Ocean Biogeochemistry Control on the Atmospheric Chemistry

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NATIONAL CENTER FOR ATMOSPHERIC RESEARCH

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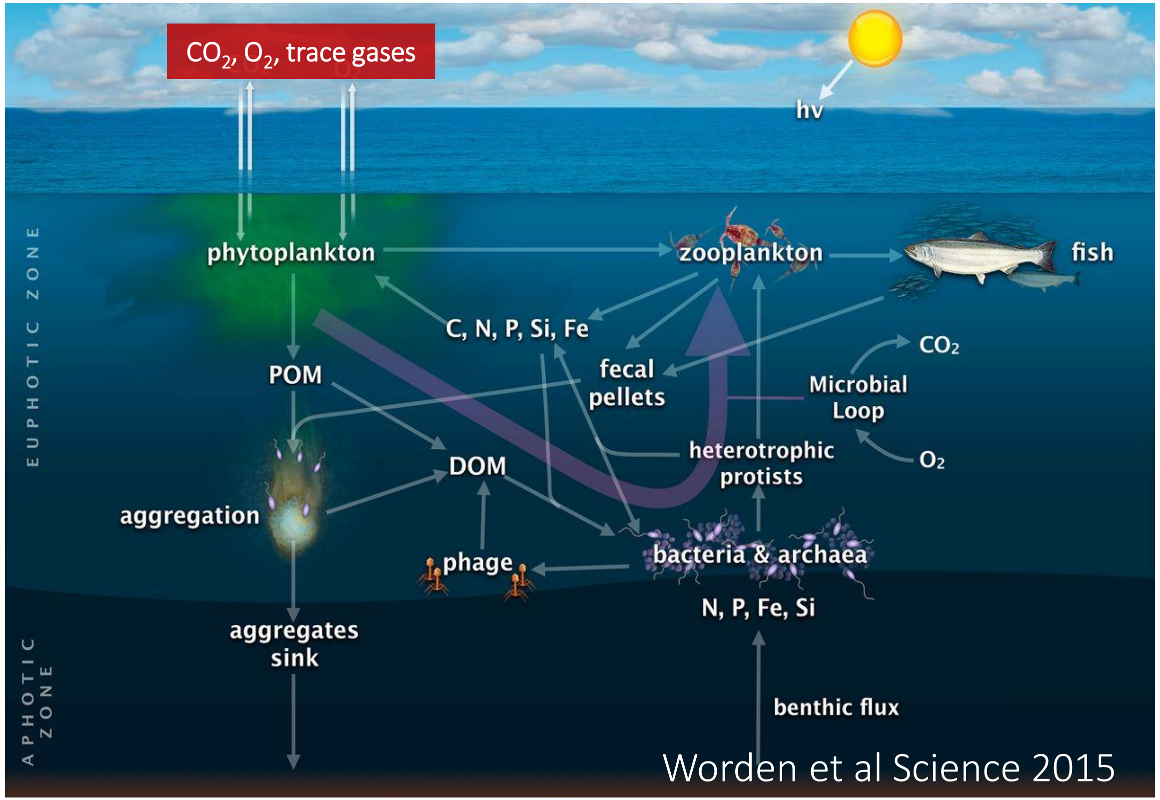
Ocean emits climate-relevant gases

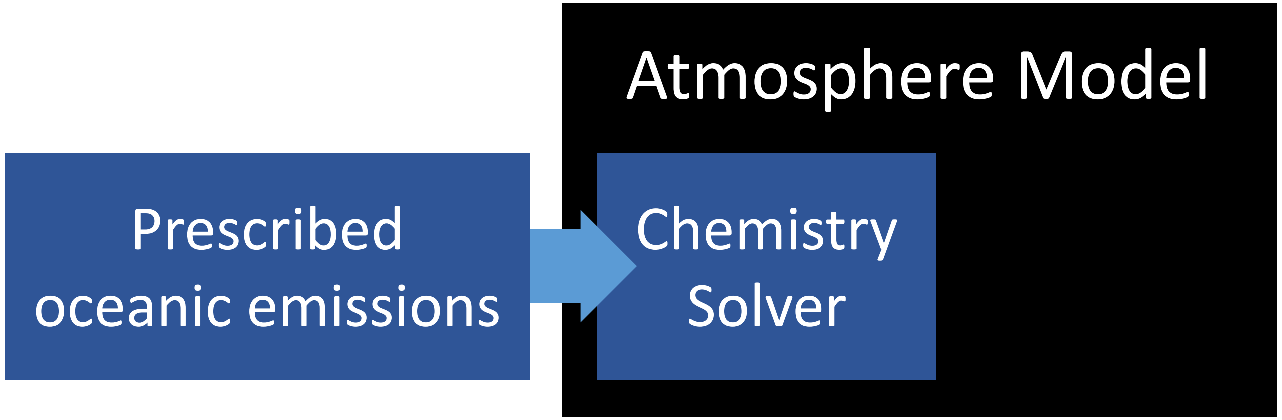
- Photochemistry of dissolved organics in seawater produces biologically labile compounds, volatile organic compounds (VOCs), and CO (Kieber et al., Nature 1989; Kieber et al., Limnology and Oceanography, 1990; Mopper et al., Deep-Sea Research 1991; etc), which is also the rate-limiting step for the removal of a large fraction of oceanic DOC (Mopper et al., Nature 1991).

- Many of the ocean-emitted trace gases have profound impact on the atmosphere:
  - DMS (aerosol / cloud)
  - Organohalogens (stratospheric O_3)
  - VOCs (O_3, oxidative capacity)
  - Reactive nitrogen (O_3, oxidative capacity)



Worden et al Science 2015

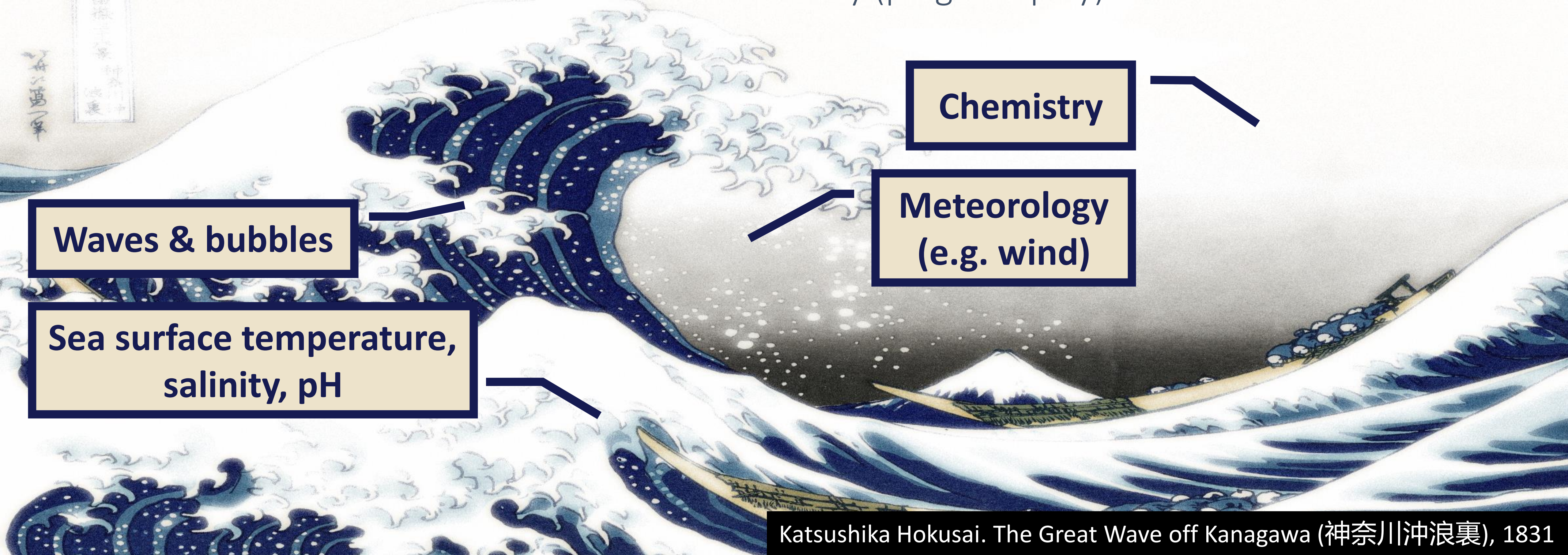
Ocean biogeochemistry control: previous



- Current approach: prescribed oceanic emissions for climate-relevant trace gases, e.g. DMS, organohalogens, ...
- This is easy, but not entirely skillful and has very limited predictibility. For example:
  - Emission fluxes do not response to changes in local conditions
  - Poorly justfied future / past climate projections

