

# Anthropogenic very short-lived halocarbons from ballast water treatment

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## Halocarbons as disinfection by-product (DBP)

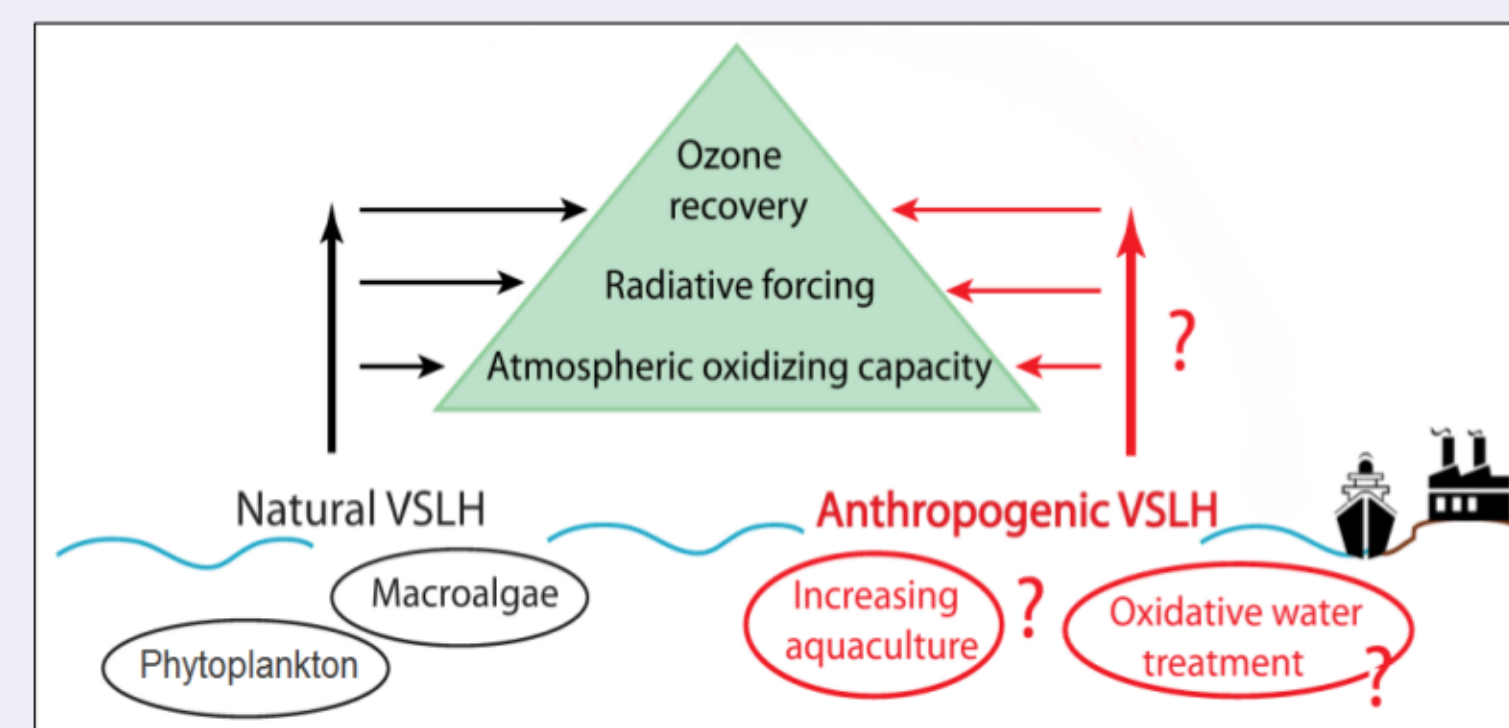


Fig. 1: Atmospheric impact of VSLH from natural and new anthropogenic sources (adapted from S. Tegtmeier).

Anthropogenic very short-lived halocarbons (VSLH) are formed as by-products during disinfection (DBP) of seawater as in ships and power plants (Fig. 1). In the atmosphere, VSLH like bromoform are photolysed and thus involved in ozone depletion.<sup>[1]</sup> The environmental impact of anthropogenic VSLH is still unknown.

