

DEPARTMENT OF HEALTH
Office of Drinking Water

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TO: Bob James, Derek Pell, Scott Torpie, Mike Means, Garin Schriever
FROM: Steve Deem, Virpi Salo-Zieman, Jolyn Leslie
SUBJECT: Disinfection By-Product Formation Study (DBPF) – Initial Conclusions & Action Items

Summary

We have completed the data-gathering and data analysis phases of the **DBP Formation in Coastal Groundwater Study**. The study was funded by SRF set aside money and led by NWRO ODW staff in collaboration with the University of Washington Civil Engineering Department.

The study entailed collecting four (4) sets (quarterly) of water quality samples from eighteen (18) groundwater sources representing 15 Group A water systems, and collecting and evaluating relevant water system operating parameters over a one-year period. The water systems all practice continuous chlorination treatment and are located in San Juan and Island Counties. The regulatory DBP monitoring resulted in an exceptionally high proportion of DBP MCL exceeders in these counties. A few systems do not exceed the MCL for TTHMs and were selected specifically to be controls. The other systems all exceed or have exceeded the MCL for TTHMs; six of these have primarily brominated THMs.

The key questions for this study were:

- What water quality parameters lead to DBP formation in disinfected water systems using groundwater sources of supply in San Juan and Island Counties? (Why do adjacent water systems with similar well settings exhibit very different DBP compliance results?)
- What are the limiting factors for creation of brominated by-products?
- Are there certain water quality indicators that could be used to evaluate DBP formation potential in other groundwater systems?
- Do these parameters vary by season, pumping rate, seawater influence, or some other yet unidentified reason?
- What can systems do to minimize DBP formation, or to treat for DBPs?

Water quality parameters monitored included Chloride (Cl^-), Bromide (Br^-), Iodide (I^-), total dissolved solids (TDS), conductivity, ammonia nitrogen ($\text{NH}_3\text{-N}$), heterotrophic plate count (HPC) (both standard plate count method and R2A agar method), adenosine triphosphate (ATP), total and dissolved organic carbon (TOC and DOC), and UV absorbance at 254 nm, as well as 7-day maximum formation potentials for total THMs (TTHMs), HAA5, and HAA9, and associated 7-day free available chlorine (FAC) demand. Operational water quality parameters monitored during sampling at each location included pH, free and total available chlorine (FAC and TAC) concentrations, and water temperature. In addition, the dissolved organic matter (DOM) in each water sample was characterized by (a) fluorescence spectroscopy – to obtain fluorescence excitation-emission matrixes for subsequent processing by parallel factor analysis (PARAFAC), as a means of identifying characteristic signatures of fluorescent components present in the DOM, and (b) HPLC/size exclusion chromatography with online UV/visible,

fluorescence, and dissolved organic carbon (DOC) detection (HPLC/SEC-UV/fluorescence/DOC) – to characterize and quantify the distribution of various size fractions of DOM present in the samples.

Study data and reports can be found at S:\EPH\DW\Field Operations\Northwest\PROGRAMS\D-DBP\DBP Formation Study.

Key findings / conclusions:

1. Dissolved organic carbon (DOC) in the source water appears to be the primary factor affecting DBP formation. Other parameters including microbial activity and inorganics do not appear to affect total formations with exception of bromide that plays a role in the amount of brominated DBPs that a system forms.
2. Total organic carbon (TOC) is almost all dissolved in this setting. (TOC = DOC).
3. Quarterly source water testing revealed significant variability in some source water quality parameters. (Example: San Juan Ranchos DOC varied from low of 1.3 mg/L to a high of 7.8 mg/L and many systems showed seasonal variability in chloride and ammonia). This observed seasonal variability has implications for DOH source monitoring and treatment design approaches. (i.e. reliance on a single sample as representing ground water quality may be wrong).
4. Accurate knowledge of DOC concentrations in source water can be used to anticipate if a water system may develop DBPs above the regulatory limits. This study indicates that sources with less than 1.2 mg/L DOC would be unlikely to exceed TTHM MCLs. Sources with less than 2.1 mg/L DOC would be unlikely to exceed HAA5 MCLs. The DOC concentrations in source water correlated linearly with DBP formation potentials. DOC should be considered a critical design parameter for treatment processes that include chlorine addition (currently not required or even anticipated by the reviewers or design engineers). Currently, DOC is not part of any regulatory monitoring.
5. Speciation of DOC revealed organics originating primarily from decayed vegetation. (Not coming from algae, wastewater, surface water, etc.). The organic matter was dominated by moderate to high molecular weight aromatic compounds commonly related to humic substances and their building blocks.
6. UV₂₅₄ Absorbance correlates very well with DOC concentrations and DBP formation potentials (UV₂₅₄ Abs can be completed in the lab or field by the operators and could serve as an inexpensive surrogate parameter for DOC).
7. SUVA₂₅₄ (UV₂₅₄nm/DOC) was fairly uniform across the sample set with an average value of 2.86 (mg/l/m)⁻¹ and did not show a seasonal trend. This means that the organic matter is of similar character year round across the study area.
8. DOH field-testing and review of WTP operating and reporting practices suggests that water system chlorination facilities are operating inconsistently. Systems did not maintain a stable free available chlorine (FAC) residual in the distribution. We observed variations from 0.0 to 3.5 mg/L FAC in the same month. Utility monitoring practices appear to be inconsistent and not representative of distribution conditions. Additionally, utilities are not routinely monitoring for total available chlorine (TAC).

