reuse and recycling to address, where appropriate, expected water supply shortfalls over the next ten years in 40 of 50 US states [45]. More common is unplanned wastewater reuse which occurs, for example, when treated wastewater is discharged to surface waters upstream of a drinking water intake [39]. Rice et al. [46] estimated that wastewater contributes >50% of the flow in 900 streams across the contiguous US. Even in water-rich areas of the country, such as Indiana, unplanned wastewater reuse constitutes a sizeable fraction of the water supply (3 – 134%, with the larger end of the range referring to circulation of wastewater through multiple water systems as it flows downstream) [47].

Human health and ecological concerns associated with IPR and unplanned wastewater reuse typically focus on the impacts of discharged nutrients, micropollutants, and endocrine disrupters on receiving water quality [48-50]. These wastewater reuse practices also have the potential to exacerbate the FSS. This is because salt entering a sewage collection system, or added during the treatment process, is not removed by conventional wastewater treatment processes. However, based on the literature, the contribution of treated wastewater to the FSS appears to be strongly climate and context dependent [51,52]. For example, in a study of salt retention in a rural watershed in New York State, “salt used for deicing accounted for 91% of the sodium chloride input to the watershed, while sewage and water softeners accounted for less than 10% of the input” [12]. On the other hand, a study of sodium and chloride surface water exports from the Dallas/Fort Worth region of Texas found that, “the single largest contributor was wastewater effluent...” [21]. A reasonable inference from these and other studies is that treated wastewater is a significant source of freshwater salinity in warmer climates, while deicers drive freshwater salinization in colder climates that receive snowfall [10,12,18,21,53-59]. This conclusion is supported by the strong south-to-north increasing trend in stream specific conductance along the US east coast [16]. Untreated wastewater can contribute to the FSS across all climates, as documented by the contribution of aging sanitary infrastructure to stream chloride concentrations in Baltimore and Puerto Rico [60-62].

We hypothesize that two common methodological shortcomings in the literature may obscure the contribution of IPR and unplanned wastewater reuse to the FSS in colder climates: (1) the focus is often on characterizing salt mass loads (i.e., salt mass per time) discharged from wastewater treatment plants, whereas many endpoints of human and ecological concern are concentration based (e.g., EPA acute and chronic criteria for instream chloride concentrations [63] and the taste thresholds and health advisory for sodium concentrations in drinking water [36-38]); and (2) salt mass loads discharged from wastewater treatment plants are typically aggregated to annual averages, thereby removing higher frequency processes (e.g., seasonal and day-to-day streamflow variability) that can strongly influence the dilution of wastewater flows in inland freshwaters [47,64-66].

We test this hypothesis by analyzing a unique >25-year time series of flow and sodium concentration measurements in the tributaries and reclaimed wastewater that collectively drain to a regionally important drinking water reservoir in Northern Virginia. We quantify, using regression and a copula-based conditional probability analysis [67], how sodium inputs to the reservoir from watershed and reclaimed wastewater sources are modulated by climate and other environmental factors. We then explore how the contributions of treated wastewater to inland freshwater salinization might be reduced through locally tailored interventions that increase a region's salt productivity, defined here as the goods and services produced per unit of salt discharged to inland freshwaters.

**Field Site**

[Figure 1 about here]

The Occoquan Reservoir, located approximately 30 km southwest of Washington D.C. in Northern Virginia, is one of two primary sources of water supply for nearly 2 million people in Fairfax County, Virginia, and surrounding communities (Figure 1a). Sodium concentration in the reservoir began increasing around 1995 (purple curve in Figure 1b) and now frequently exceeds the EPA's lower taste and health advisory thresholds (horizontal black solid and dashed lines). This trend prompted the local water purveyor, Fairfax Water, to explore planning-level options to address the rising sodium concentration in the reservoir, including the possible construction of a reverse osmosis treatment upgrade. The irony of desalinating freshwater and the estimated cost ($1B USD, not including operating and maintenance costs and a vastly higher carbon footprint

[68]) makes identifying, and ideally mitigating, sources of sodium in the reservoir a top regional priority.

On an annual basis, approximately 95% of the water flowing into the reservoir comes from its Occoquan River and Bull Run tributaries. Water from Bull Run includes baseflow and stormwater runoff from the Bull Run watershed ($1.94 \times 10^8$ $m^3$ $year^{-1}$) together with reclaimed water discharged from a wastewater reclamation facility (Upper Occoquan Service Authority, UOSA) ($3.28 \times 10^7$ $m^3$ $year^{-1}$) located approximately 1.5 km upstream of Bull Run's confluence with the reservoir (red star in Figure 1a). One of UOSA's missions is to improve drinking water security in the region by augmenting streamflow into the Occoquan Reservoir with a high quality and drought proof source of water. Conceived and built in the 1970s, UOSA was the US's first planned application of IPR for surface water augmentation and a model for the design and construction of similar reclamation facilities around the world [39,69]. Water discharged from the Occoquan River comes primarily from baseflow and stormwater runoff from the Occoquan River Watershed ($3.43 \times 10^8$ $m^3$ $year^{-1}$). Thus, possible sources of sodium in the reservoir include deicer use and other land-based anthropogenic sodium sources in the rapidly urbanizing Occoquan River and Bull Run watersheds, which have experienced population increases of 200,000 and 220,000 residents, respectively, over the past 20 years [70], and salt added to UOSA's sewershed from its >350,000 residential and commercial connections [71]. Possible sources of sodium within UOSA's sewershed include the down-drain disposal of sodium-containing drinking water and sodium-containing household products [72-74], use of water softeners in commercial and residential locations [53], as well as permitted and non-permitted sodium discharges from industrial and commercial customers. The sodium concentration in UOSA's effluent may also be elevated due to structural and non-structural water conservation measures that concentrate salts in wastewater streams [75,76]. Indeed, sodium concentration measured in daily flow-weighted composite samples of UOSA's discharge are consistently higher than sodium concentrations measured in grab samples collected downstream on the Bull Run at station ST45 and on the Occoquan River at station ST10 (Figure 1b).