## Bromoform (CHBr<sub>3</sub>) as mayor DBP

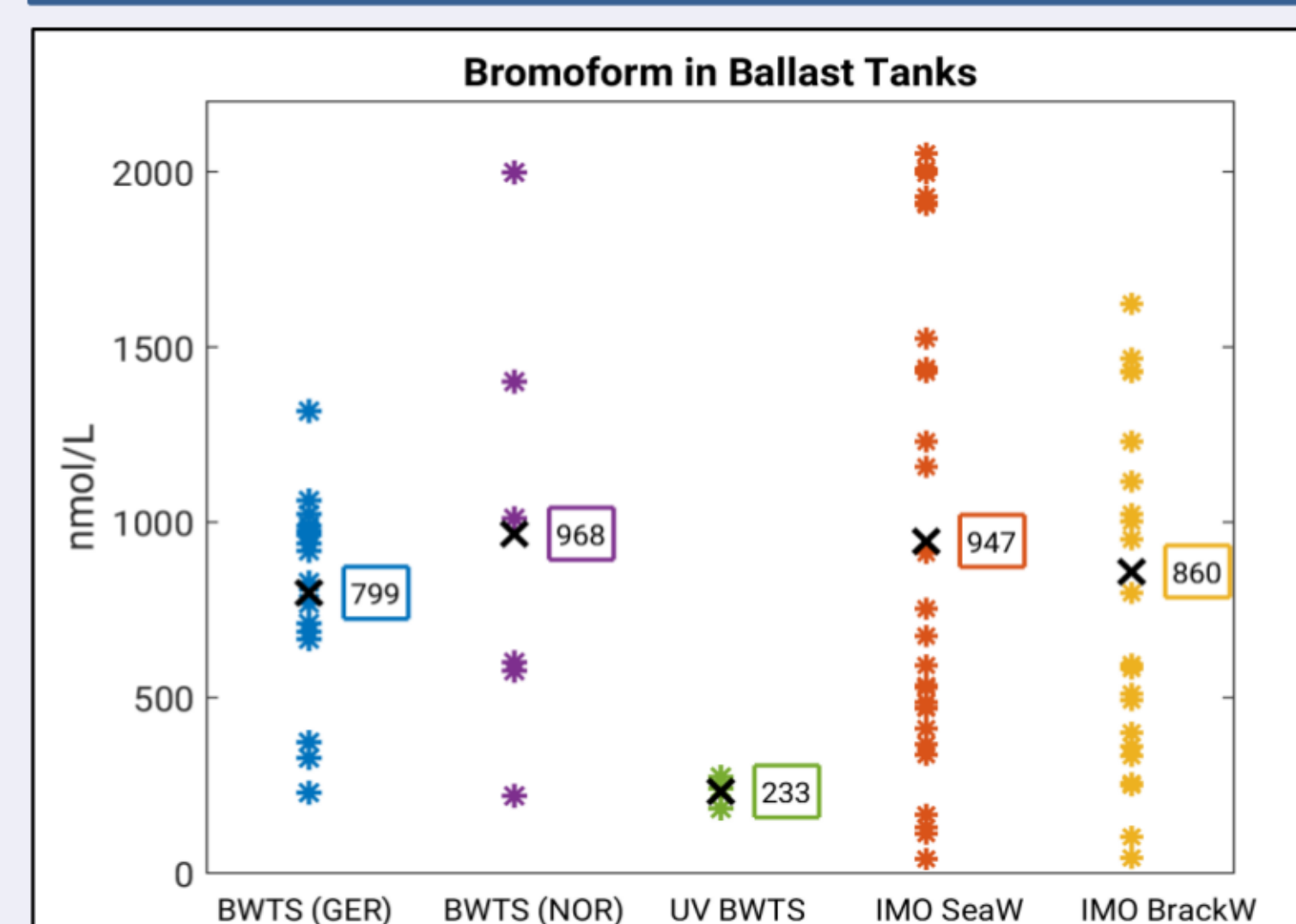


Fig. 2: Measurements of bromoform from BW samples (1-3) and values from MEPC reports<sup>[3]</sup> from BW treatment systems (4-5).

