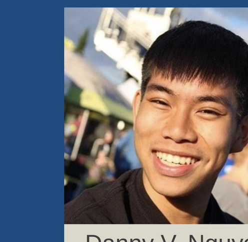
# Disinfection byproduct formation from chlorocyanurates, alternative sources of free chlorine (RRS9)

*Direct potable reuse*



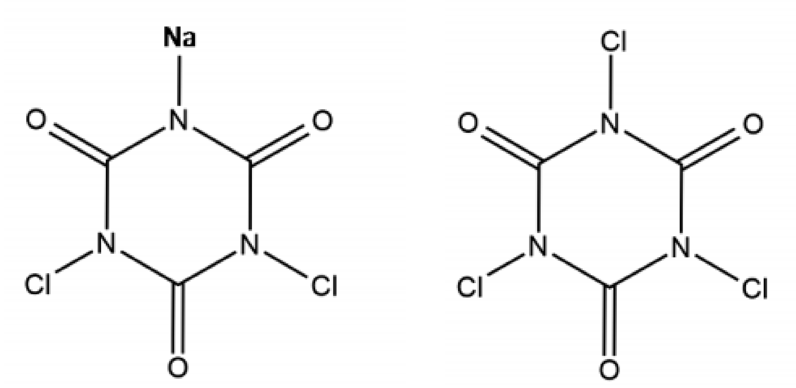

Re-Inventing the Nation's Urban Water Infrastructure (ReNUWIt)

**Danny V. Nguyen, Kirin Emlet Furst, William Mitch**
Stanford University

## Background

Chlorine disinfection is a treatment for water sanitation to remove pathogens like bacteria and viruses. However, one concern is disinfection byproducts (DBPs), which are produced from the reaction of disinfectants with dissolved organic matter. Chlorine is typically applied to drinking water as sodium hypochlorite (NaOCl), to form free chlorine (HOCl). Alternative sources of free chlorine such as the solid chlorocyanurates are becoming more common (Figure 1). Sodium dichloroisocyanurate (dichlor) and trichloroisocyanuric acid (trichlor) are solid disinfectants that are typically used for point-of-use disinfection and in swimming pools. These disinfectants dissociate in water to produce some free chlorine, which is also the active agent in bleach, while the rest of it remains bound to the cyanurate molecule. Little is known about DBP formation from these alternative forms of chlorine, even though they were recently approved for use by public water utilities in the US.

**The goal of this project is to compare DBP formation from NaOCl, dichlor, and trichlor.**



Sodium Dichloroisocyanurate

Trichloroisocyanuric Acid

**Figure 1. Dichlor as NaDCC and trichlor as TCCA (adapted from Wahman 2018)**

## Approach

- **Sampling:** Water samples for these experiments were collected from drinking water sources in Dhaka, Bangladesh, and from Lake Lagunita on campus.
- **Disinfectants:** Dilute NaOCl (bleach) was dosed as a liquid. Dichlor was purchased as Aquatabs, and trichlor was purchased as solid pellets; both were ground to a fine powder for dosing as a solid (Figure 2).
- **Chlorine analysis:** Free and total chlorine residuals were measured using the DPD colorimetric method and a UV-Vis spectrophotometer (Figure 3).
- **Experiment:** After dosing water samples with chlorine, the samples were stored in a 37℃ temperature stable room for a 24 hour reaction time.
- **DBP analysis:** DBPs were extracted using a liquid-liquid extraction protocol adapted from the US EPA. Gas-chromatography mass-spectrometry (GC-MS) method was used to measure the concentrations of 25 volatile DBPs (Figure 4).