**Results**

*MLR Models for Sodium Concentration*. Multiple linear regression (MLR) models of sodium concentration generated for each monitoring station (ST10, ST45, and UOSA) were ranked by Bayesian Information Criterion (BIC) and then validated using leave-one-out cross validation root mean square error (LOOCV-RMSE) and the hold-out method [77-81] (see Methods and Supplementary Information for details). The top-ranked MLR models (Supplementary Table 1) are significant ($p<0.001$) and capture between 31 and 87% of the measured variance in log-transformed sodium concentration (adjusted $R^2$ values reported in Supplementary Table 1). The top-ranked MLR model for sodium concentration at ST45 captures the most variance ($R^2$=87%, hold-out $R^2$=81%) and its predictor variables include in situ specific conductance (positive correlation), maximum snow depth over the previous two weeks (positive correlation), log-transformed flow (negative correlation) and season (higher sodium concentration during the winter season). The top-ranked MLR model for sodium concentration in UOSA's discharge captures the second most variance ($R^2$=54%, LOOCV-$R^2$=51.6%) and has as its only predictor variable specific conductance measured on flow-weighted composite final discharge samples (positive correlation). The top-ranked MLR model for sodium concentration at ST10 explains the least variance ($R^2$=31%, hold-out $R^2$=15%), presumably because in situ specific conductance measurements were not available at this station. Predictor variables for sodium concentration at ST10 include log-transformed flow (negative correlation), maximum snow depth over the previous two weeks (positive correlation), and number of days below freezing in the previous two weeks (positive correlation). In summary, sodium concentration at these three stations is: (1) positively correlated with specific conductance measured either in situ (ST45) or on flow weighted composites of the final discharge (UOSA); (2) positively correlated with environmental variables (antecedent snow, freezing weather and winter season) likely to be associated with deicer use (ST10 and ST45); and (3) negatively correlated with flow (ST10 and ST45), implying that stormwater tends to dilute instream sodium concentration.

[Figure 2 about here]

*Daily Timeseries of Sodium Mass Load and Concentration.* Synthetic time series of sodium concentration (generated using the top-ranked and validated MLR models described above) were combined with daily flow measurements at ST10, ST45, and UOSA to generate daily predictions (from 2010 through 2018) of sodium mass load and concentration in flows from the three putative sources evaluated in this study—Occoquan River Watershed, Bull Run Watershed, and UOSA water reclamation facility (see Methods). When these daily predictions are aggregated to annual averages, the results are in line with previous reports for regions that experience seasonal snowfall; namely, annual mass loading of sodium to the Occoquan Reservoir is dominated by the two watershed sources, not by UOSA (Figure 2a). Consistent with Figure 1b, however, the annualized sodium concentration in UOSA's discharge ranges between 60-70 mg/L, well above EPA’s lower threshold for taste (30 mg/L), and >1.5 and >4.5 times above the annualized sodium concentration in flow from the Bull Run and the Occoquan River watersheds, respectively (Figure 2b).

[Figure 3 about here]

These annualized results could be interpreted to mean that UOSA contributes a relatively minor portion of sodium mass loading to the Occoquan Reservoir. However, the story is more nuanced when evaluated on a day-by-day basis (Figure 3). During extended periods of reduced precipitation, sodium mass load from UOSA frequently exceeds mass loads from either the Occoquan River or Bull Run watersheds (see four vertical gray stripes, Figure 3b). During wet weather, on the other hand, sodium mass loads from the two watersheds consistently exceed those from UOSA, often by >200-fold (note that the sodium mass load axis in Figure 3b is logarithmic). Spikes in wet weather sodium mass loading from the two watersheds dominate the annual load estimates, giving the potentially misleading impression that UOSA is a minor contributor to sodium in the reservoir (compare with Figure 2a). These daily and annual sodium mass load estimates should be relatively robust to uncertainty in the MLR-generated synthetic sodium concentration timeseries, because most of the mass loading variance ($R^2$= 66%, 91% and 82% for Occoquan River watershed, Bull Run watershed and UOSA, respectively) is attributable to measured daily average flow at each station.

Consistent with the annualized results (Figure 2b), on a day-to-day basis the sodium concentration in UOSA's effluent is nearly always higher than the sodium concentration in outflows from the Occoquan River and Bull Run watersheds (Figure 3d). Sodium concentration in outflow from the Bull Run watershed is generally higher than in outflow from the Occoquan River watershed, consistent with the latter's greater impervious surface fraction (Supplementary Table 2).

[Figure 4 about here]

*Influence of Weather on Sodium Mass Loading*. Application of a copula-based conditional probability analysis to daily predictions of sodium mass load for the period 2010 to 2018 (see Methods) confirms that UOSA's discharge dominates the sodium mass load entering the reservoir from the Occoquan River and Bull Run during dry and median weather conditions (Figure 4). UOSA's percentage contribution to sodium mass loading varies from 60 to 80%

during dry conditions (corresponding to cumulative flow from the Occoquan River and Bull Run of $\langle Q_{\text{Total}} \rangle = 90$ cubic feet per second (cfs)), 30 to 50% during median conditions ($\langle Q_{\text{Total}} \rangle = 244$ cfs), and 5 to 25% during wet conditions ($\langle Q_{\text{Total}} \rangle = 1095$ cfs). The Occoquan River and Bull Run watersheds exhibit the opposite pattern, contributing a greater percentage of the overall sodium load during wet weather periods. During wet weather, sodium mass loading from the Bull Run watershed is, on average, higher than sodium mass loading from the Occoquan River watershed, consistent with the land use data in Supplementary Table 2.