Commercial ships discharge  $\sim 10^7$  m<sup>3</sup> of ballast water (BW) in ports every day. Treatment of BW helps to prevent biofouling and the invasion of non-indigenous species.

BUT: Chemical BW treatment produces high concentrations of VSLH as DBPs especially bromoform (CHBr<sub>3</sub>).<sup>[2]</sup> We measured bromoform in BW with mean concentrations of 900 nmol/L  $\approx$  230 g/L (Fig. 2).

## Research area

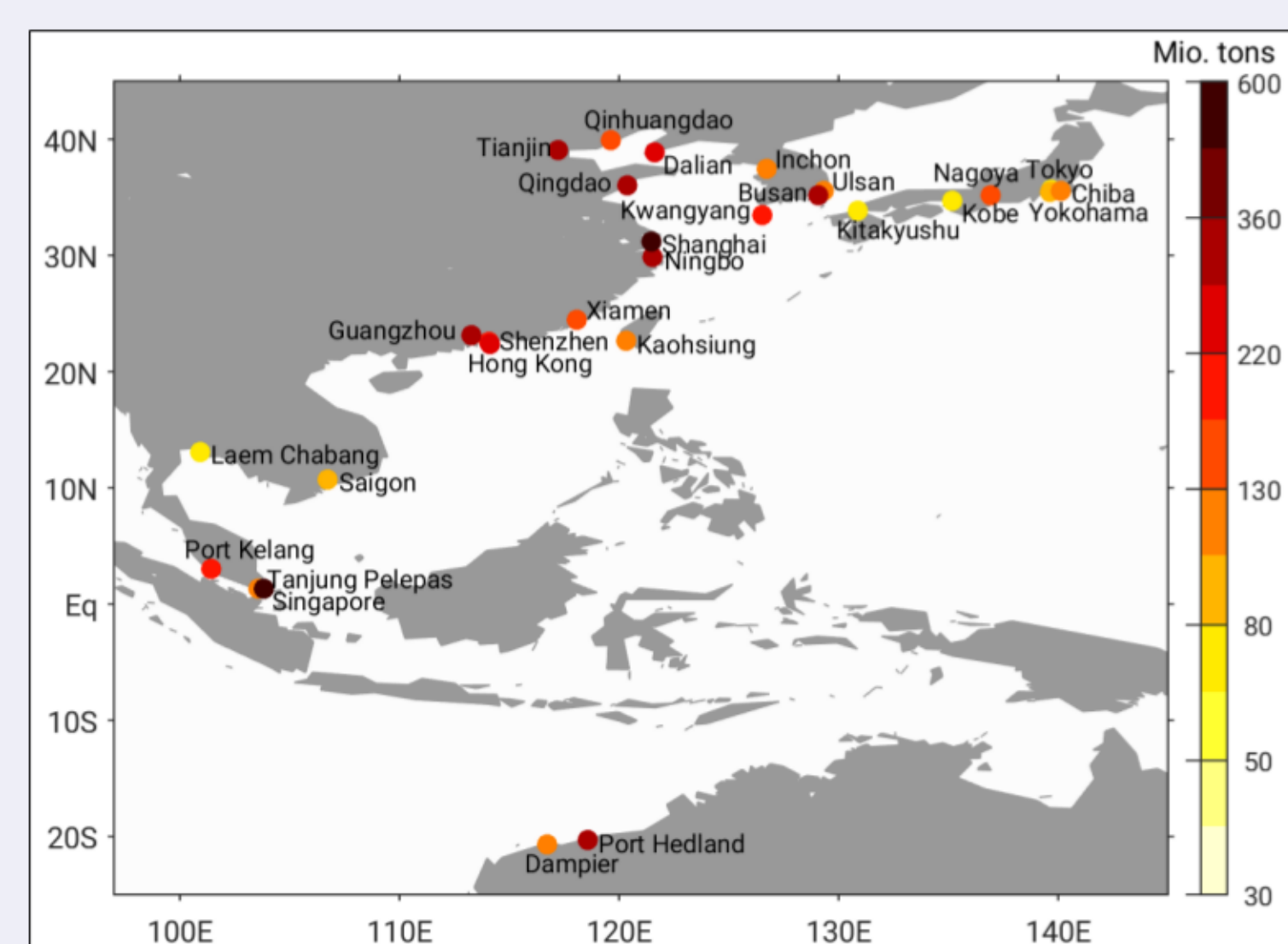


Fig. 3: Largest harbours according to cargo throughput in southeast Asia, in Mio. (10<sup>6</sup>) tons.

VSLH require strong tropical convection to reach the upper troposphere and stratosphere. We focus on the highly industrialised area of tropical southeast Asia where 28 of world's 50 largest ports are located accounting for over 50% of commercial shipping worldwide (Fig. 3).

## Numerical simulation of bromoform spreading

### Methods

- NEMO-ORCA high-resolution 1/12° ocean model.
- Lagrangian simulation of DBP pathways near big harbours, e.g. Singapore and Hong Kong.
- Continuous discharge of particles representing bromoform mass in BW.
- We calculate concentrations within the upper 20m and outgassing from the mixed layer over one year.