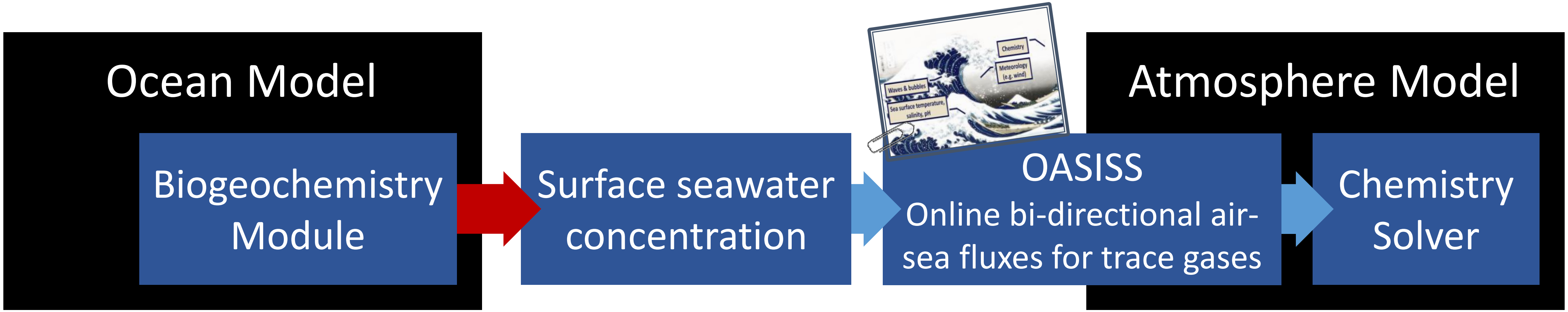
Fully Coupled Air-Sea Exchange Interface

- An Online Air-Sea Interface for Soluble Species (OASISS) is developed for NCAR CESM2 | CAM-Chem to predict the bi-directional oceanic flux of trace gases.
- The model framework is flexible and user-friendly (plug and play)



Katsushika Hokusai. The Great Wave off Kanagawa (神奈川沖浪裏), 1831

Ocean biogeochemistry control: ideal

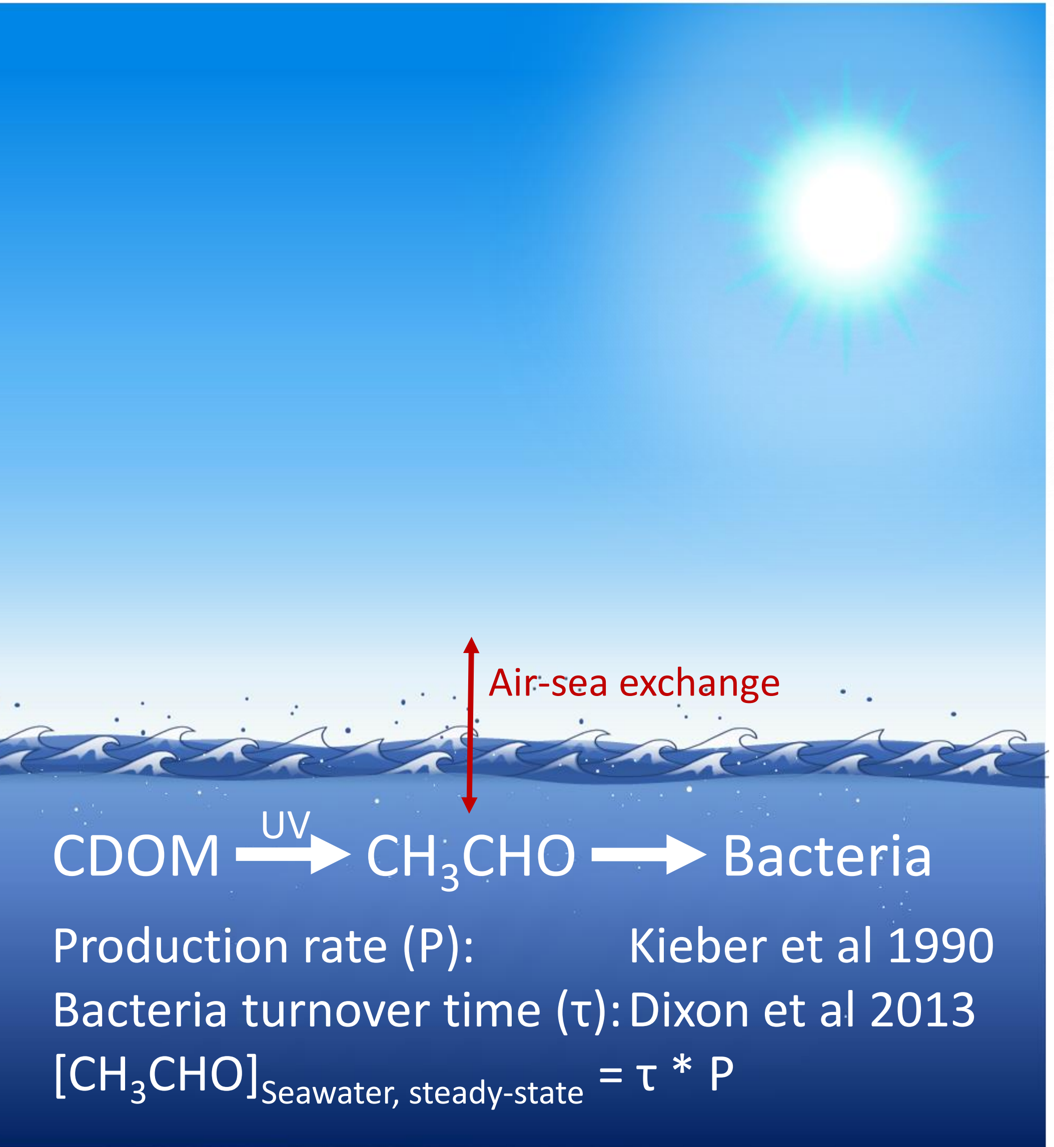


- Ideally, we should explicitly describe the sources, sinks, transport, and air-sea exchange processes of these compounds in the ocean.
- Surface seawater concentration is the key connection between the atmospheric chemistry and the ocean biogeochemistry. Currently this connection is missing for most of the climate-relevant gases.
- **Biggest challenge: the lack of quantitative and mechanistic understanding of the biogeochemical processes that control the production and removal of these compounds in the seawater.**

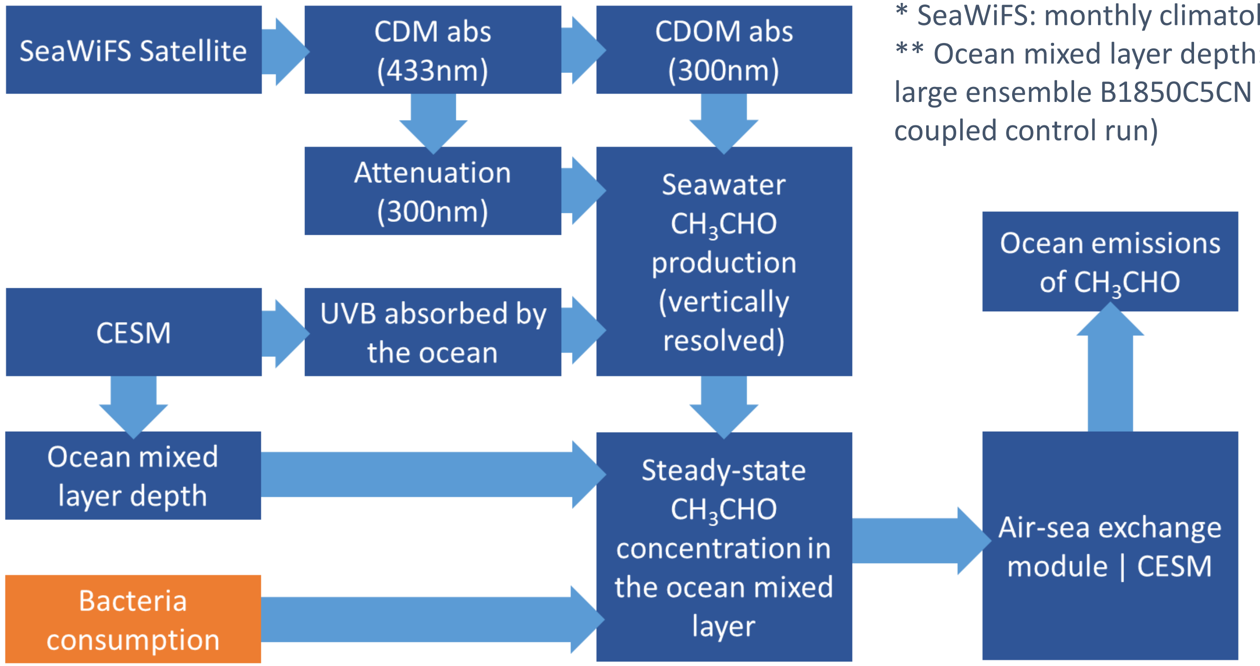
Ocean biogeochemistry control: current

- **Old-fashioned "Bottom-up" approach (sort of):**
  - ➢ Acetaldehyde (CH_3CHO): photochemical production from the colored dissolved organic matters (CDOM) in the seawater, coupled to the atmospheric model.
  - ➢ This CDOM photochemistry framework can certainly be expanded to other compounds ← need help from the experimentalists.