[Figure 5 about here]

*Sources of Wastewater Salts*. The results presented above support our hypothesis that, when evaluated on a daily basis, discharge from wastewater reclamation facilities can be a significant component of the freshwater sodium budget even in colder climates, like the mid-Atlantic US, where deicers are a well-documented cause of inland freshwater salinization [9,16-20]. Where is the sodium in UOSA's discharge coming from? UOSA's sewage collection system serves as a conduit through which sodium from myriad sources (watershed deicers, water treatment processes, household products, commercial and industrial discharges, and wastewater treatment) are focused into a single point source discharge (Figure 5a). Based on data provided by the utility we estimate that, on an annual average, 46.5% of the daily sodium mass load from UOSA (7600 ± 590 kg day$^{-1}$) is partitioned between chemicals used in water and wastewater treatment (for pH adjustment, chlorination, dechlorination, and odor control), a single permitted discharge from a microfabrication facility, and human excretion; the latter was estimated by multiplying UOSA's service population (351,906) [71] by a mean excretion rate of 3.608 g $Na^+$ day$^{-1}$ [82] (Figure 5b). The source of the remaining 53.5% is unknown, but presumably includes contributions from the down-drain disposal of sodium-containing drinking water (~2.5 ($Na^+$

mg)/L) from Lake Manassas, the Potomac River and the Occoquan Reservoir, as well as sodium-containing household products that eventually end up in the sanitary sewer system.

*Generalizable Lessons*. Given these results for the Occoquan reservoir, how can the potential conflict between reducing the FSS and promoting water security through IPR and unplanned wastewater reuse be addressed? One possible conceptual framework, borrowed from soft-path approaches for enhancing human water security [83,84], focuses on a variety of approaches, applied at various scales, for increasing the goods and services produced per unit of salt discharged to inland freshwaters; i.e., improving “salt productivity.” As applied to sodium, there are at least four ways in which salt productivity could be improved: (1) reduce watershed sources of sodium that enter the water supply (such as from deicer use); (2) enforce more stringent pre-treatment requirements on industrial and commercial dischargers; (3) switch to low-sodium water and wastewater treatment methods; and (4) encourage households in the sewershed to adopt low-sodium products. We consider each in turn.

Because potable water supply and sewage collection systems are inextricably linked (e.g., Figure 5a), factors that contribute salt to the former ultimately contribute salt to the latter as well. As mentioned earlier, many different sources (apart from treated wastewater) contribute salt to inland freshwaters, most notably deicer use in northern climates but also untreated sewage (e.g., from failing septic systems [85]) and erosion of civil infrastructure (e.g., pavement [86]). With respect to deicers, their use on roadways can be curtailed without a reduction in public safety (e.g., through precision deicer application [87]). However, interventions at the watershed scale raise many questions across various domains, including human behavior (e.g., how do we induce residents to be more conservative about their use of deicers on parking lots and driveways, and what is the “right amount” of deicer they should be using?); hydrology (what are the hydrologic pathways by which salt moves through watersheds, and what are their timescales?); ecology (how do the changing concentrations and compositions of salinized waters alter biological communities and ecosystem processes?); and engineering design (are we unintentionally creating legacy salt pollution by adopting stormwater best management practices that transfer road salts to groundwater?). In such complex socio-hydrological-ecological systems, well intended interventions can have adverse consequences and so-called "aggregation effects" in which "desirable outcomes at a larger scale conceal inequalities and, as such, distributional injustices at the local scale" [88]. For example, deicer use might be reduced by lowering expectations for clean roads and public transportation during winter storms, but such actions could also limit access to free and subsidized school breakfast and lunch programs for low-income children and thereby exacerbate child hunger [89].

Sodium reductions can be achieved by the imposition of more stringent pre-treatment requirements on commercial and industrial dischargers, although this will inevitably raise questions regarding potential economic trade-offs. For example, nearly 14% of the annual sodium load discharged by UOSA can be traced to a single chip fabrication facility (Figure 5b). The fabrication facility is currently undergoing a major expansion that will both increase the load of sodium entering UOSA's sewershed and add up to 1000 high-tech jobs to the local economy [90].

Changes in centralized water and wastewater treatment practices can be implemented. Chlorine is a cost-effective and well-established method for destroying viruses, bacteria and protozoa, including those responsible for waterborne human disease [91]. Wastewater treatment plants that use chlorine to disinfect their water must also dechlorinate to prevent harm to downstream aquatic life. Dechlorination is typically achieved through the addition of sulfur dioxide or sulfite salts, including sodium sulfite, sodium bisulfite, or sodium metabisulfite [92] thereby increasing the sodium content of the water [93]. Dechlorination dosages depend on the compound used; e.g., sodium sulfite, sodium bisulfite, and sodium metabisulfite require 1.8-2.0, 1.5-1.7, 1.4-1.6 mg per mg $L^{-1}$ of chlorine residual, respectively [94]. Therefore, judicious choice of a dechlorinating agent or the use of alternative disinfectants (e.g., ultraviolet (UV) light) can help reduce sodium mass loading from wastewater treatment. Interestingly, the use of UV light for disinfection might also reduce micropollutant concentrations in the reclaimed wastewater [95].

Likewise, there are multiple steps in the drinking water treatment process where sodium can be introduced (Table 1). A drinking water facility looking to decrease sodium use should begin by identifying which of their processes contribute sodium and what alternative chemicals or processes might be adopted, while being mindful of potential unintended consequences. As an example of the latter, adoption of the coagulant ferrous sulfate for drinking water treatment, while potentially minimizing the addition of sodium, could accelerate the corrosion of downstream sewer infrastructure [96]. As with the chip manufacturing example above, economic constraints and a risk averse culture among public sector utilities [97-99] may also limit what can be achieved in practice.