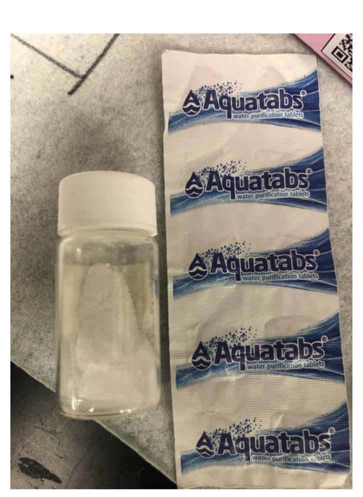



**Figure 2. Trichlor and dichlor (Aquatabs) as powders**

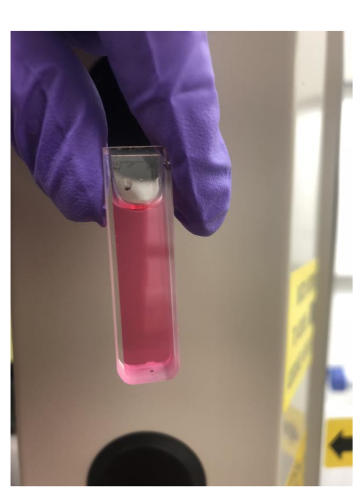


**Figure 3. Cuvette with water sample for measuring chlorine residual by UV-Vis**

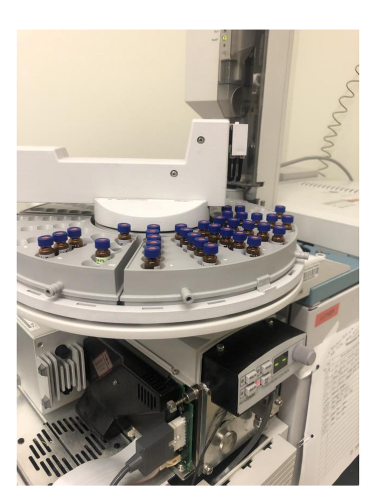


**Figure 4. The autosampler of a GC-MS; vials with sample extracts**

## Results

- Chlorine demand was typically lower with dichlor and trichlor than bleach, indicating that less free chlorine was available to react (Figure 5).
- While overall DBP formation was reduced with dichlor relative to bleach in the surface water, DBP formation was fairly constant in groundwater (Figure 6).
- In the surface water from Dhaka, dichlor formed less THM4 compared to bleach. However, in groundwater from Dhaka, there was no significant difference in THM4 formation (Figure 6).

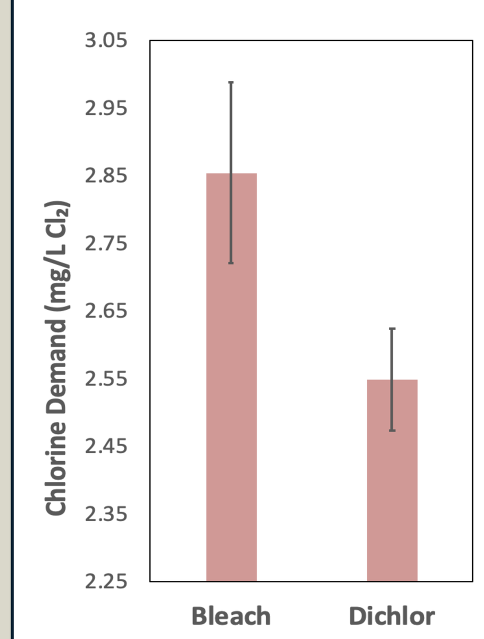



**Figure 5. Example chlorine demand results: chlorine residual as $Cl_2$ subtracted from dose. In the surface water sample from Dhaka, dichlor had 12% lower chlorine demand than free chlorine.**