Example: air-sea exchange of CH_3CHO



- Satellite-based approach: Millet et al ACP (2010).
- Diurnal surface UV (<320nm) net absorption (CESM)
- CH_3CHO production from CDOM (Kieber et al 1990) and bacteria-induced turnover timescale updated based on recent study (Dixon et al JRL 2013)



* SeaWiFS: monthly climatology
** Ocean mixed layer depth: CESM large ensemble B1850C5CN (fully-coupled control run)

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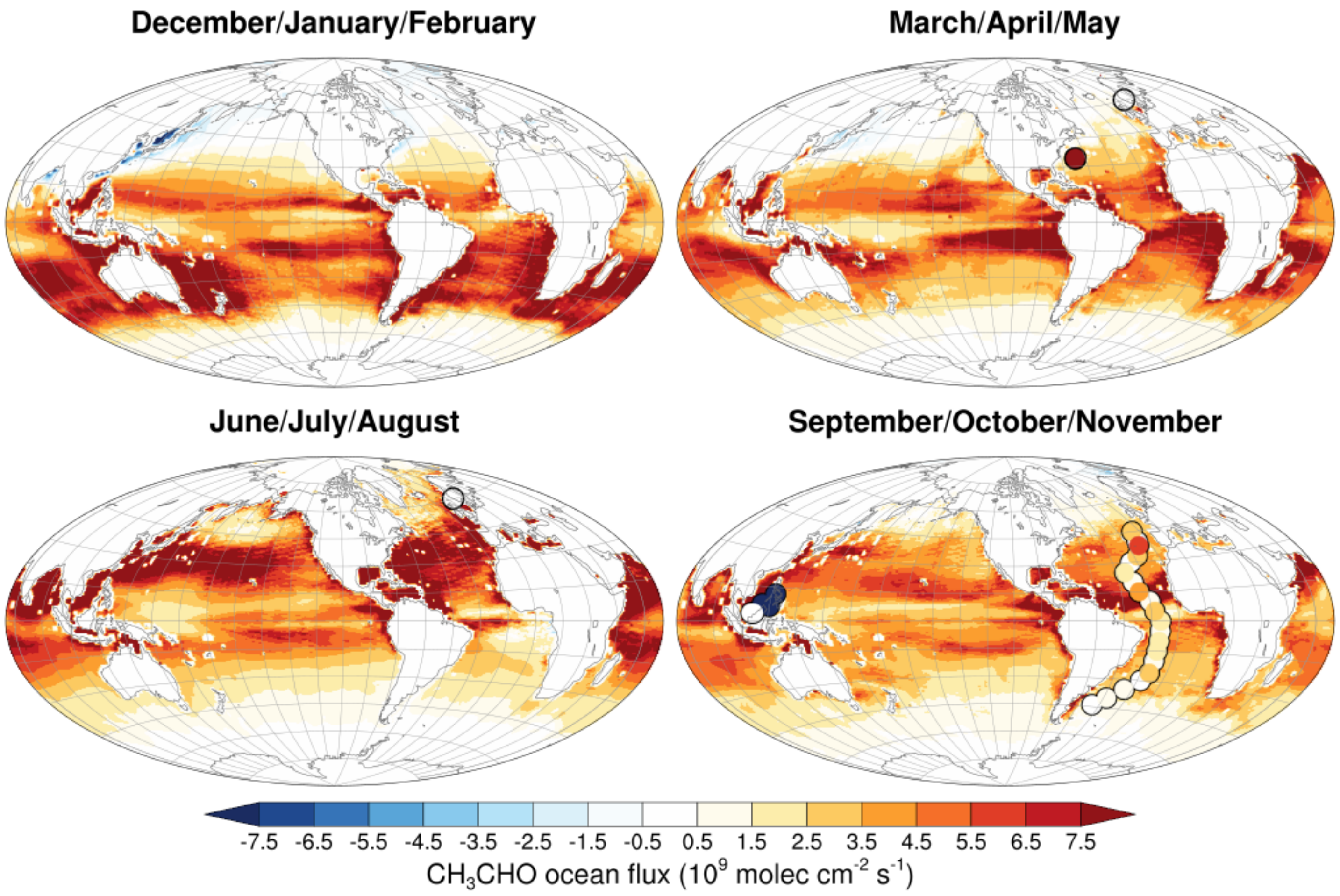

Flux measurements used for model validation:

- Schlundt et al (2017)
- Yang et al (2014) ← Eddy covariance
- Beale et al (2013)
- Sinha et al (2007) ← mesocosm
- Zhou and Mopper (1997)

Wang et al, in review by GRL

AMS talk: https://ams.confex.com/ams/2019Annual/videogateway.cgi/id/51193?recordingid=51193

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  - ➢ This CDOM photochemistry framework can certainly be expanded to other compounds ← need help from the experimentalists.
  - ➢ Fundamental challenge: lack of mechanistic understanding for many other species!

ROAD CLOSED
LACK OF MECHANISTIC
UNDERSTANDING

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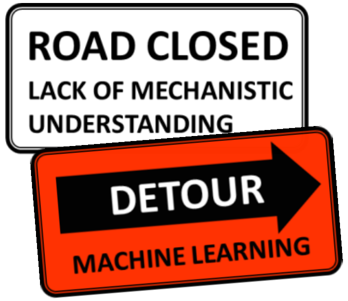
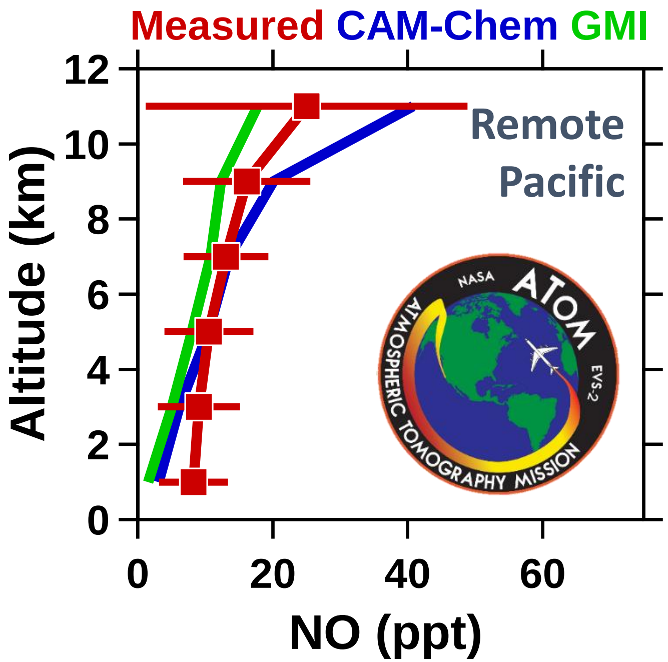
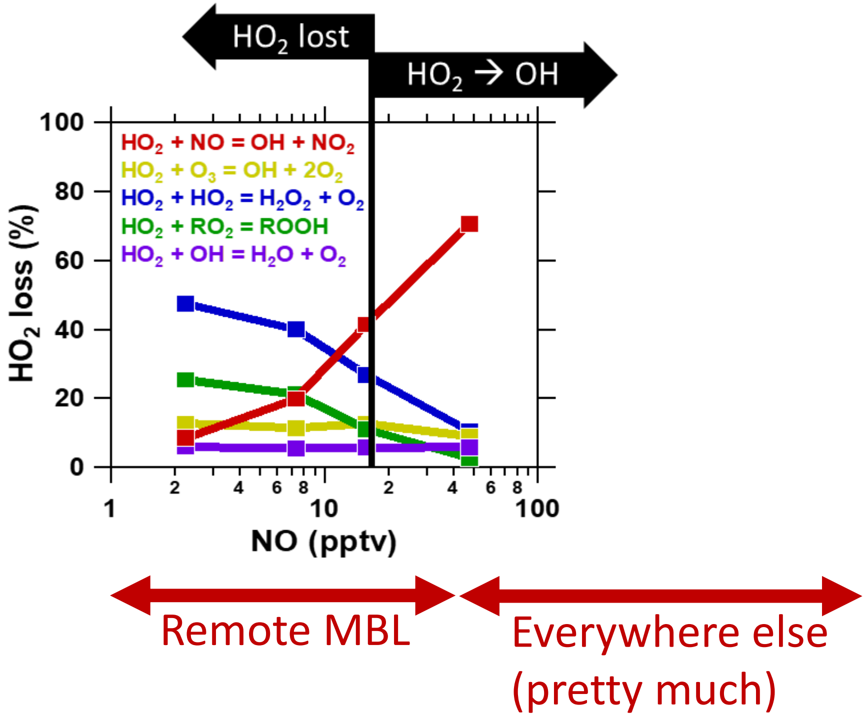
  - Fundamental challenge: lack of mechanistic understanding for many other species!