**Table 1. Steps during the drinking water treatment process that introduce sodium and alternative low-sodium or sodium-free methods or compounds.**

| Treatment Process | Sodium Introducing Compound(s) | Sodium-free Alternatives | Reference |
|---|---|---|---|
| Softening | Soda ash (sodium carbonate) or by ion-exchange processes | Electrically induced precipitation, template assisted crystallization, magnetic water treatment, and electrically induced precipitation or capacitive deionization, polyphosphate, | Shammas and Wang, 2016 [113]; AWWA, 1999 [114]; Wiest et al., 2011 [115]; Wang et al., 2017 [116]; Richards et al., |

| | | | |
|---|---|---|---|
| | | or lower water heater temperature set points | 2018 [117] |
| Increasing pH for corrosion control, or to counter any acid producing reactions | Soda Ash ($Na_2CO_3$), Sodium bicarbonate ($NaHCO_3$) or sodium hydroxide ($NaOH$) | Use potassium or calcium hydroxide (lime) to increase pH, or reduce/eliminate the acid producing reactions (i.e., coagulation) by using alternative such as membranes | Rehring et al., 1996 [118]; Shammas and Wang, 2016 [113] |
| Chlorine gas generation | NaCl brine can leak into potable water if $Cl_2$ gas is generated onsite | Stop brine leaks | Nguyen et al., 2010 [119] |
| Anion Exchange | NaCl regeneration of columns used for nitrate, arsenic, uranium removal | Adsorption, biological treatment, coagulation as appropriate. | Nguyen et al., 2010 [119] |
| Disinfection | Sodium hypochlorite or sodium chlorite or chloramine | $Cl_2$ gas. UV, ozone, membrane filtration, reverse osmosis can reduce doses | Dotson et al., 2012 [120]; Collivignarelli et al., 2017 [121] |
| Fluoridation | Sodium fluoride, sodium fluorosilicate | Hexafluorosilicic acid | AWWA, 1999 [114] |
| Corrosion inhibitor | Sodium silicates, sodium phosphates | Replace the antiquated infrastructure at risk of corrosion, or use lime columns to adjust pH-alkalinity | Tang et al., 2018 [122]; Benjamin et al., 1992 [123] |
| Coagulation | Sodium aluminate, sodium alginate (coagulant aid) | Aluminum sulfate, ferric sulfate, ferrous sulfate | Sahu and Chaudhari, 2013 [124], AWWA and ASCE, 1990 [125] |

Finally, salt productivity improvements are possible at the household scale. Most research on household product ionic composition has been conducted in countries interested in greywater recycling as a water conservation strategy [73]. For example, in 2008 a comprehensive study of sodium mass loads from household products in Melbourne, Australia reported that [74]: (1) laundry and dishwashing products contribute orders of magnitude more to sodium mass loads than do other household products; (2) median sodium mass loads from household products are

58-300% higher than those from human excretion; (3) mass loads of sodium can vary significantly across product brands, which leads to high variability in the salinity of household wastewater streams; and (4) product switching has the potential to significantly reduce sodium mass loading to the sewershed. Assuming human excretion accounts for about 14% of the UOSA sodium mass loads (Figure 5b), these Australian results suggest that household products could account for another 10 to 51%; notably, the upper limit would nearly close UOSA's annual sodium mass balance. Educational and social marketing campaigns aimed at informing consumers and manufacturers about the FSS, and fostering product and behavioral changes, could ultimately reduce salt loading from common household products such as detergents [100].

Thus, addressing the contribution of IPR to sodium pollution at our field site, and the FSS more generally, will require site-specific combinations of behavioral and technological interventions tailored to the local political, social and environmental context.

**Methods**

*Historical Monitoring Data.* To characterize the relative sodium contributions of the Bull Run watershed, the Occoquan River watershed, and UOSA's discharge in the Occoquan Reservoir, we utilized data from a long-term (>25 year) sampling program that was originally established to monitor UOSA's impact on water quality in the reservoir [69]. We focused specifically on a twelve year time period, 2006 through 2018, during which discrete surface water samples were collected weekly or semi-weekly from the Occoquan River and the Bull Run monitoring stations (ST10 and ST45, N=395 and 338, blue circles, Figure 1a) and analyzed for a suite of water quality parameters including sodium concentration. Continuous measurements ($f$ = 1 hour$^{-1}$) of specific conductance (N=106,708 at ST45) and flow (N=160,446 and 170,179 at ST10 and ST45, respectively) were also available during this time frame. Daily average measurements of discharge from UOSA were provided by the utility for the period 2010 to 2018 (N=2,941), along with measurements of specific conductance (N=2,943) and sporadic measurements of sodium concentration (N=68) on daily flow-weighted composite samples of effluent discharged to their final detention reservoir.

*Daily Average Timeseries of Sodium Concentration and Mass Loads*. From the monitoring data described above we set out to evaluate the relative contribution of three key sources—the Occoquan River watershed, the Bull Run watershed, and UOSA—to sodium mass load (mass per time) and concentration (mass per volume) entering the Occoquan Reservoir under various weather and environmental conditions. Several limitations with the monitoring data had to be overcome (c.f., [47]): (1) flow and sodium concentration measurements at ST45 reflect the combined inputs from the Bull Run Watershed and the UOSA treatment plant; (2) at ST10 and ST45 sodium concentrations were measured on grab samples, whereas sodium concentrations reported by UOSA were measured on daily flow-weighted composites of the final effluent; (3) the sampling schedules at ST10 and ST45 were asynchronous (i.e., grab samples were collected at different times on any given day, or on different days); and (4) while sodium measurements at ST10 and ST45 were collected every other week for the entirety of the study period (2010 to 2018), sodium measurements on UOSA's composite samples were sporadic and infrequent (see Figure S1, Supplementary Materials).