### Ocean surface concentration

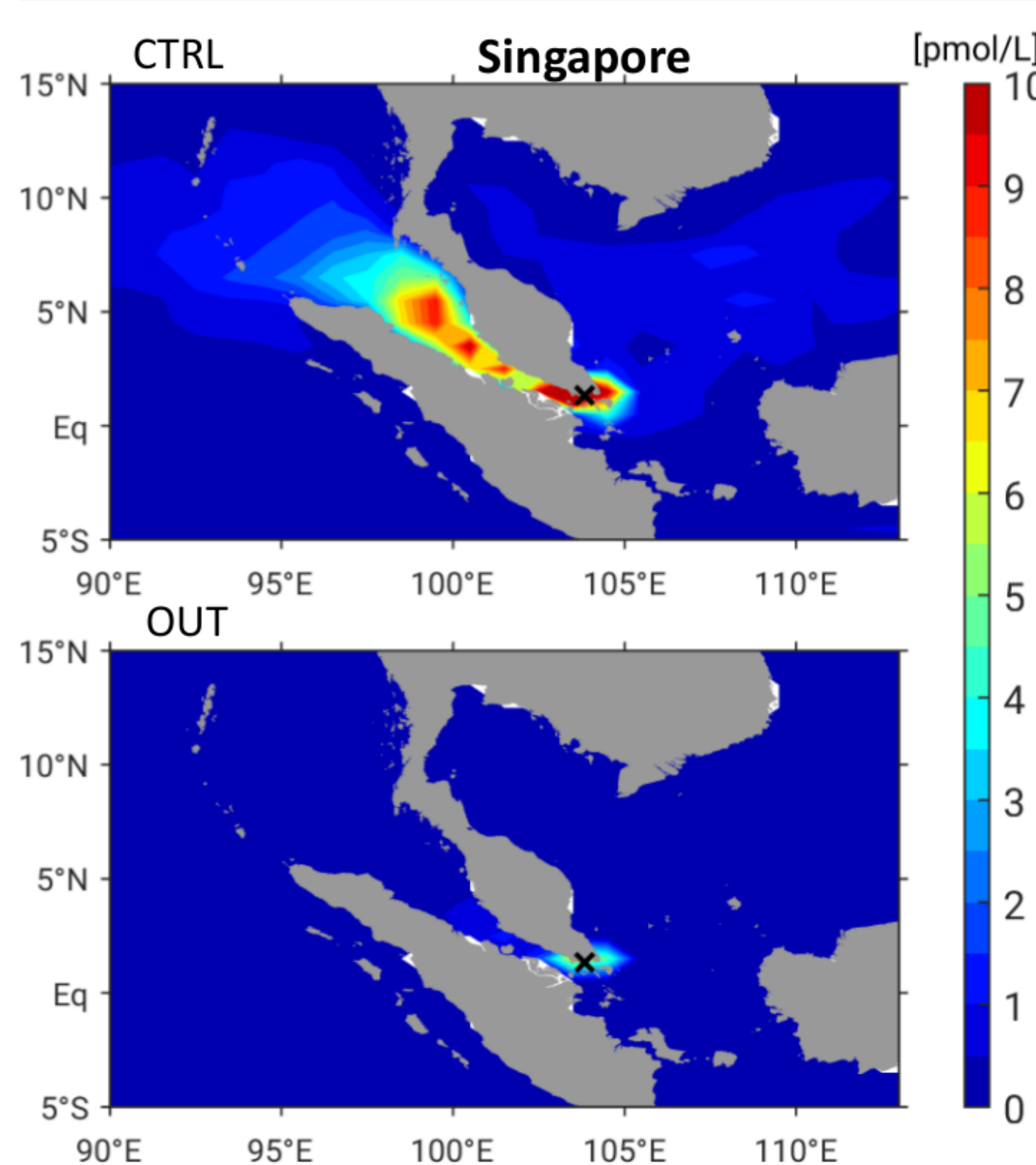


Fig. 4: Surface bromoform concentration from two experiments (OUT and CTRL).

Tab. 1: Bromoform concentration and outgassing over one year near discharge location from OUT experiment. Neighbouring ports from Singapore and Hong Kong are included.

Port	Concentration [pmol/L]	Flux [pmol/m <sup>2</sup> /hr]
Singapore	11.5	956.7
Hong Kong	10.7	1739.5

Over one year, BW can spread fast over large regions (Fig. 4, CTRL). Bromoform concentrations are highest close to the discharge location.

Only 15% of bromoform stays in the surface ocean when outgassing is included (OUT). Air-sea flux prevents large-scale transport in the ocean.