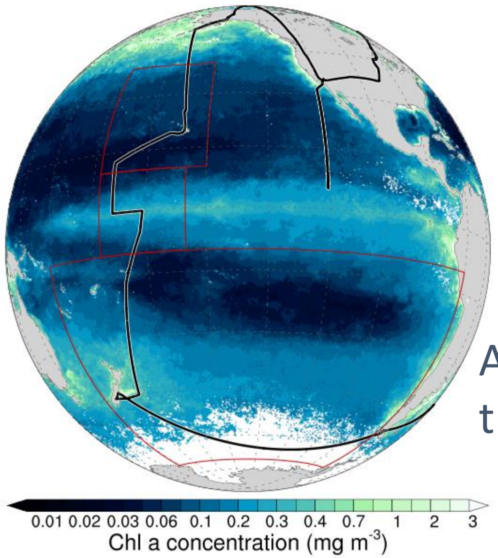
- **Statistical tricks to get around the fundamental challenges:**
  - Machine learning
  - Need a lot of data ← need help from the experimentalists.
  - This is not ideal, but can get things done (i.e. can be operational) and has some predictability too. May provide insights into future research directions.
  - Examples: air-sea exchange of NO and $CHBr_3$.



Example: air-sea exchange of NO



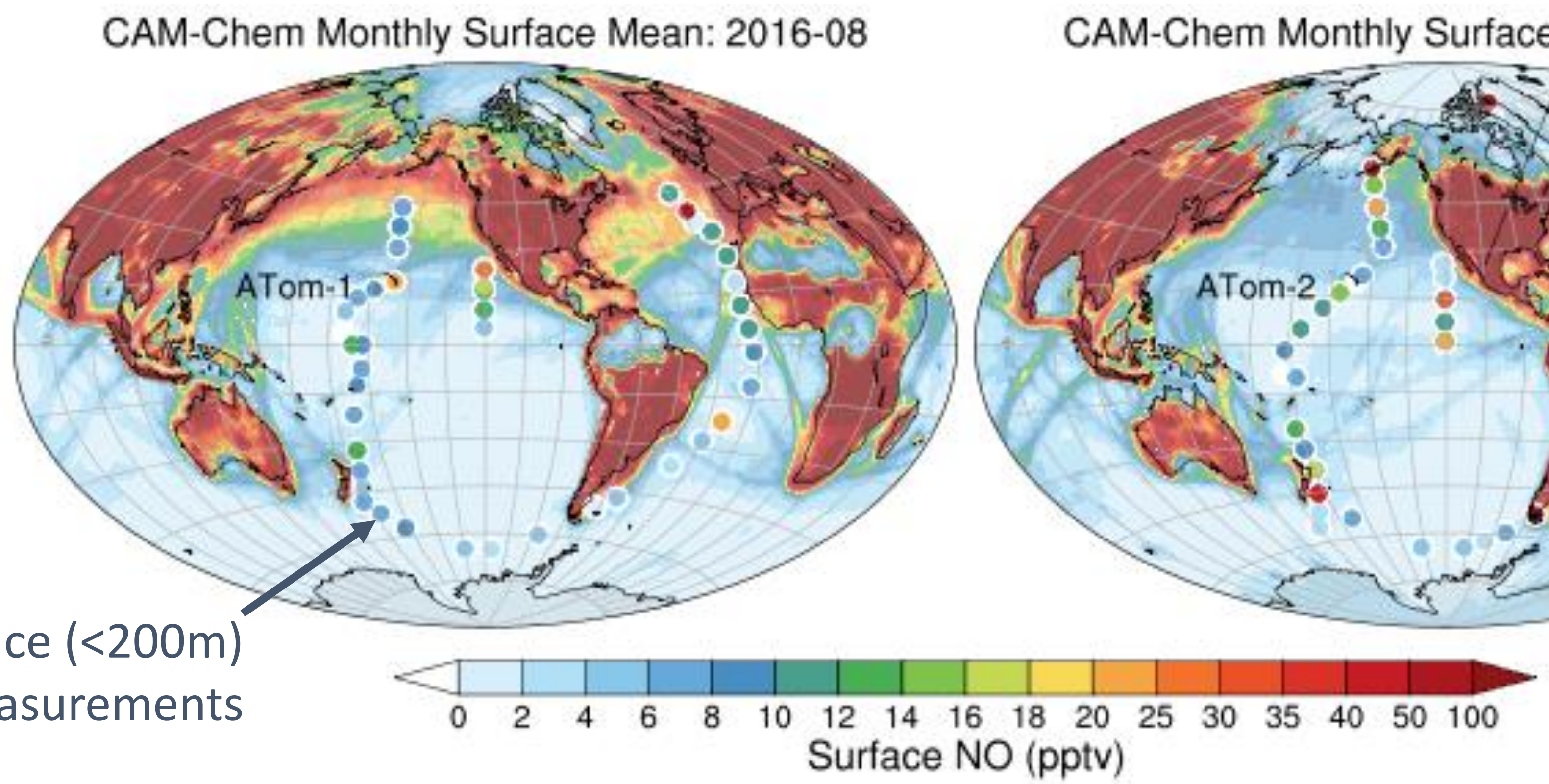




ATom flight tracks

- Recent aircraft campaigns (ATom, CONTRAST, TORERO) suggest that in the remote marine boundary layer (especially in the tropics), both NO and NO_y are consistently underestimate by models (Nicely et al JGR 2015; Anderson et al JGR 2017; Thompson and Murray et al, in prep.).
- Adding ocean emissions of alkyl nitrates doesn't help (Fischer et al 2018)
- Box model shows that HO_x chainlength is quite sensitive to NO in this range.

NO in the remote MBL: underestimated



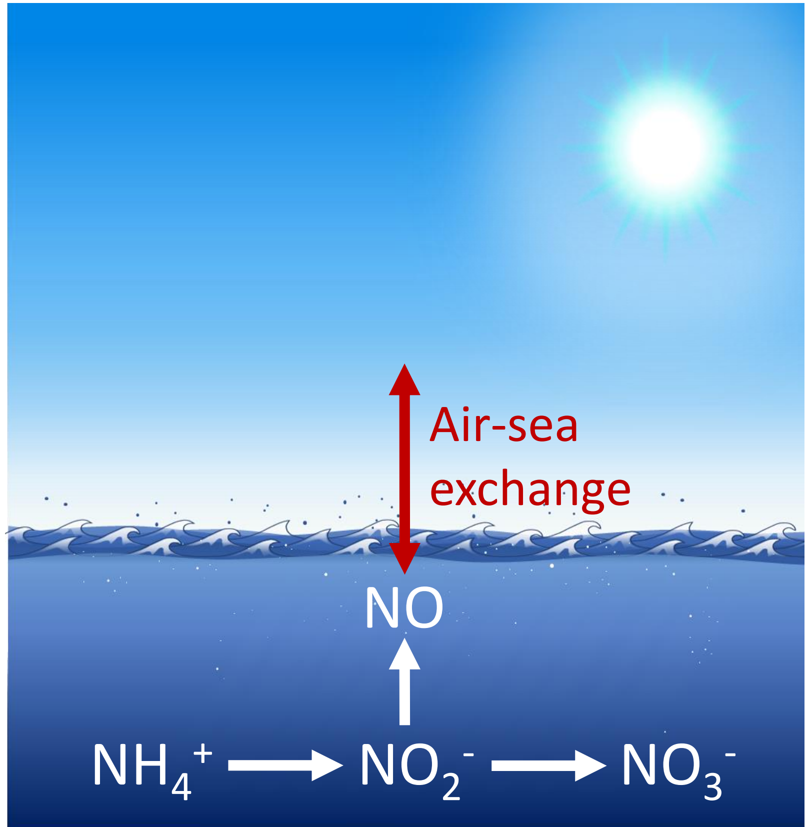
Surface (<200m) measurements

Note the scale is saturated at 100 pptv

- The low bias is likely widespread. Especially in the tropical and southern hemisphere oceans, i.e. roughly 1/3 of the world's ocean
- Is NO coming out of the ocean?