To address these challenges, for the period 2010 to 2018 (for which all of the required data resources were available) we constructed synthetic daily time series of average sodium mass load and concentration at the three monitoring locations as follows: (Step 1) at each monitoring station a multiple linear regression (MLR) model of log-transformed sodium concentration (dependent variable) was prepared (glmulti package in R [101]) by adopting, based on stakeholder recommendations, the following set of potential environmental covariates (independent variables): (a) hourly stream flow (ST45 and ST10) or daily average final flow discharged to Bull Run (UOSA), (b) maximum daily rainfall in the preceding two weeks, (c) maximum daily snow depth in the preceding two weeks, (d) number of days below freezing in the preceding two weeks, (e) season (as represented by sine and cosine functions with annual periodicity), and (f) either hourly in situ measurements of specific conductance (ST45) or measurements of specific conductance on daily flow weighted composites (UOSA). For model validation we used the hold-out method at ST10 and ST45 [102] and leave one out cross-validation root mean square error (LOOCV-RMSE ) at the UOSA station (see Supplementary Information for details); (Step 2) the population of MLR models generated for each monitoring station in Step 1 were ranked according to Bayesian Information Criterion (BIC) to identify the most parsimonious model, accounting for the tradeoff between model fit and model complexity [103,104]. If the top-ranked models for a given station were within two BIC units, they were further ranked by LOOCV-RMSE [105]; (Step 3) the final top-ranked MLR model for each station from Step 2 was then used to generate an eight-year (2010 to 2018) synthetic timeseries of hourly (ST10 and ST45) or daily (UOSA) sodium concentration; and (Step 4) the synthetic sodium concentration time series from Step 3 were combined with hourly (ST10 and ST45) or daily (UOSA) flow measurements at each station, and then aggregated to daily and annual sodium concentration and mass load using the *aggregateSolute* command in the USGS software package Loadflex (for error propagation we adopted the default data correlation structure, which adopts a unit correlation if two samples are collected on the same calendar date, and zero correlation otherwise [106]). The result was three fully aligned eight-year synthetic timeseries of daily and annual average sodium mass load and concentration (denoted here by the symbols $\langle L \rangle$

and $\langle C \rangle$, respectively) and associated estimates of error at each of the three monitoring stations. As noted above, ST45 receives water and sodium from both the Bull Run Watershed and the UOSA water reclamation facility. The contribution of the Bull Run Watershed to sodium concentration and mass load was therefore isolated by mass balance where $\langle Q \rangle$ denotes daily average flow measurements and the subscript "BR" refers to the Bull Run Watershed:

$$\langle C_{\mathrm{BR}} \rangle = \frac{\langle L_{\mathrm{ST45}} \rangle - \langle L_{\mathrm{UOSA}} \rangle}{\langle Q_{\mathrm{ST45}} \rangle - \langle Q_{\mathrm{UOSA}} \rangle} \tag{1a}$$

$$\langle L_{\mathrm{BR}} \rangle = \langle L_{\mathrm{ST45}} \rangle - \langle L_{\mathrm{UOSA}} \rangle \tag{1b}$$

From these synthetic timeseries we constructed daily timeseries for the percent contribution of the Occoquan River Watershed ("OccRiv"), Bull Run Watershed ("BullRun"), and UOSA discharge ("UOSA")) to the total sodium mass entering the reservoir from the Occoquan River and Bull Run (which, as noted earlier, contributes 95% of freshwater flow into the reservoir):

$$\%\mathrm{Load}_{\mathrm{OccRiv}} = \frac{\langle L_{\mathrm{ST10}} \rangle}{\langle L_{\mathrm{ST10}} \rangle + \langle L_{\mathrm{ST45}} \rangle} \tag{2a}$$

$$\%\mathrm{Load}_{\mathrm{BullRun}} = \frac{\langle L_{\mathrm{BR}} \rangle}{\langle L_{\mathrm{ST10}} \rangle + \langle L_{\mathrm{ST45}} \rangle} \tag{2b}$$

$$\%\mathrm{Load}_{\mathrm{UOSA}} = \frac{\langle L_{\mathrm{UOSA}} \rangle}{\langle L_{\mathrm{ST10}} \rangle + \langle L_{\mathrm{ST45}} \rangle} \tag{2c}$$

*Construction of Bivariate Distributions and Conditional Probabilities*. Equations (2a) – (2c) provide daily predictions for the relative contribution of each source to sodium mass discharged to the reservoir from the Occoquan River and Bull Run. How are these predictions modulated by local weather conditions? To answer this question, we adopted the cumulative daily discharge of water flowing into the reservoir from the Occoquan River and Bull Run as a proxy of local weather conditions: $\langle Q_{\mathrm{Total}}\rangle = \langle Q_{\mathrm{ST10}}\rangle + \langle Q_{\mathrm{ST45}}\rangle$. Marginal probability distributions of percent sodium mass load from equations (2a)-(2c) ($\%\mathrm{Load}_{\mathrm{OccRiv}}$, $\%\mathrm{Load}_{\mathrm{BullRun}}$, $\%\mathrm{Load}_{\mathrm{UOSA}}$) and log-transformed values of cumulative streamflow from the Occoquan River and Bull Run ( $\ln\langle Q_{\mathrm{Total}}\rangle$) were then joined by a copula to yield three bivariate cumulative distribution functions (CDFs) of the form, $F_{LQ}(\ell,q) = C\left[F_L(\ell), F_Q(q)\right]$, where $L$ and $Q$ are random variables for the percent sodium mass load from a particular source and cumulative discharge from the Occoquan River and Bull Run, respectively, $\ell$ and $q$ are specific predictions of these random variables, and $C$ is the CDF of the copula function. The copula was selected based on BIC ranking [104] of the Plackett and Archimedean copula families [107] optimized to our daily timeseries of percent mass load (from equations (2a) – (2c)) and measured daily cumulative discharge from the Occoquan River and Bull Run using the MATLAB software package, MvCAT [108]. The probability density function (PDF) of percent sodium mass load from each of the three sources conditioned on a specific cumulative discharge was then calculated as follows [107]:

$$f_{L|Q}(\ell|q) = c\left[F_L(\ell), F_Q(q)\right] f_L(\ell) \tag{3}$$

Here, the function $c$ is the PDF form of the copula and $f_L(\ell)$ is the marginal distribution for the percent of sodium mass load to the Occoquan Reservoir from a particular source. We focused on three conditioning events corresponding to low (10$^{\mathrm{th}}$ percentile), medium (50$^{\mathrm{th}}$ percentile), and high (90$^{\mathrm{th}}$ percentile) cumulative discharge ($\langle Q_{\mathrm{Total}}\rangle = 2.55$ m$^3$ s$^{-1}$, 6.91 m$^3$ s$^{-1}$, and 31.01 m$^3$ s$^{-1}$, respectively). These three conditioning events represent dry, average, and wet weather conditions, respectively.

*Stationarity*. The time-series data used for the copula analysis and to generate the MLR models were tested for stationarity (*tseries* package in R [109]) using the Augmented Dickey-

Fuller (ADF) test [110], Phillips-Perron (PP) test [111] and the Kwiatkowski-Phillips-Schmidt-Shin (KPSS) test [112]. These test statistics indicate that measured sodium concentration and all independent variables are stationary over the time period for which the MLR and copula analyses were conducted (2010-2018) (see Supplementary Table S4 and Supplementary Note S1).

**Data Availability**

All data used in this study are publicly available at: https://doi.org/10.4211/hs.61a19724394643fca62a4fb3ce881efe

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## Author Contributions

SVB and SBG conceived and drafted the article. EAP, MAR, AG, PV, AM, ME, GP, NS, and SC contributed text and analysis. All co-authors contributed edits.

## Competing Interests

The authors declare no conflicts of interest.

## Additional Information

Supplementary Information includes MLR results, percent imperviousness data for both watersheds and figures and information on MLR validation and stationarity tests.

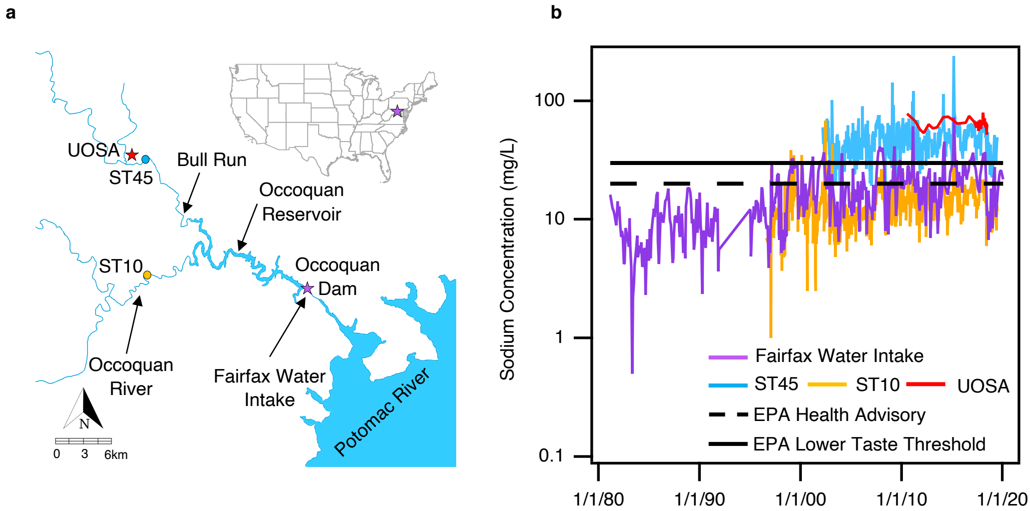


**Fig. 1. a,** The Occoquan Reservoir in Northern Virginia, USA. More than 95% freshwater inflow to the reservoir is from the Occoquan River and Bull Run which drain mixed undeveloped, agriculture, ex urban and urban landscapes. Shown are key geographical features including the Occoquan Dam (where Fairfax Water sources its raw water), ion and flow monitoring sampling sites on the Occoquan River and Bull Run (monitoring stations ST10 and ST45), and the location on Bull Run where reclaimed water is discharged from the Upper Occoquan Service Authority (UOSA). Water from the Occoquan Reservoir is treated by Fairfax Water, the water wholesaler, and from there passes to various water distributors. **b,** Forty years of sodium concentration measurements at the Fairfax Water intake and upstream stations (ST10, ST45), and the final reclaimed water discharged by UOSA. Also shown are the EPA Health Advisory and Lower Taste Threshold for sodium.