### Experiments

#### CTRL

- Constant particle mass
- No outgassing, particle conservation

#### OUT

- Oceanic degradation
- Sea-to-air flux in the mixed layer

### Sea-to-air flux (OUT)

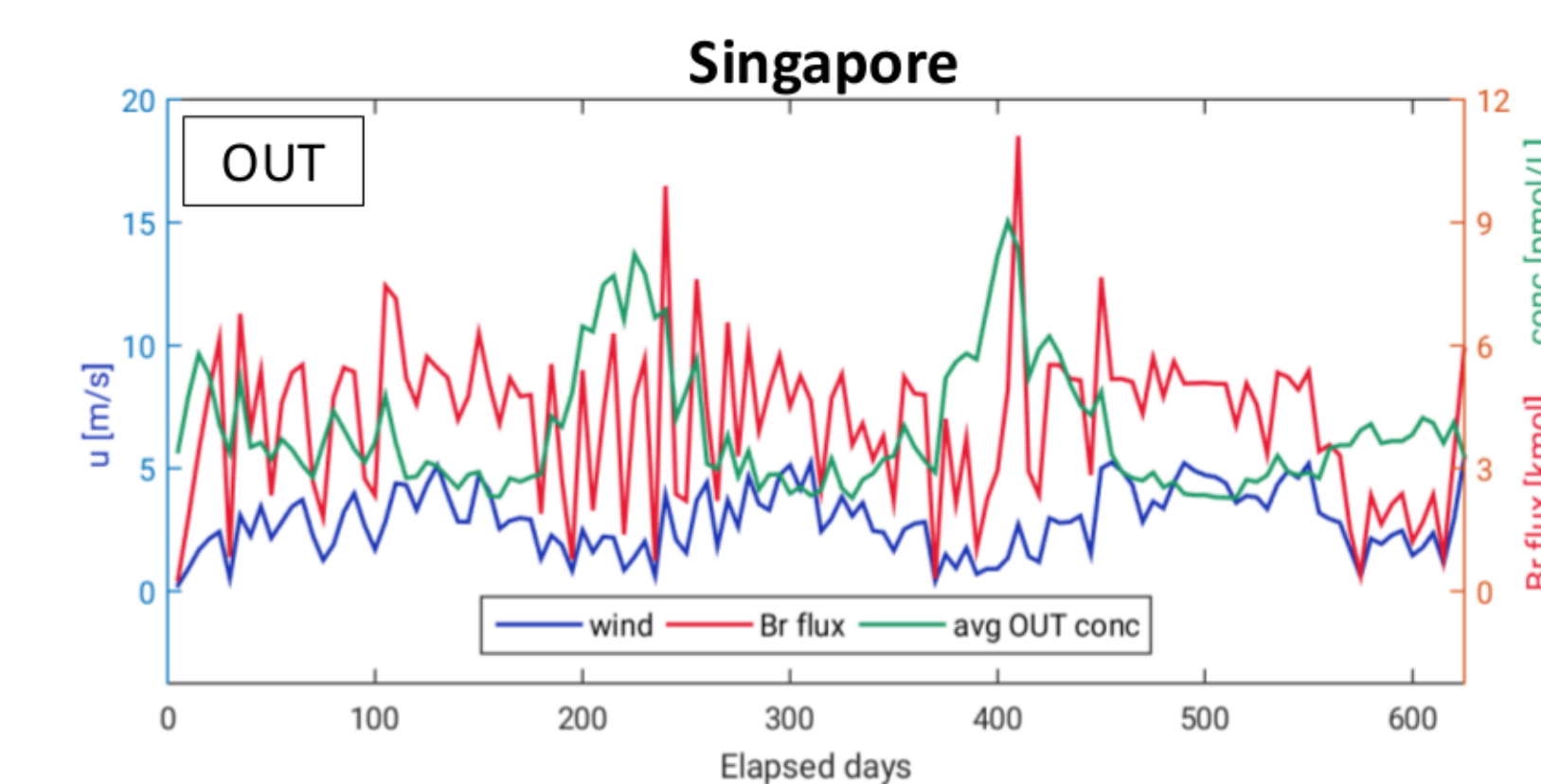


Fig. 5: 5-day values of wind, bromine flux and bromoform concentration close to discharge.