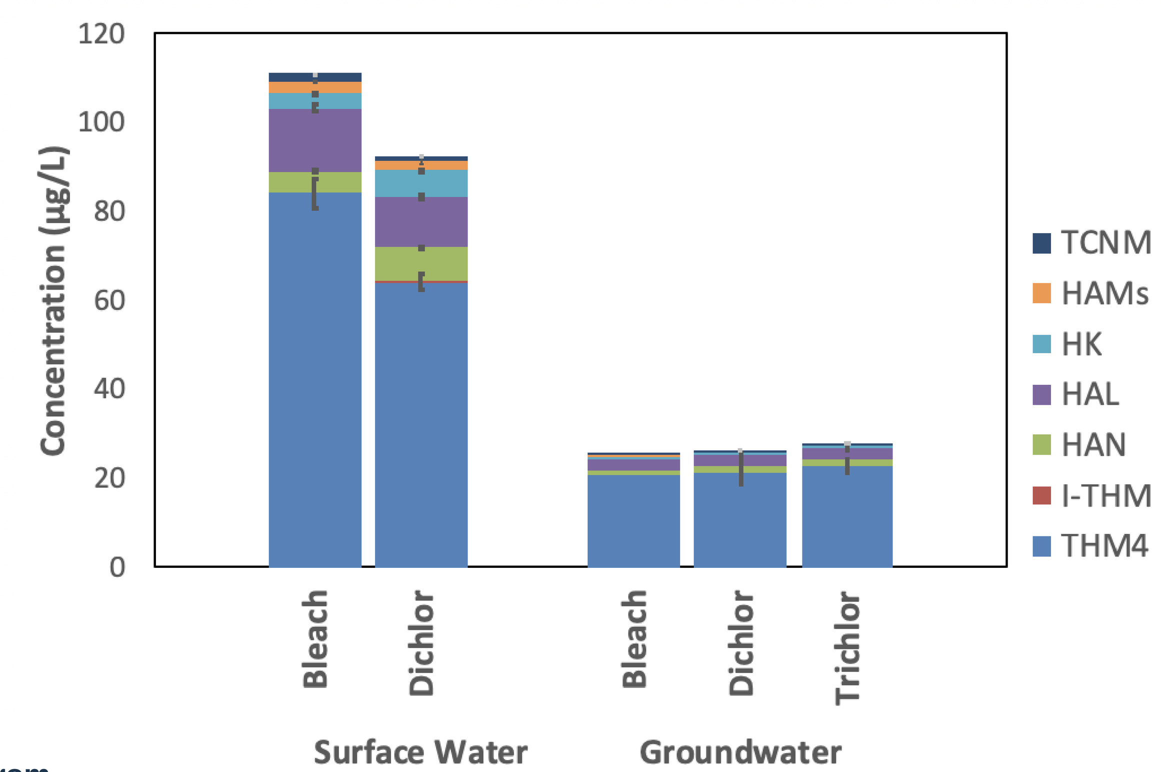



**Figure 6. DBP formation in surface water and groundwater from Dhaka. Error bars indicate the standard deviation of triplicate or range of duplicate experimental replicates.**

- THM4 formation in Lake Lagunita water was not significantly different between disinfectants when no halides were added. After adding 0.2µg/L bromide however, THM4 formation increased (Figure 7).
- With the addition of 0.1µg/L iodide, samples dosed with trichlor showed significantly increased concentrations of iodinated THMs (I-THMs) (Figure 7).