Ocean does emit NO, dominated by nitrite

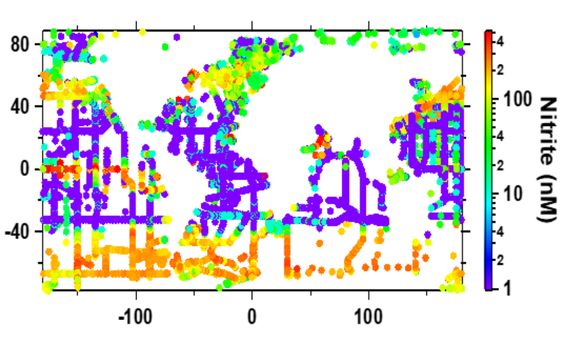
- Surface seawater is supersaturated with NO (Torres et al 1993; Zafiriou et al 1981; Zafiriou et al 1980; McFarland et al 1979; etc).
- Olasehinde et al (EST 2010) reported NO production rates correlate perfectly with dissolved nitrite (NO_2^-).
- Zakem et al (Nat Comm 2018): In general, nitrite is an intermediate of nitrification, the microbially mediated oxidation of NH_4^+.
- Sources and sinks of nitrite in the surface seawater remains poorly understood. CESM2 BGC currently does not represent nitrite. What can we do?



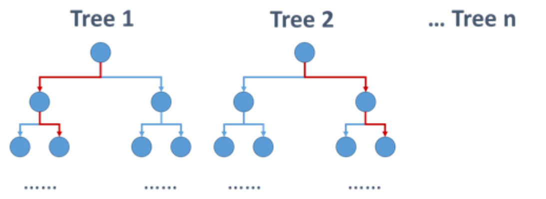
Seawater nitrite: Machine learning

- GLODAP v2 dataset (Olsen et al 2016) compiles over 700 scientific cruises since 70s covering the global ocean.
- This dataset is used to train a random forest algorithm which is then used to predict seawater nitrite (validated at this point), and finally to calculate NO production.

Observations

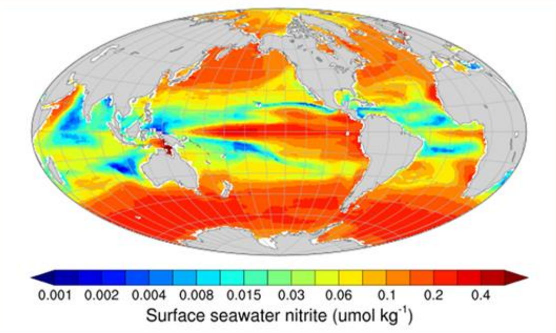


Machine Learning

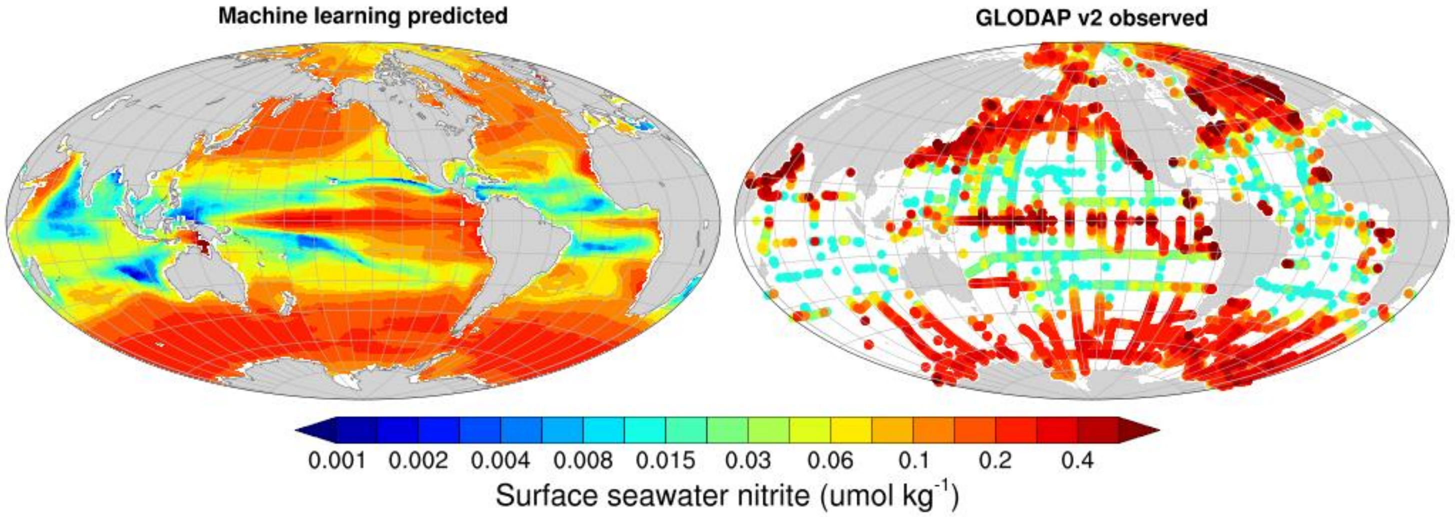


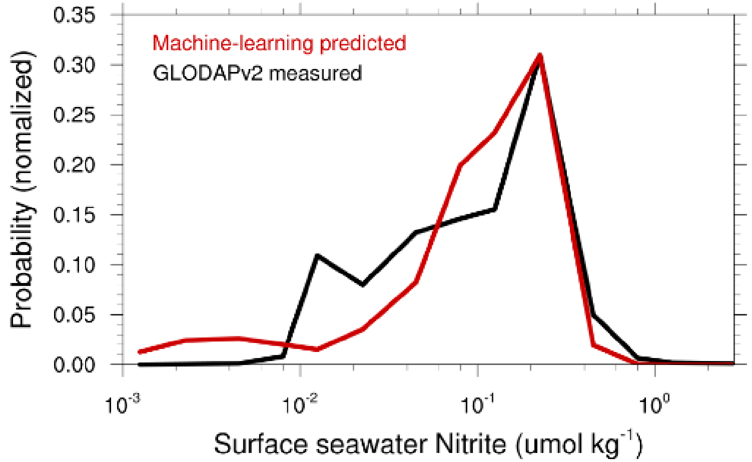
Random forest algorithm trained by the observations

Predictions



Surface seawater nitrite: machine learning





- This approach captures large scale features of the observed surface seawater nitrite.
- FYI, near-explicit nitrate aqueous-chemistry (Mack and Bolton 1999; etc) in the euphotic zone can explain <10% of this observed nitrite.

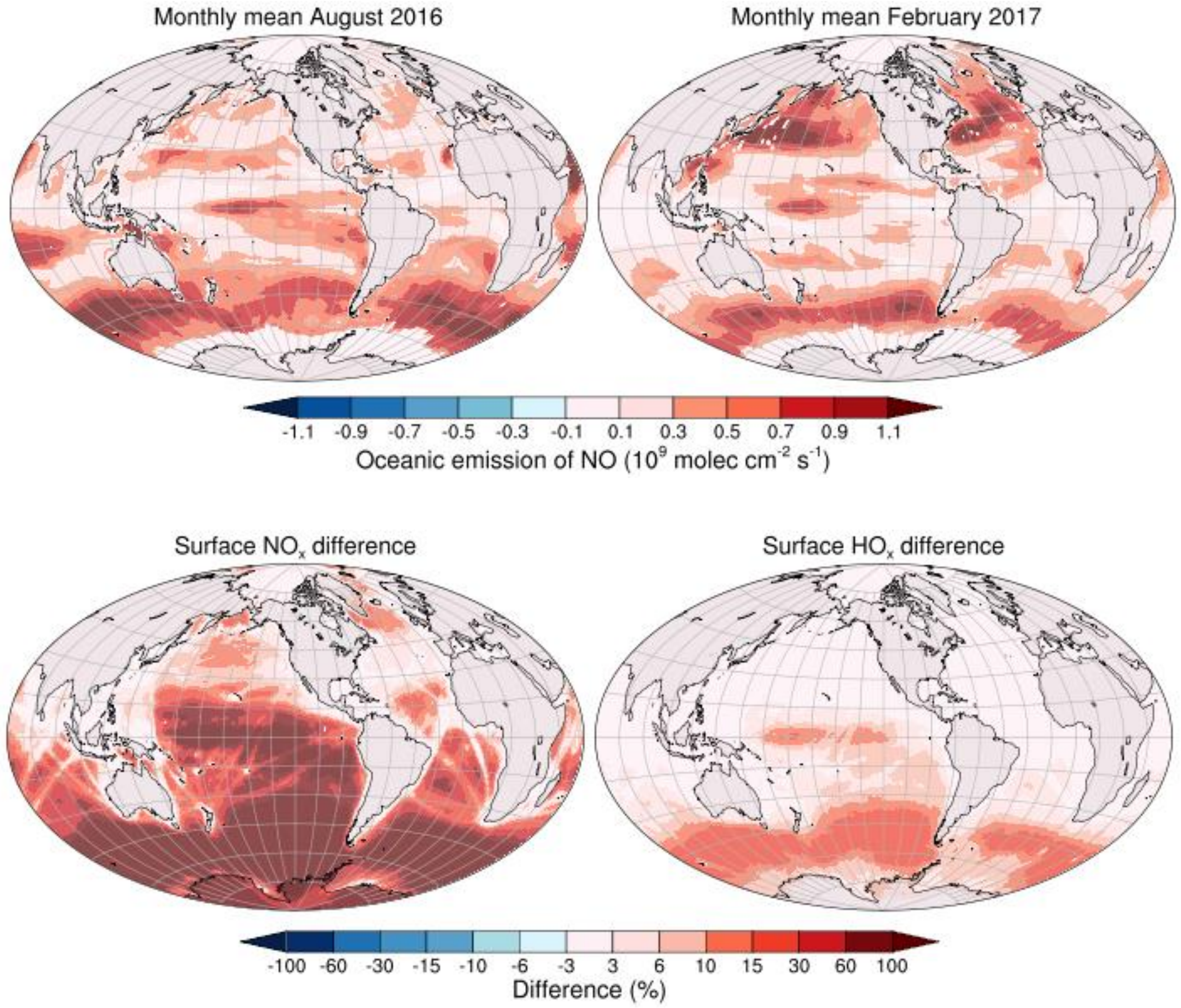
NO_3^- (aq) + hv → NO_2 (aq) + OH (aq)

