Revised Scope of Work for the MWCOG Project:

Establishing a Science Partnership to Support Understanding of the Freshwater Salinization Gradient in the Metropolitan Washington, D.C. Region

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In response to Technical Advisory Committee (TAC) feedback on our MWCOG freshwater salinization project, we would like to propose the following modifications to the scope of work for Phase II, encompassing the period **July 2, 2022 through July 1, 2025**.

Specifically, the TAC suggested that Phase II research should focus on answering the following set of questions:

1. If we do nothing, what will salt concentrations (at least of Na and Cl) at drinking water intakes or streams in the region be in 10 years? In 25 years? What will be the exceedance frequency for various drinking water or stream health metrics?
2. What are the drinking water basins in the region most vulnerable to increases in salinity?
3. What are the HUC 12 watersheds in the region most vulnerable to increases in salinity?
4. What will be the impact (on exceedance frequency, annual loads or on other parameters) of a reduction in deicing salt loads in those basins? What will be the impact of a reduction in the sodium content of household products in those basins?
5. Should we be concerned about changes in the loading, fate and transport of any other salt ions other than Na and Cl?
6. How do stormwater BMPs affect the fate and transport of salt ions in the environment and how is BMP performance affected by salt loading?
7. What is the effect of salt loading on groundwater concentration of salt ions and what is the transport time of salt ions through groundwater to surface water?

We propose three general approaches (or Tasks) to address these questions. Each Task will result in the publication of one or more peer-reviewed journal articles in an appropriate scientific journal, and the findings will be documented in slide presentations and presented to MWCOG in a resource management context. These tasks will be pursued and accomplished at a rate commensurate with the resources provided by MWCOG, and as such may require greater time to complete than the period of this agreement.

Task 1: Scaling of Salt Production Factors. To address **Questions (1) through (3)**, we will utilize long-term measurements of streamflow and stream ion concentrations in the MWCOG region to calculate historical trends in watershed-specific salt production rates, in units of salt mass exported from the watershed per year per watershed area (e.g., tons sodium/year/km^2 or tons chloride/year/km^2). Watershed-specific salt production rates will be calculated on an annual basis from historical flow and ion concentration data using USGS LOADEST software, and then regressed against potential drivers of salt production, including physiographic province, as well as growth in watershed population, percent imperviousness cover, road network density, and informal (septic) sewer system density. The outcome of this analysis will be a tool for estimating the salt production rate for any watershed in the MWCOG region, that can be scaled up to address the first three questions posed by the TAC. For example, our estimated salt production rates can be combined with MWCOG Transportation Area Zone (TAZ) estimates of population and road network growth, together with solute and streamflow models (e.g., using the modeling framework presented under Task 2 (see below) or, at a larger scale, USGS SPARROW), to yield geographically explicit predictions for annual average salt concentrations over a 10 to 25 year horizon under a business-as-usual scenario, and under various climate change scenarios, directly