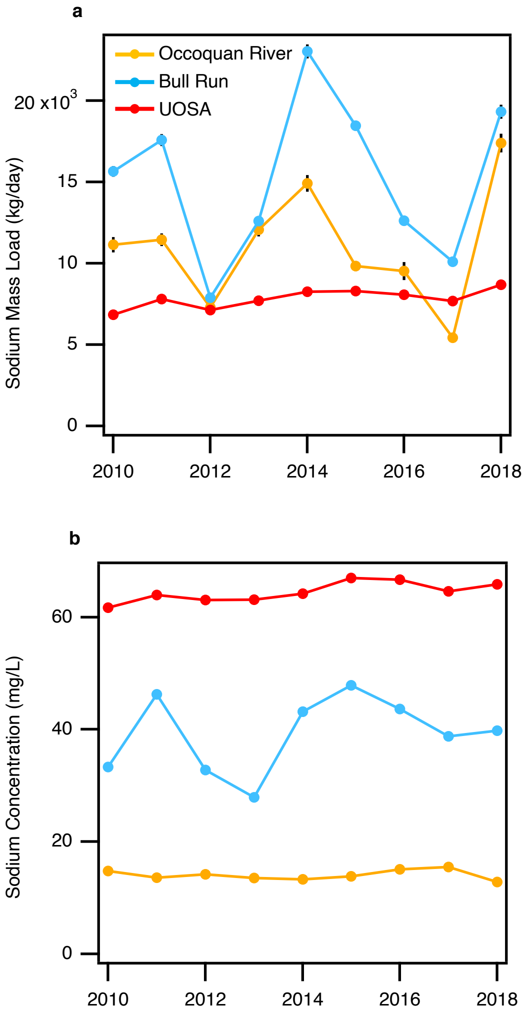


**Fig. 2. Annualized sodium contributions from Occoquan River, Bull Run and UOSA water reclamation facility. a,** Sodium mass loads. **b,** Sodium concentration. Error bars represent 95% prediction intervals (some error bars are hidden behind points).

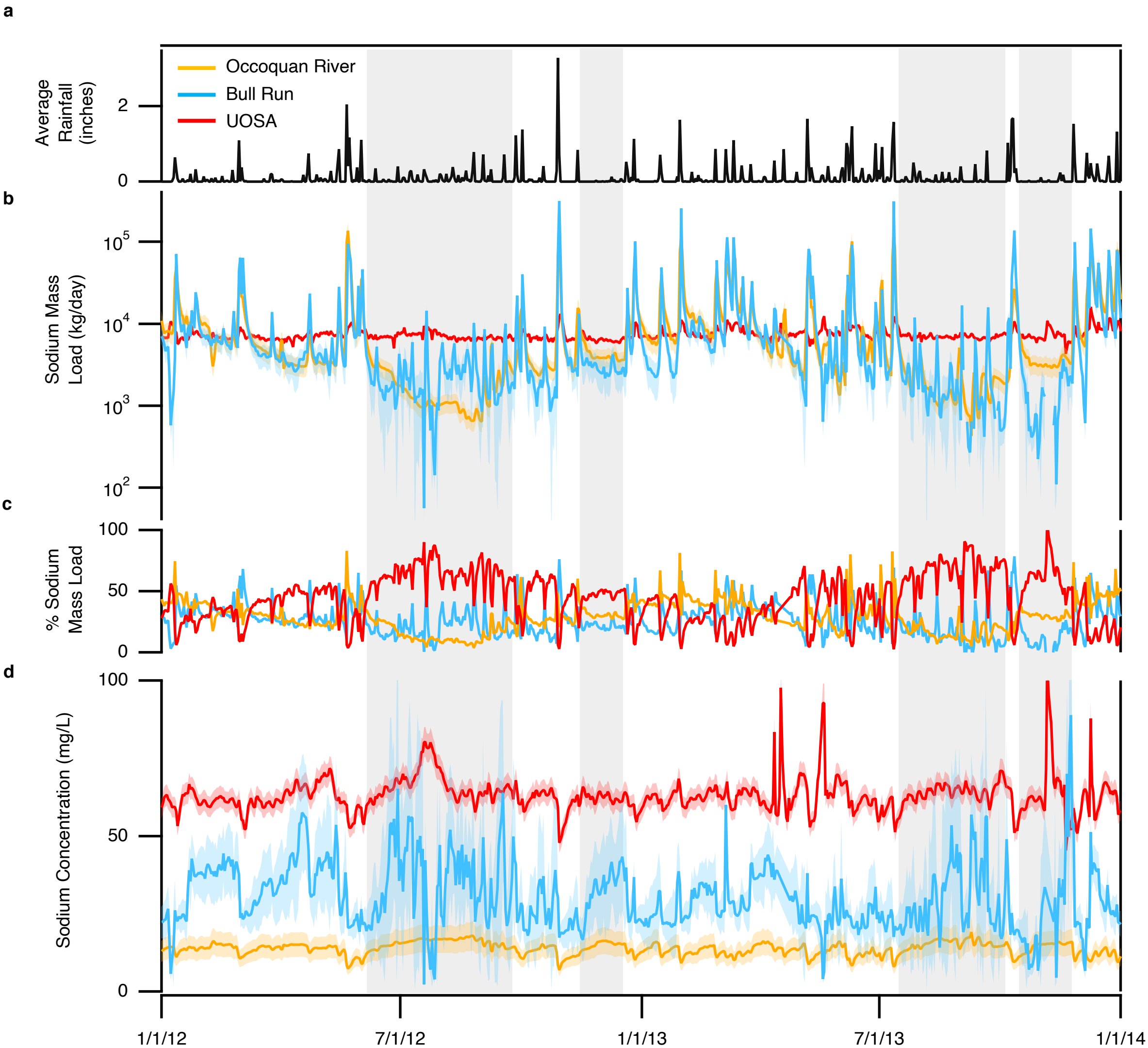


**Fig. 3. Daily sodium contributions from Occoquan River, Bull Run and UOSA water reclamation facility for an illustrative two-year period (2012-2013). a,** Daily average rainfall in the watershed calculated using the Thiessen polygon method. **b,** Predictions of sodium mass load from the three sources. **c,** Percentage of total sodium mass load entering the reservoir from the three sources. **d,** Predictions of sodium concentration in outflow from the three sources. Gray vertical stripes indicate extended periods of reduced precipitation. 95% prediction intervals for sodium mass load and concentration are also shown.