NO_3^- (aq) + hv → NO_2^- (aq) + O^3P (aq)

NO_2^- (aq) + hv → NO (aq) + OH (aq)

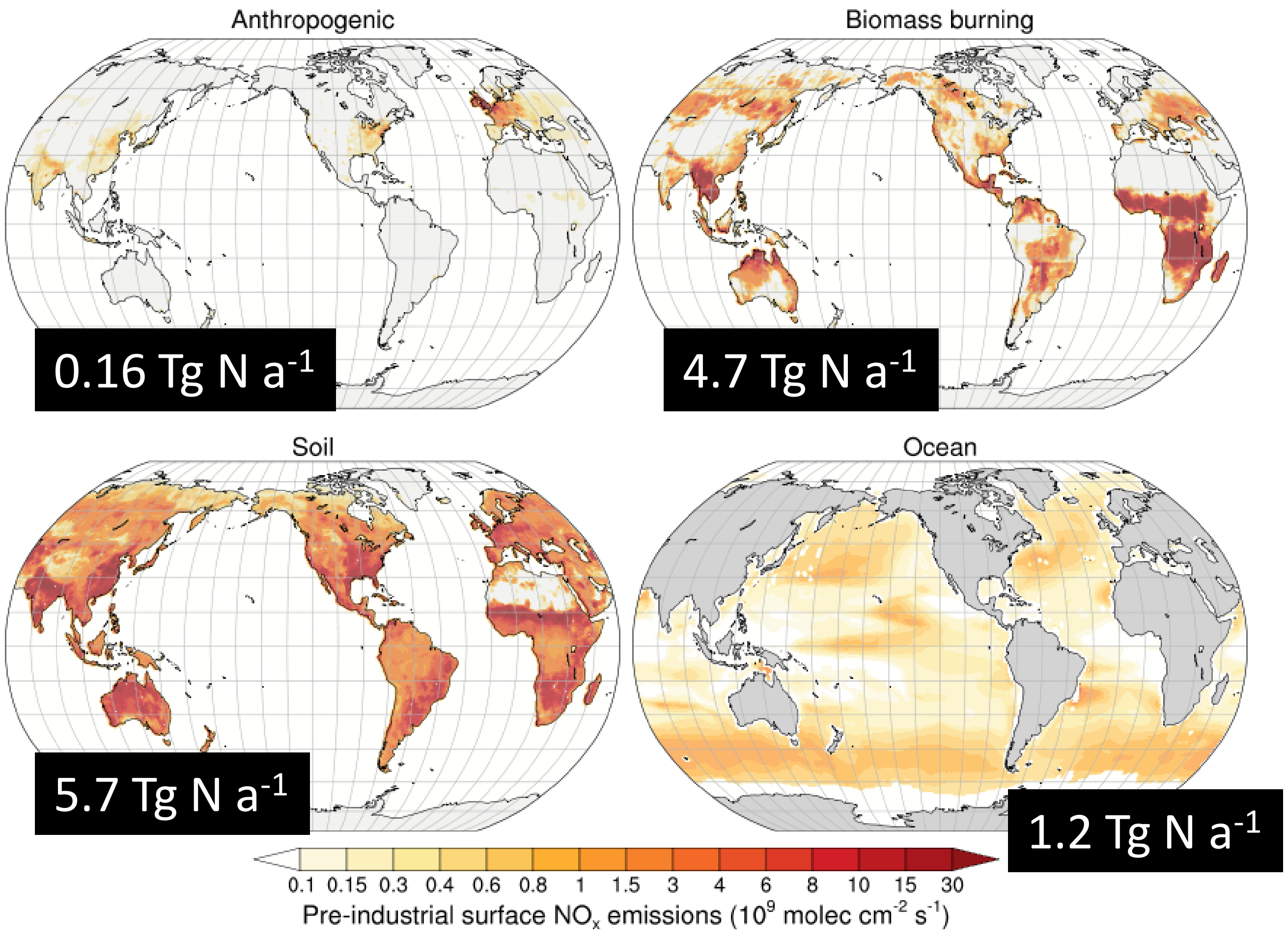
…

Air-sea exchange of NO: present-day



- Our approach predicts that the global oceanic is a small net source of NO: 0.9 Tg N per year.
- Fairly small compared to other NO_x sources (present-day)
- … but the impact (present-day) in the remote MBL is significant: average NO_x difference: +114%; average difference in HO_x and O_3: +10% both.
- No big deal globally, but quite substantial impact over the remote oceans (1/3 of the ocean coverage).

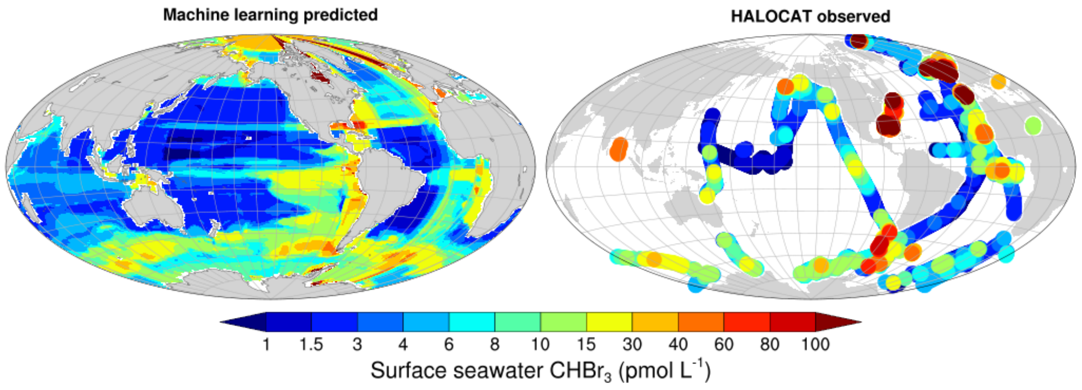
Possibly bigger pre-industrial impacts?

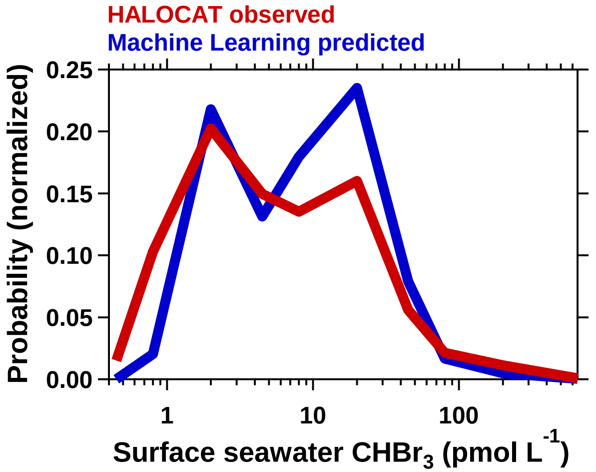


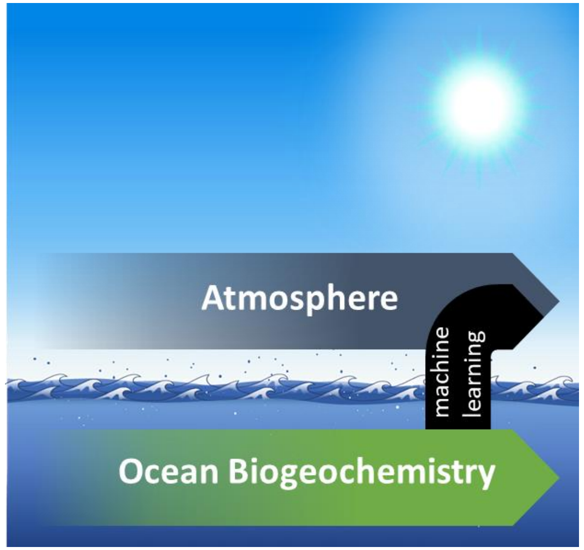
CMIP6 Pre-industrial (year of 1850)

- Algorithm trained using present-day data (GLODAP), then use Large Ensemble Community Project (LENS) dataset (Key et al BAMS 2015) to predict pre-industrial oceanic NO emissions.
- Pre-industrial total NO_x: ~16 Tg N per year (ACCMIP: Young et al ACP 2013).
- Ocean accounts for ~7% total NO_x emissions in pre-industrial days, but is a major source over the remote ocean!!!
- How does this affect the pre-industrial ozone budget and radiative forcing? ← working in progress

Last example: air-sea exchange of $CHBr_3$







- $CHBr_3$ is the most important brominated short-lived O_3-depletion substance in the stratosphere, and ocean is the dominant global source (Hossaini et al ACP 2016; etc). It's production and removal in the seawater remains poorly understood.
- HALOCAT dataset compiles historical cruise observations of $CHBr_3$ (and others too).
- We couple the air-sea exchange of $CHBr_3$ with the ocean BGC workhorse via machine learning, leading to improved predictability than current approaches (Ziska et al JAC 2017). ← Working in progress!