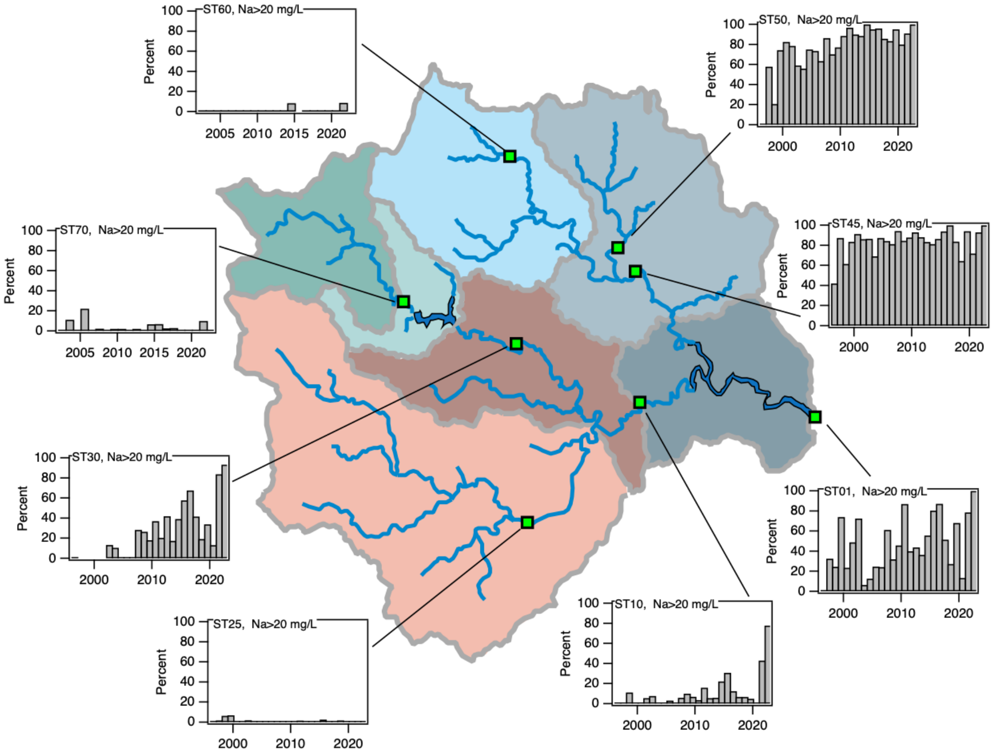

Figure 1. Sodium exceedance trends in the seven sub-drainages tributary to the Occoquan Reservoir. Annual exceedance rates represent the fraction of samples collected at a sampling site (green squares) each year that exceeded the EPA health advisory (for individuals on a severely restricted salt diet) of 20 mg/L. These spatial and temporal trends presumably reflect variations in population and impervious cover across the sub-drainages. Importantly, each monitoring station also has continuous streamflow measurements, allowing for the calculation of salt production rates, as outlined in Task 1.

addressing **Questions (1) through (3)**.

To develop the loading model, we will first leverage the long-term dataset available for sub-watersheds tributary to the Occoquan Reservoir (**Figure 1**). The model will then be validated in several additional watersheds in the MWCOG region (depending on available flow and ion data), for example in the Watts Branch and the Patuxent River watersheds.

Similar procedures can be used to estimate population normalized salt production rates for treated wastewater effluent, with the goal of quantifying how wastewater contributions to inland freshwater salinization scale with the number of sewer connections and other attributes (e.g., permitted discharges) in the sewershed (e.g., as a starting point for tackling the second half of **Question 4**).

We anticipate completing a preliminary version of the loading model (based on an analysis of flow and ion measurements in the Occoquan subdrainages), along with its initial application to Watts Branch or the Patuxent, by late September, 2023.

Task 2: Salt Sources, Transport, and Transformation along Flowpaths. Answering **Questions 4 and 7** is challenging, because the flowpaths that transport salt from their point of origin in the watershed (e.g., from the application of deicers on a road or a parking lot) to streams and reservoirs are spatially complex and temporally variable, including conventional stormwater drainage systems, but also natural flowpaths through the vadose zone and shallow and deep groundwater.[1] Further, interpretation of salinity measurements in streams is complicated by the tendency of some ions to undergo ion exchange[2] and the contribution of diffuse ion sources beyond deicers, including septic systems, mineral dissolution, and leaking sewage collection systems. We propose two approaches for addressing these challenges, including: (a) a next-generation modeling framework that utilizes high-frequency measurements of streamflow and stream specific conductance to infer salt transport along surface and subsurface flowpaths; and (b) field and experimental measurements of salt signal attenuation and transformation along stream and river flowpaths. Much previous work has focused on understanding these dynamics at stream reach scales, but it is now necessary to generate this detailed information across a range of watershed scales (from local to regional) in support of salt management efforts.

Modeling Salt Transport along Flowpaths. Modeling of salt transport and transformation along flowpaths will occur in two steps. In the first step, surface and subsurface flowpaths are inferred

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[1] Hester, E.T., Fox, G.A. (2020) Preferential flow in riparian groundwater: gateways for watershed solute transport and implications for water quality management. *Wat. Resour. Res.* 56, e2020WR028186.

[2] Haq et al. (2018) Episodic Salinization and Freshwater Salinization Syndrome Mobilize Base Cations, Carbon, and Nutrients to Streams across Urban Regions. *Biogeochem.* 141, 463–86.

from high-frequency (hourly) measurements of precipitation, air temperature, evapotranspiration, and streamflow. Specifically, these data are used to infer the dynamic routing of water through a simple two-box model of the sub-drainage that captures the flow of rain and snowmelt directly to a stream (e.g., through storm drainage systems), through the vadose zone to the stream (e.g., through interflow), and through shallow groundwater to the stream (**Figure 2a**).