9. Total Maximum Formation potential tests (for the control systems) for THMs and HAA5 do not correlate with regulatory TTHM and HAA5 testing results. The implications are significant. Results suggest that some systems may not exceed regulatory TTHM levels (when their source water DOC is higher than 1.2 mg/L) because of inconsistent disinfection treatment practices and the limited DBP distribution monitoring (a single sample collected annually or quarterly) that does not detect nor account for this variability.
10. The HAA9 results indicate that the additional non-regulated and more brominated DBPs are also formed at high levels in these systems. The four additional HAA compounds (that makes it the HAA9 test panel) are included in the next UCMR. The DBP rule is currently under the 6-year review process and the regulatory framework may change in the future and impact more systems in coastal areas.
11. The iron and manganese treatment facilities and one water softener treatment device that were included in the study did not remove any significant amount of DOC and had no impact on DBP formation.
12. Bromide (Br^-) is a key parameter concerning formation of the brominated DBPs. The formation of brominated DBPs correlated poorly with bromide alone, but appears to depend most strongly on the ratios of $[\text{Br}^-]/[\text{DOC}]$ in each sample, with higher $[\text{Br}^-]/[\text{DOC}]$ values generally leading to a higher tendency to form brominated HAAs and THMs. The highest proportions of brominated HAA and THM formation can be expected for sites exhibiting relatively low DOC concentrations and higher $[\text{Br}^-]$ levels (i.e., high $[\text{Br}^-]/[\text{DOC}]$ ratios).
13. Measurements of Chloride (Cl^-) and Br^- concentrations identified Cl^- concentrations in excess of 100 mg/L, and $[\text{Br}^-]/[\text{Cl}^-]$ ratios in excess of or approaching the natural seawater $[\text{Br}^-]/[\text{Cl}^-]$ ratio (1.54×10^{-3}) in several sources. This suggests that multiple sites may be at risk of or already under the influence of seawater intrusion, which could have important consequences for managing DBP formation and speciation in the future (primarily due to consequent increases in $[\text{Br}^-]$ under such circumstances).
14. Microbial testing of HPC, HPC R2A and ATP revealed very low levels in most of the study water system sources. These results are consistent with DOC speciation noted in #5 above. (The DOC speciation showed no sign of biopolymers or high molecular weight hydrophilic compounds that are related to organic compounds of recent biological origin).
15. The initial sample collection effort in September 2016 revealed a number of source sample collection sites that were poorly constructed and / or not properly located. Several of these sampling sites would not be adequate for RTCR source sampling.
16. Ammonia is present in some sources. These water systems are / may be actually employing chloramines. (Related to #8 above; if systems are not measuring total available chlorine, they may not be aware that they have chloramines). Ammonia will exert high chlorine demand and consequently, systems may not be applying adequate oxidant doses for filtration treatment to work correctly, or may not be reaching breakpoint chlorination leading to uncontrolled chloramination, nitrification, or high total chlorine levels in the distribution system. During the study, we measured total chlorine above the MRDL of 4 mg/L at two systems. Ammonia is a regulated drinking water

contaminant in other countries (i.e. U.K. and Denmark). We do not require ammonia measurements during source approval or as part of regular monitoring. Breakpoint chlorination may promote DBPs. Alternative or additional treatments may be needed to address the presence of ammonia.

17. Sampling protocols by some utilities are clearly not best practices! There is lack of consistency, lack of written standard operating procedures, and inappropriate monitoring equipment.

Next Steps / Action Items:

1. Update Bob, Derek, Scott, Mike and Garin. (complete)
2. Finish DOH additions to UW-DOH Final Report March 2017. (Sd)
3. Compile final project documentation notebook. (Vs)
4. Release last UW\$. (Sd & Dp) (Final report acceptance sent 3/6)
5. Recommend DOH next steps. (All)
6. Update – send copy of results to participating utilities as promised. (Vs / Sd / JI)
7. Disseminate findings / conclusions to State ODW, Utilities, Region 10 and National (2017 WQTC) as appropriate. (All)
8. Brief DBP and disinfection workgroups – evaluate possible changes in implementation. (Issues include compliance samples collected when chlorine residuals at zero and sporadic chlorine WTP operation) (JI)
9. Prepare source-monitoring guidance for GW system chlorination design (DOC/UV₂₅₄, Br⁻). (Design Manual addition S. Perry?) (Sd)
10. Review DOH chlorination reporting practices and follow up. Develop and provide direct / explicit expectations for water system monitoring and reporting. Include residual monitoring equipment guidance. Develop guidance on SOPs for chlorination treatment plants. (RO managers? / Disinfection workgroup?)
11. Evaluate including ammonia (NH₃-N) sampling in source water sampling requirement for all ground water systems / systems chlorinating. And add requirement for TAC monitoring after chlorination. (DBP Workgroup / RO managers / Disinfection workgroup?)
 - cc: Krista Chavez, DBP Workgroup, Disinfection Workgroup, Sam Perry,