Summary

- Ocean biogeochemistry control on the atmospheric chemistry: poorly represented in chemistry-climate models.
- We show two coupling approaches:
  - ➢ A “bottom-up” model framework of CDOM photolysis.
  - ➢ A machine-learning-based approach, connects the ocean BGC to the atmosphere, which is a compromised approach providing predictability.

THANK YOU

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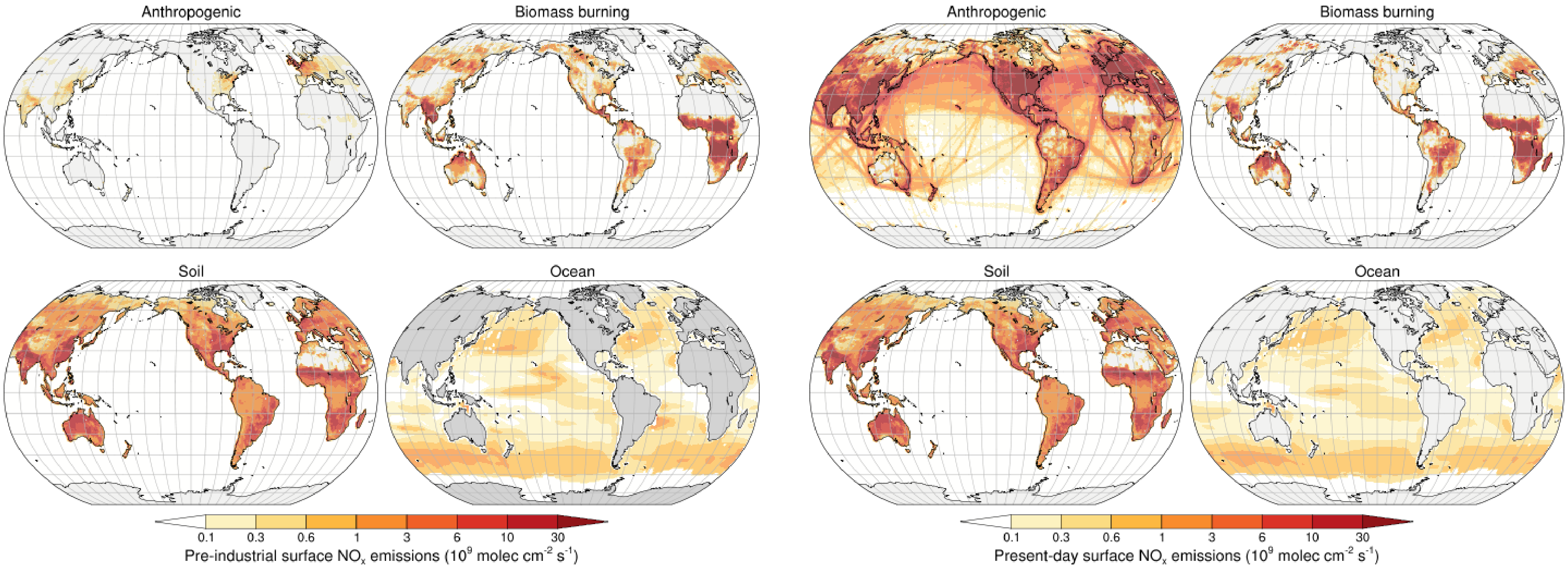
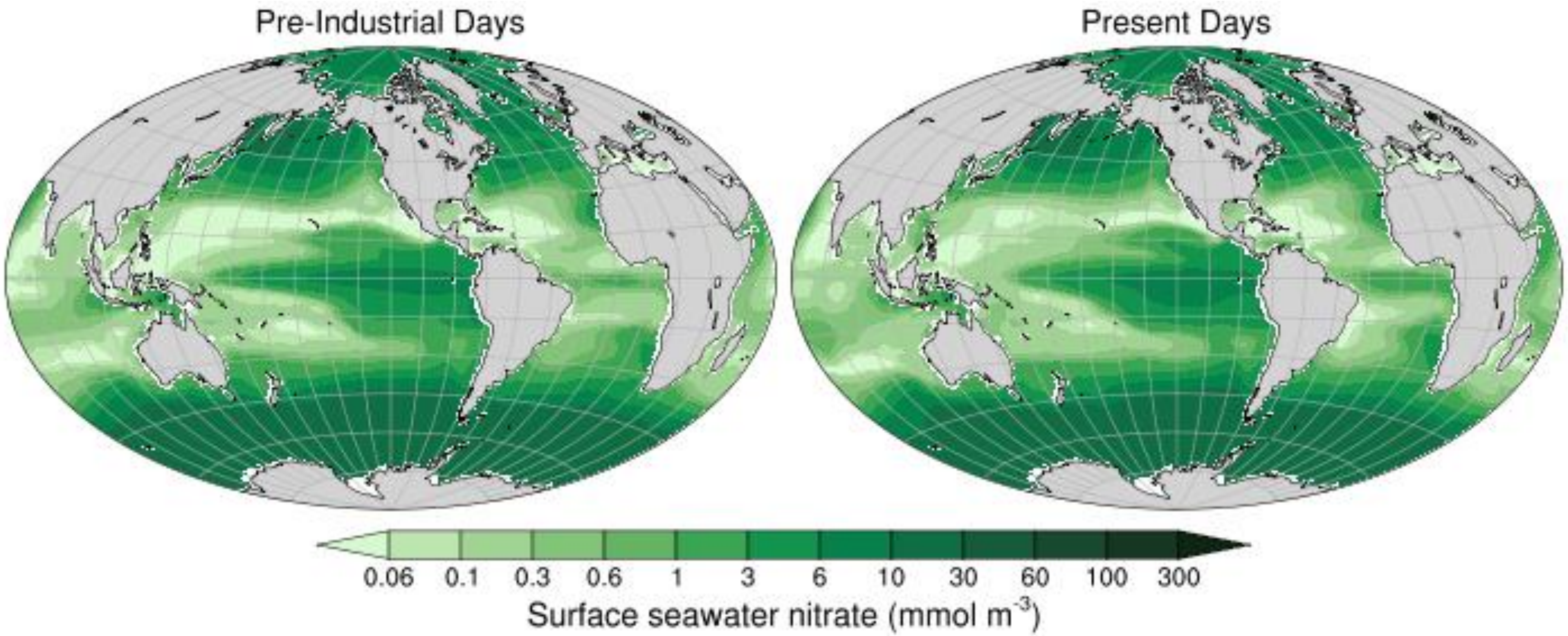
Backup