In the second step, hourly measurements of stream specific conductance (or more infrequently sampled ion-specific concentrations) are used to infer the specific conductance (or ion-specific concentrations) of water in rainfall and snow melt (which can vary by storm event, depending on deicer mobilization levels) (**Figure 2b**), as well as precipitation/dissolution reactions that drive

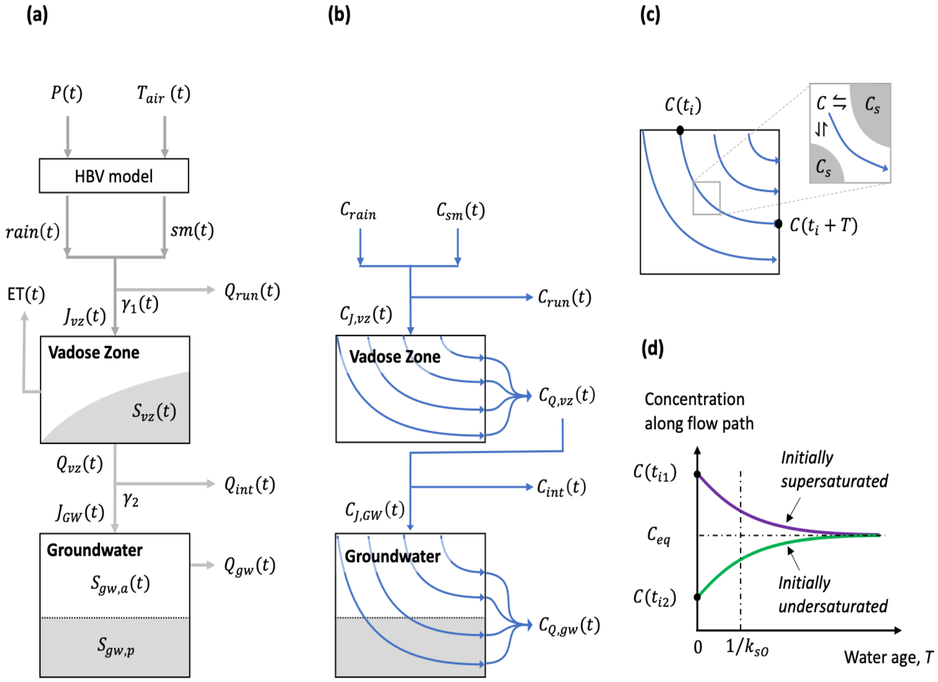

Figure 2. Conceptual representation of the (a) hydrologic model, (b) salt transport model, (c) dissolution/precipitation reaction framework, and (d) age-evolution of ion concentration along flowpaths for super-saturated and under-saturated initial conditions. Inputs to the hydrologic model (panel a) include NASA Land Surface Model estimates of hourly evapotranspiration (*ET(t)*) as well as hourly precipitation and snow melt (*rain(t)* and *sm(t)*) calculated from hourly measurements of precipitation and air temperature (*P(t)* and $T_{air}(t)$). Streamflow is the sum of direct runoff (e.g., from storm drain networks, $Q_{run}(t)$), interflow from the vadose zone ($Q_{int}(t)$) and baseflow from groundwater ($Q_{gw}(t)$). Inputs to the salt model (panel b) include ion concentrations in rain and snowmelt (C_{rain} and $C_{sm}(t)$, where the latter may vary with deicing mobilization levels). Ion concentration in the stream consists of the flow-weighted concentrations predicted for direct runoff ($C_{run}(t)$), interflow ($C_{int}(t)$) and groundwater ($C_{gw}(t)$).

the concentration of a water parcel toward some (geological- and physiographic province-specific) equilibrium concentration as a water parcel travels along a flow path through the vadose zone or groundwater (**Figures 2c and 2d**).

This modeling framework is currently being applied to 10+ year measurements of flow and specific conductance at a USGS streamgage in Fairfax County (on Flatlick Branch). The end result will be a mechanistic approach for simulating, across the MWCOG region, how reductions in deicing salt loads (e.g., associated with reductions in area-normalized salt application rates associated with different deicer or anti-icer mobilization levels) will impact salt concentrations in streams (**Question 4**), and the build-up of salt ions in the subsurface and associated transport times through the vadose zone and groundwater (**Question 7**). Indeed, the transit time distribution framework adopted here (which builds on recent work by one of the project investigators[3]) focuses specifically on tracking the age of water parcels as they move along flowpaths from rainfall and snowmelt to streams, and thus is ideally suited to address questions of transport times (**Question 7**). In addition, the modeling framework can be used to estimate salt transport and transformation through green stormwater infrastructure,[4] at least partially addressing **Question 6**.