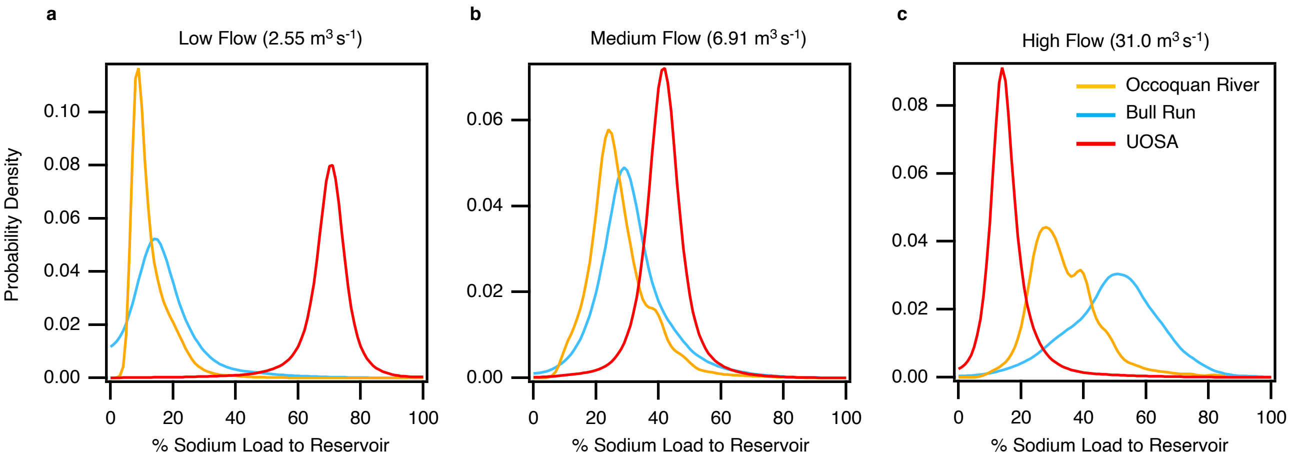


**Fig. 4. Probability density functions of the percent sodium mass load entering the reservoir from the Occoquan River, Bull Run and UOSA, conditioned on low, medium and high flow into the reservoir (a, b, and c, respectively).** The salient feature of each curve is the range of values on the horizontal axis for which there is non-zero probability density. The peak height of each curve is determined by the unit area of each PDF.

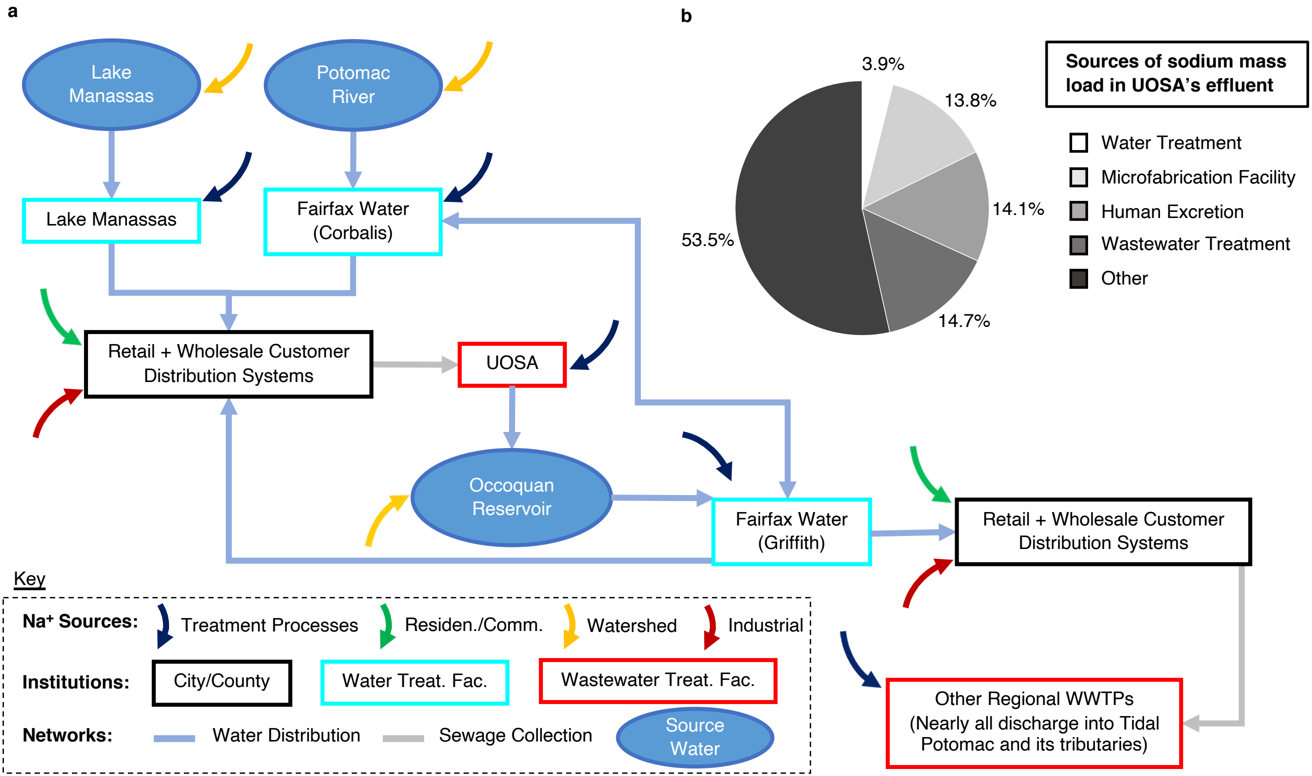


**Fig. 5. a,** Schematic representation of the drinking water and sewage collection network for the Occoquan watershed and surrounding area. Under normal conditions, the portion of the sewage network draining to UOSA receives water from the Fairfax Water's Corbalis water treatment plant, although some water from Fairfax Water's Griffith water treatment plant and Lake Manassas may also contribute to UOSA's inflow (forming a system-scale semi-closed loop for the circulation of sodium through the Occoquan Reservoir). **b,** Source breakdown for the annual sodium mass load in UOSA's reclaimed water.