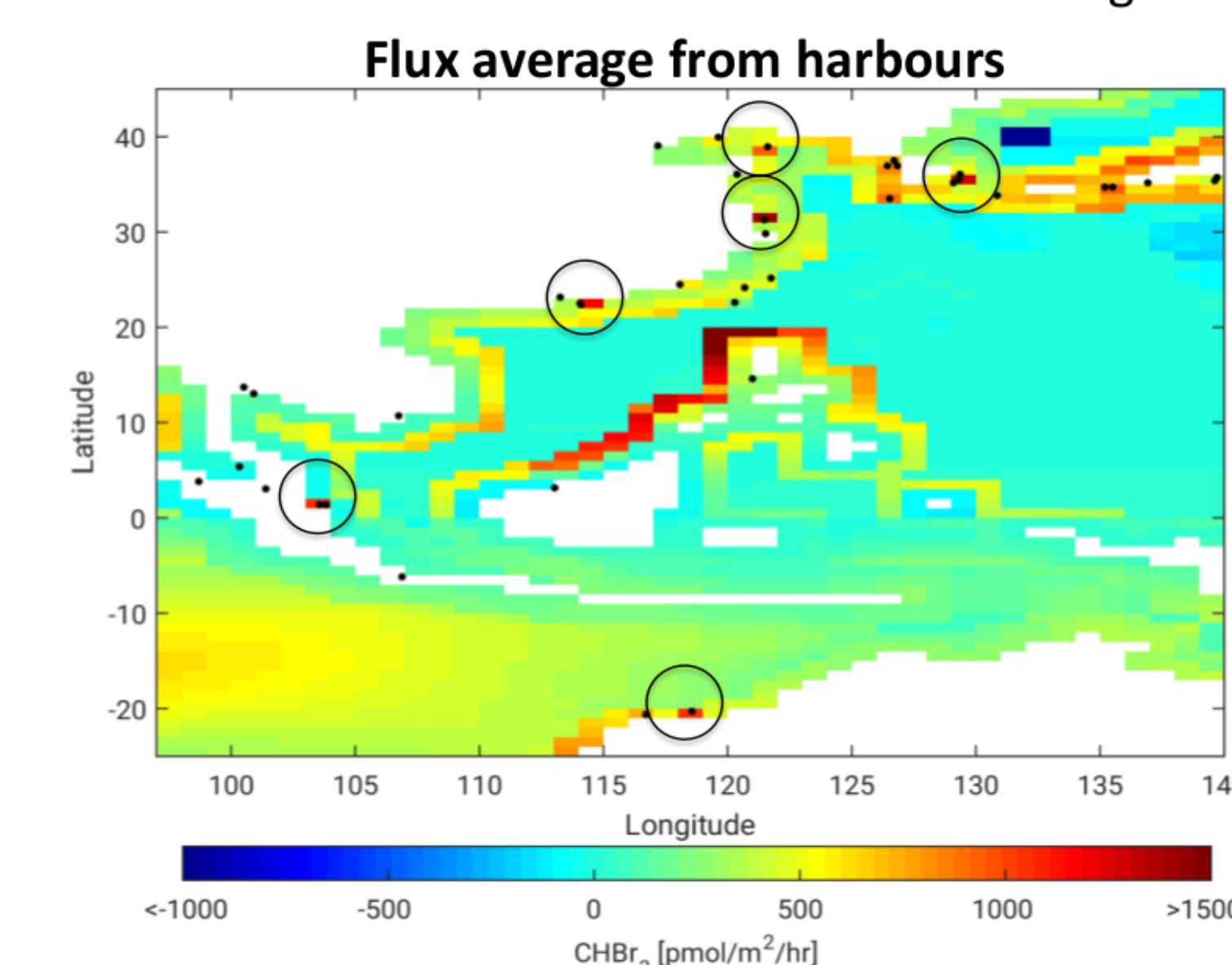


Fig. 6: BW bromoform fluxes (circles) added to modelled background fluxes by Ziska et al. (2014).<sup>[4]</sup>

High wind variability leads to large fluctuations of sea-air flux (Fig. 5). Weak winds cause accumulation of particles near the source and less sea-to-air flux.

Regions of large harbours add substantially to the natural bromoform flux (Fig. 6). Fluxes from BW discharges add locally to background fluxes.<sup>[4]</sup> 90% of bromoform from BW is instantly outgassed at discharge location.

## Conclusions

- Bromoform is 900  $\pm$  560 nmol/L in treated ballast water (BW).
- Peak values regionally reach up to 30-65 pmol/L in the ocean.
- Sea-to-air flux happens very fast: 85% of Br from Singapore BW is emitted at discharge location; 100% of Br from Hong Kong.
- Fluxes are highly variable and reach up to 2000 pmol/m<sup>2</sup>/hr near the discharge region.

## Outlook

- Discharge of treated cooling water from industrial power plants is even larger than BW discharge.
- Economic growth and population rise lead to annual increase in water treatment.
- From regional to global: What are global anthropogenic VSLH emissions?

## References

- [1] Carpenter, L. J., & Liss, P. S. (2000). *JGR: Atmospheres*, 105(D16), 20539–20547.
- [2] Werschun, B., Sommer, Y., Banerji, S., 2012. *Water Research*. 46, 4884–4901.
- [3] Marine Environmental Protection Committee (MEPC). *International Maritime Organization*, London, UK.
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## Acknowledgements

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