Measuring Salt Transport and Transformation along Flowpaths. UMD and VT will, commensurate with resources provided, investigate changes in sources, concentrations, and fluxes in salt ion concentrations along flowpaths in Watts Branch and select Occoquan subdrainages (see Task 1) and Anacostia River and its tributaries. These studies will provide insights into the spatial extent of the problem and hot spots of sources, transport and transformation. For example, by extending our monitoring along flowpaths, we can determine whether freshwater salinization is mostly a problem in small watersheds or whether freshwater salinization is spreading to larger watersheds (**Question 2**). We can also create high-resolution maps of salinization along streams across different spatial scales (see Task 1).

By measuring changes along flowpaths in salt ion mixtures and associated metals and nutrients, we will be able to elucidate whether we should be concerned about different chemicals mobilized by salt transport (**Question 5**). When possible, we will also compare changes in salt sources, transport, and attenuation along flowpaths draining different land uses and stormwater management BMPs, stream restoration sites and conservation areas (**Question 6**). By measuring changes in salt ion concentrations and chemical mixtures along stream flowpaths during baseflow and wet weather events, we can also learn about the relative importance of groundwater *vs.* surface contributions as watershed size increases (**Question 7**). This can yield important

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[3] Grant, S.B. and Harman, C.J. (2022) Solute transport through unsteady hydrologic systems along a plug flow-to-uniform sampling continuum. Water Resources Research. 58, e2022WR032038.

[4] Parker, E.A., Grant, S.B. et al. (2021) Predicting solute transport through green stormwater infrastructure with unsteady transit time distribution theory. *Water Resources Research*. 57, e2020WR028579.

information regarding the persistence of freshwater salinization issues across not only time but varying spatial scales and watershed sizes.

Multiple synoptic sampling locations will be located throughout Occoquan subdrainages, Watts Branch, and Anacostia watershed (identified based on leveraging resources and time and ongoing monitoring by investigators) to measure longitudinal changes in downstream concentrations and mixtures of ions and associated contaminants. Within a watershed, the synoptic sampling will occur throughout the same day and/or consecutive days with similar streamflow conditions. We will sample along the length of the watershed to evaluate where urban degradation occurred and/or restoration activities were implemented; in some cases, these flowpaths can extend from headwaters to the stream outflow to receiving waters. Sampling locations for the synoptic sites along each mainstem will be chosen based on accessibility, presence of tributary junctions, and positioning of conservation and restoration features. When possible, stream water samples will be collected at the mouth of major tributaries and at a sufficient distance downstream from the tributary confluence along the mainstem (to ensure well-mixed conditions). Latitude and longitude for synoptic sites will be recorded using GPS applications. Longitudinal patterns in chemical concentrations will be classified into increasing, decreasing, stepwise changes, and/or trends with increasing distance downstream to determine: (a) spatial patterns in downstream vulnerability including the HUC 12 scale; (b) the degree to which other ions and metals are mobilized along flowpaths; (c) the influence of BMPs, restoration efforts, and conservation on fate and transport of salts downstream; and (d) the relative influence of groundwater *vs.* surface water sources across seasons and along flowpaths. These data can also be related to surrounding land use characteristics and other GIS layers using various statistical approaches. These results will be linked to modeling efforts (above) for calibration and validation, and for evaluation of model representations of ion exchange and contaminant mobilization reactions along flowpaths.

Initial results from the Flatlick Branch model and synoptic monitoring of the Occoquan subdrainages and Watts Branch should be completed and ready to share with MWCOG stakeholders by January 2023.