Influence



Anthropogenic
Biomass burning
Soil
Ocean
0.1 0.3 0.6 1 3 6 10 30
Pre-industrial surface NO_x emissions (10^9 molec cm^{-2} s^{-1})
Anthropogenic
Biomass burning
Soil
Ocean
0.1 0.3 0.6 1 3 6 10 30
Present-day surface NO_x emissions (10^9 molec cm^{-2} s^{-1})




```
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csw_specifier = 'CH3CHO   -> 1.0 * /glade/work/siyuan/SeaWaterConc/Csw_c
                'CH3COCH3 -> 1.0 * /glade/work/siyuan/SeaWaterConc/Csw_c
                'NO       -> 1.0 * /glade/work/siyuan/SeaWaterConc/Csw_c
csw_type = 'SERIAL'
! csw_type = 'CYCLICAL' !!!! 'SERIAL'
! csw_cycle_yr = 2016
bubble_mediated_transfer = .FALSE.
```
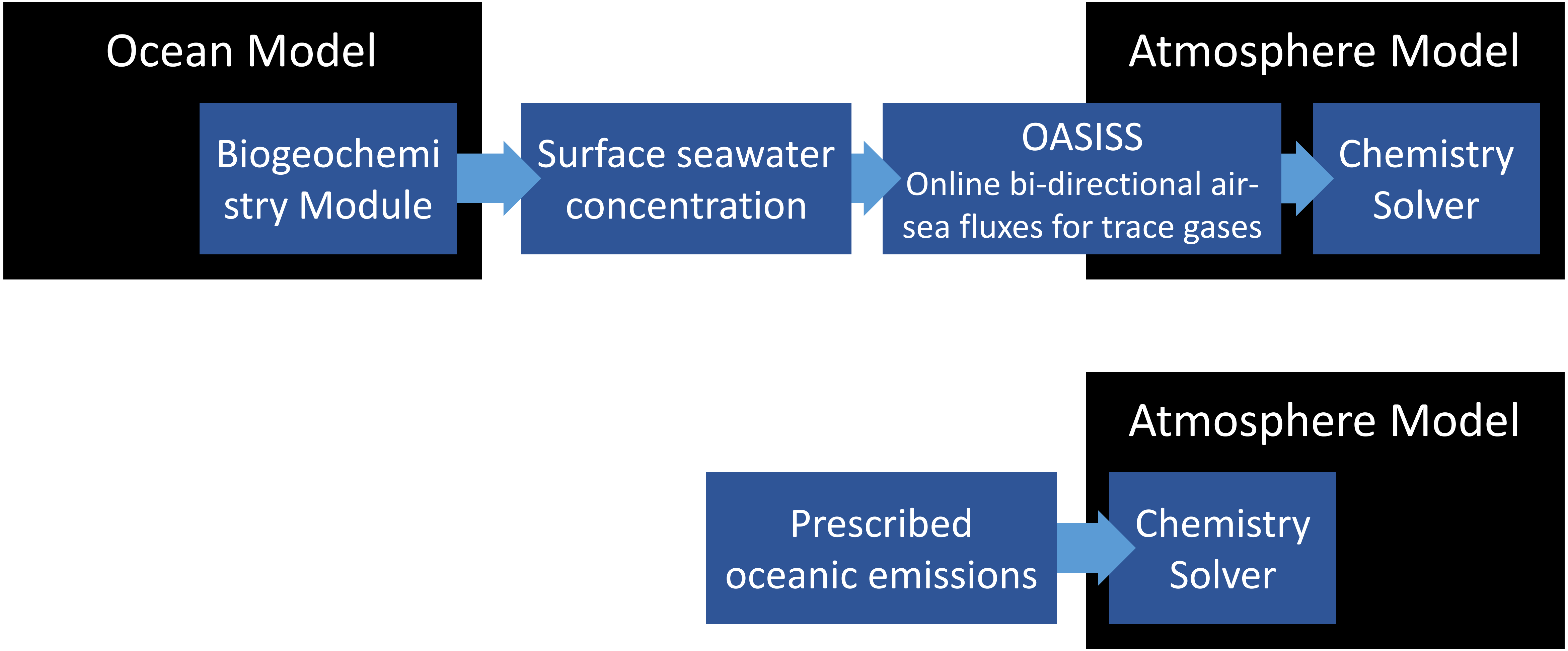
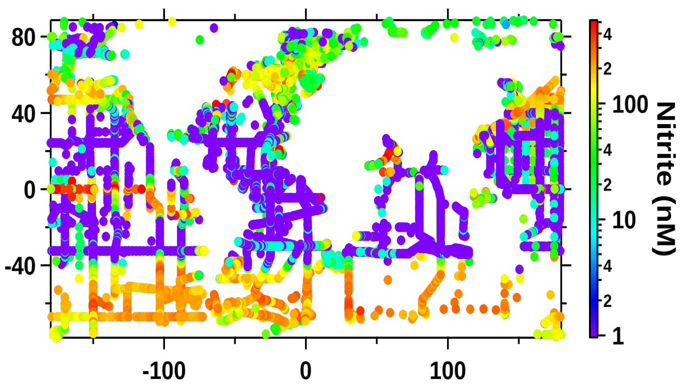
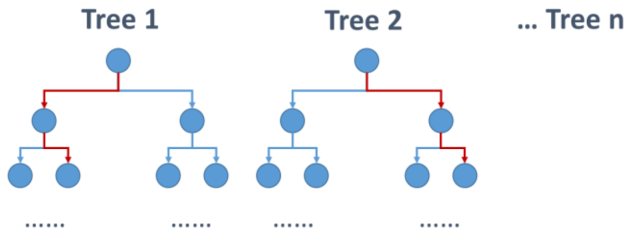


Ocean Model
Biogeochemistry Module
Surface seawater concentration
Atmosphere Model
OASISS
Online bi-directional air-sea fluxes for trace gases
Chemistry Solver
Atmosphere Model
Prescribed oceanic emissions
Chemistry Solver

Observations



Machine Learning



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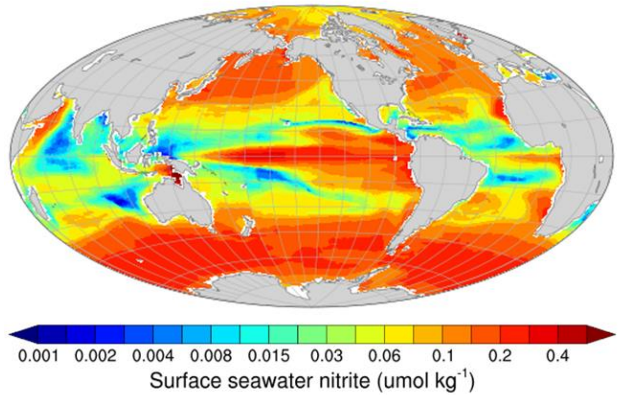
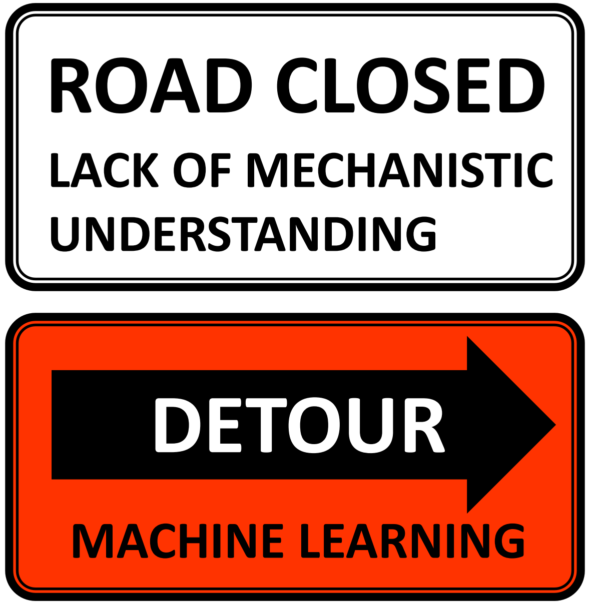
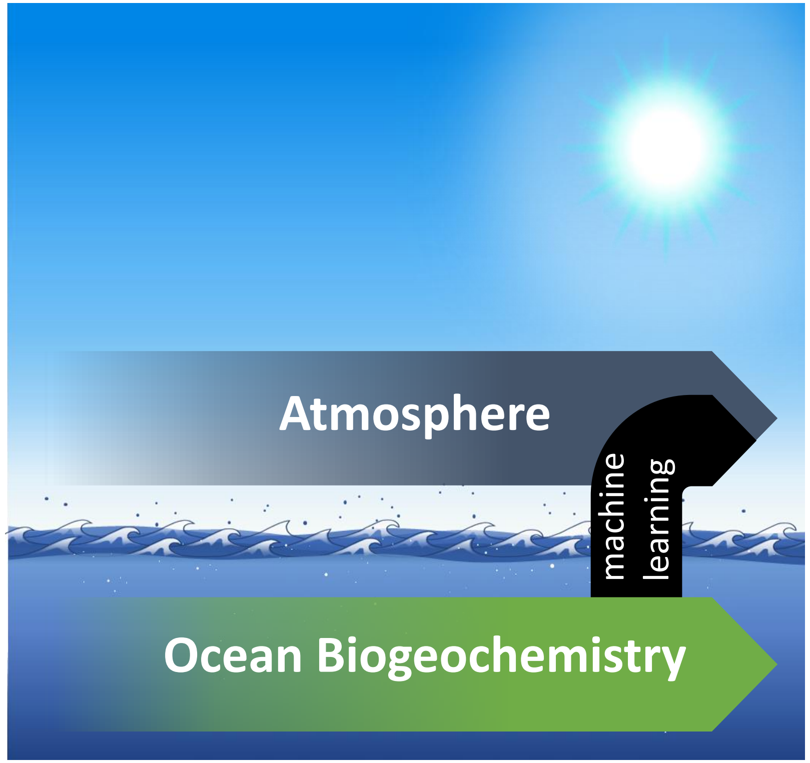



ROAD CLOSED
LACK OF MECHANISTIC UNDERSTANDING
DETOUR
MACHINE LEARNING


Atmosphere
machine learning
Ocean Biogeochemistry