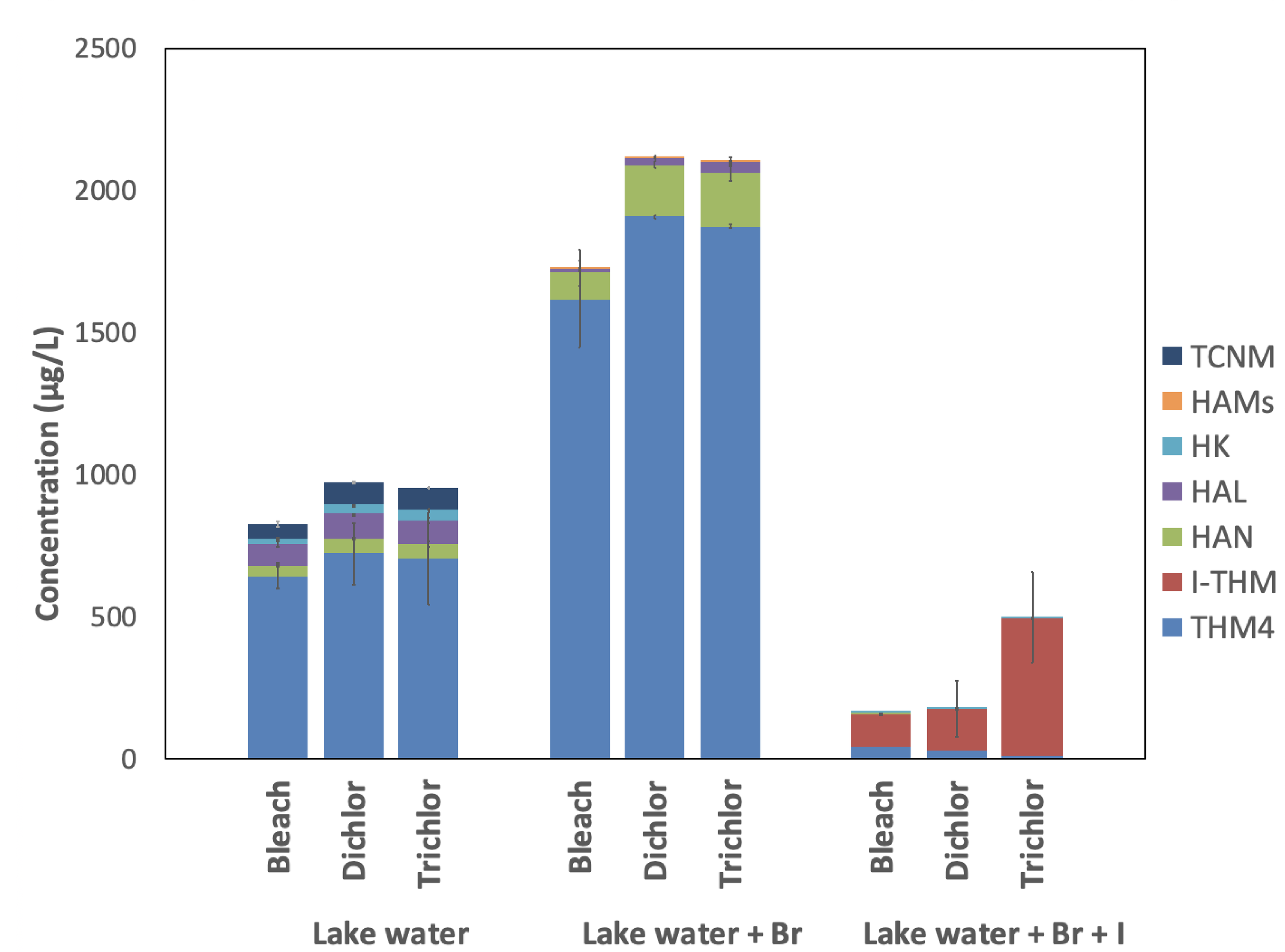



**Figure 7. DBP formation in Lake Lagunita water with no detectable bromide and iodide, with 0.2µg/L bromide added, and with 0.5µg/L bromide and 0.1µg/L iodide added.**

## Conclusions

- In some samples, chlorocyanurates reduced THM4 formation. However, this trend was not present in all samples. (Figure 8). Because THM4 is regulated in many countries, reducing THM4 formation is a favorable feature of alternative disinfectants.
- Dichlor and trichlor consistently formed higher concentrations of HANs by ~30-50% (Figure 8). This result is concerning because research shows HANs may be more genotoxic and cytotoxic than THM4.
- The DBP formation behavior of chlorocyanurates resembles that of chloramines. However, since chloramines consistently reduce THM4 formation and that was not the case with dichlor and trichlor in these experiments, parallels should be drawn with caution until more is known about the mechanisms.

| | | THM4 | I-THM | HAN | HAL |
|---|---|---|---|---|---|
| Surface Water | Dichlor | -31% | 21% | 41% | -29% |
| Groundwater | Dichlor | 2% | 0% | 30% | -5% |
| | Trichlor | 8% | 0% | 29% | 4% |
| Lake | Dichlor | 11% | 0% | 37% | 7% |
| | Trichlor | 9% | 0% | 35% | 3% |
| Lake + Br | Dichlor | 15% | 0% | 50% | 48% |
| | Trichlor | 14% | 0% | 52% | 68% |
| Lake + Br +I | Dichlor | -47% | 23% | -21% | 0% |
| | Trichlor | -278% | 77% | -238% | 0% |

| Key |
|---|
| 75% |
| 50% |
| 25% |
| 0% |
| -25% |
| -50% |

**Figure 8. Relative DBP formation from dichlor and trichlor compared to bleach. Positive percentages (blue) indicate that more of that DBP class were formed by dichlor or trichlor compared to bleach. Negative percentages in red indicate that less of that DBP class were formed by dichlor or trichlor. *Note: not all differences are statistically significant.***

## Next Steps

1) Investigate the formation of other DBP classes from dichlor and trichlor, including haloacetic acids and nitrosamines like N-nitrosodimethylamine (NDMA).
2) Determine whether the cyanurate rings in dichlor and trichlor contribute to the formation of HANs and other nitrogenous DBPs through the use of isotopic labelling.
3) Investigate the impact of pH and mixing rates on DBP formation from dichlor and trichlor.
4) Compare the pathogen removal efficacy of dichlor and trichlor to bleach, using E. coli and bacteriophage MS2 as model pathogens.

## Acknowledgements

Special thanks to Kirin Furst for her amazing mentorship and ongoing support, Pamela McLeod for her tireless efforts in building the RRS program, and Bill Mitch for his helpful expertise.

### Research Scholar Contact Information

Danny V. Nguyen | dannyn@stanford.edu

Research conducted through the ReNUWIt Research Scholars (RRS) Program.

*Supported by the National Science Foundation under EEC-1028968*