Task 3: Assessing Salinization Risk. Tasks 1 and 2 are intended to leverage a variety of regional and national monitoring data and special field studies, with the goal of directly addressing management-focused salinization-related questions of pressing interest to stakeholders in the MWCOG region. These same results (e.g., in conjunction with relationships between conductivity and certain contaminants of concern) can be used to estimate geographically distributed risks of freshwater salinization, for example to drinking water supplies, ecosystem health, and nutrient cycling (**Questions 1 and 2**). To this end, the researchers will compile local, national, and international threshold concentration data for sodium and chloride and evaluate the frequency of threshold exceedance across the region, both now and into the future (**Figure 1** is an example of where this has been done for sodium in

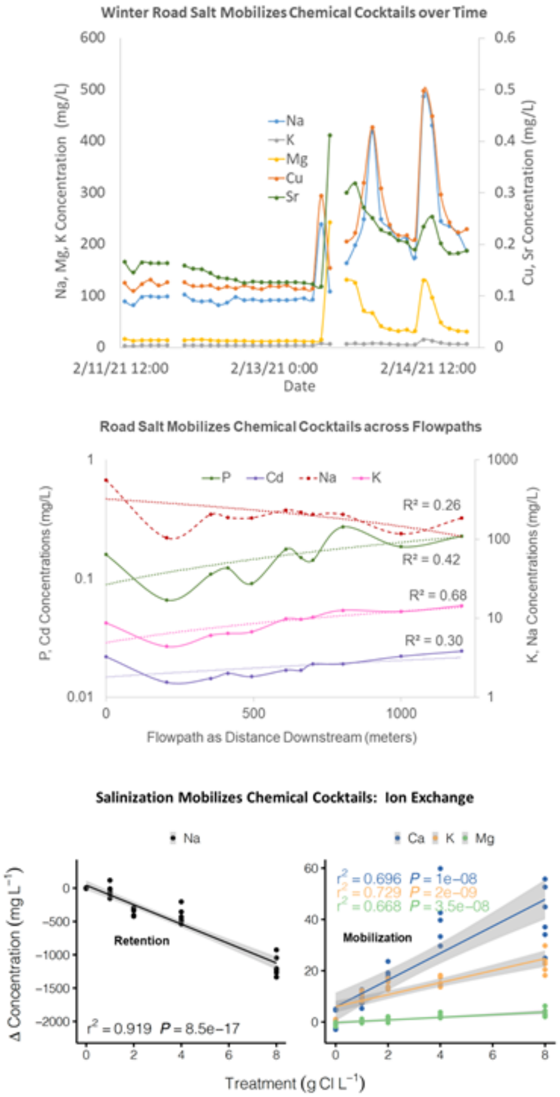

Figure 3. Freshwater Salinization Syndrome mobilizes chemical contaminants (including phosphorus) across space and time in Campus Creek, a small urban stream in College Park, Maryland in the Anacostia watershed. Campus Creek has undergone a type of stream restoration known as regenerative stormwater conveyance, which dramatically enhances floodplain reconnection through the creation of a series of step pools. (Top Panel) In Campus Creek, there are peaks in ion concentrations during a winter road salt event illustrating the importance of mobilization of multiple elements over time in response to deicer applications and winter

climate. (Middle Panel) Along the longitudinal flowpath of Campus Creek, Na concentrations decline during winter after a road salt event, as other elemental concentrations increase (all slopes are significantly different than zero); this suggests the importance of ion exchange and/or shifts in sources along the flowpath (Bottom Panel) Laboratory salinization experiments with sediments from Campus Creek demonstrates the importance of Na retention as NaCl is added at increasing concentrations (using experimental methods similar to Haq et al. 2018 and Kaushal et al. 2019); other elements are mobilized and released from sediments of Campus Creek due to ion exchange and geochemical processes.   Figure is from Kaushal…Grant…et al. (2022) in *Limnology & Oceanography*.[5]

tributaries draining to the Occoquan Reservoir). Technically, risk assessment requires quantifying both the frequency of occurrence (e.g., exceedance of a threshold) and the exposure, or likely impact of that exceedance on a particular endpoint of interest (e.g., drinking water taste, daily intake of sodium from drinking water, chloride toxicity to benthic macroinvertebrates, contaminant mobilization and so on). We will work with MWCOG stakeholders to define potential impacts relative to each of the thresholds identified and combine this information with the outcomes of Tasks 1 and 2 above to generate clear visual representations of salinization risk across the MWCOG region. We will also explore opportunities to leverage ongoing development of MWCOG's WaterSuite Tool, which is used by local water utilities for contaminant risk assessments. Because Task 3 is integrative—i.e., integrates the results from Tasks 1 and 2, and leverages ongoing development of the WaterSuite Tool—we anticipate it will be finished toward the end of the project period, in July 2025.

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[5] Kaushal, S.S. et al. (2022) Five state factors control progressive stages of freshwater salinization syndrome. *Limnology and Oceanography Letters*, in press.