# Deriving mixed layer boundary conditions from ocean transient tracer observations

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*Air-sea flux*

*Chem. Equilibria*

*Entrainment*

## Why do mixed layer transient tracer concentrations lag behind the atmospheric trend?

· Transient tracers (e.g. CFCs, $SF_6$) are human-created, passive, conservative gases acting as "clocks" for ocean ventilation and the anthropogenic $CO_2$ sink, yet their mixed layer saturation histories constitute the single largest source of error in transit time distribution (TTD) age models.[1]

Fig. 1: Observations of MML transient tracer disequilibrium vs. atmosphere in GLODAPv2.2023 dataset. Grey line represents LOESS regression in time series, negative values represent undersaturation. Regional medians calculated for the full time series using RECCAP2 biomes.

## Tracers in the maximum mixed layer (MML) derive from new and old waters

· Air-sea flux and entrainment of old water limit atmospheric equilibration of CFCs, $SF_6$,[2] leading to MML undersaturation.[3]

· A Dirichlet boundary condition may be given by an Green's function κ(t') for tracers subject to a Robin (mixed) condition.[2]

$$C^{MML} = \int_{t'=0}^{\infty} C^{atm}(t-t')\kappa(t')dt'$$

(MIXED LAYER)
(THERMOCLINE)
$z_m$

*air-MML disequilibrium*

*Tracer Concentration*          *Atmosphere*          *Unknown Age Spectrum κ(t')*

Young waters contribute the largest fraction of MML tracers.

Older contributions may still be significant.

Fig. 2: Convolution of MML tracer concentrations from atmospheric histories and Green's function age spectrum. For representative example age spectrum shown, ordinate represents water mass fraction and abscissa represents equilibration time in years, such that younger waters are heavily favored in the convolution.

## So we deconvolute a MML age spectrum from hydrographic observations

· 4+ decades of observations of transient tracers in the GLODAPv2.2023 dataset[4] were selected from the mixed layer defined by the median max. mixed layer depth.[5]

· A Markov Chain Monte Carlo inverted optimal κ(t') and posterior uncertainties from observations of all three tracers on global and regional scales with minimal prior guidance.

*GLODAPv2.2023 CFC, $SF_6$ Data*

*Likelihood Estimation*

*Posterior Age Spectra κ(t')*

**Sampling**

$$C^{MML} = C^{atm}|_{t-t'}^{t} \cdot \kappa(t')$$

*MCMC Simulation*

Fig. 3: Deconvolution scheme for the derivation of an age spectrum κ(t') from GLODAP and atmospheric transient tracer observations. Map depicts locations of all inverted observations.

## This allows reconstruction of CFC and $SF_6$ saturation throughout the industrial era

· Atmospheric histories[6,7] were convolved with κ(t') on a global scale and for neutral density outcrops associated with water mass formation regions. Reconstructions revealed **hysteresis** in air-MML disequilibrium.

Linearity observed between disequilibrium and atmospheric concentration as predicted by models,[8] later broken by emissions mitigation, indicating **departure from transient steady state**[9] c. 1970s for CFC-11 & -12.

Fig. 4: GLODAP average air-MML disequilibrium for CFCs and $SF_6$ given by convolution of derived age histories and trajectories. Solid lines represent historic reconstructions, dashed lines represent projections under SSP 3-7.0.

**Transient Tracer Measurement**
Water was collected on decadal hydrography transects using Bullister bottles. Transient tracers were extracted over CFC/$SF_6$-free gas, cold trapped, and quantified by ECD gas chromatography against standard gases on the SIO scale. QA/QC and cruise level corrections were performed in assembly of GLODAPv2.

## And we find spatial & temporal patterns of MML undersaturation drivers

Fig. 5: Age spectra derived for various neutral density levels. Posterior means are shown as solid lines with 1σ shaded uncertainties.

· **"Heavy-tailed"** age spectra indicate old waters in the MML: 40±10% of GLODAP average MML transient tracer reservoir is older than 1 year.

Mean 1.19 +/- 0.28 yr.
Variance 3.56 +/- 1.31 yr.

· Solubility as a function of **temperature drives a latitudinal gradient in saturation** consistent with published estimates.[13,14]

· This analysis provides a means of addressing bias in TTD-based studies of upper ocean circulation due to asumptions of constant tracer saturation.

Fig. 6: GLODAP mean satuation histories of CFCs and SF6 given as percent saturation relative to the global atmospheric mean over time given as years C.E.

## Finally, we produce an anthropogenic $CO_2$ MML product by rescaling κ(t')

· We convolve the atmospheric history of anthropogenic $CO_2$ with κ(t') assuming:
1) $C_{anth}$ acts as a quasi-conservative transient.[9]
2) Equilibration timescales of CFCs, $SF_6$, & $CO_2$ are limited by gas exchange.[10]
3) κ(t') can be applied to $CO_2$ by scaling t' by the ratio of their equilibration timescales.

$$\kappa^{CO_2}(t') = \kappa^{CFC,SF_6}\left(t' a_0 b \left(\frac{S_c^{CFC,SF_6}}{S_c CO_2}\right)^{-0.5}\right) \approx \kappa(15t')$$

· Surface ocean $C_{anth}$ **lags the atmospheric history** similarly to previous model estimates.[11,12]

· Determination of this product for water mass formation regions and convolution with age models may improve observation-based ocean carbon sink estimates.

Fig. 6: Reconstructed GLODAP mean MML $xCO_2$ (solid line) as a function of the convolution of the atmospheric history (dashed line) and the age spectrum determined from transient tracers, after adjusting for the longer equilibration timescale of $CO_2$. The dotted line represents the surface boundary of TRACEv1.[12]

**The Bottom Line**

Ocean transient tracer saturations depend on their atmospheric histories, yet this relationship has not been consistently applied in studies of ventilation and tracer uptake. We derive mixed layer age distributions from CFC and $SF_6$ observations using Markov Chain Monte Carlo inversion and reconstruct transient tracer and anthropogenic $CO_2$ saturations. The result is an improved observational constraint for surface ocean circulation and carbon sink investigation.

**Citations, detailed methods, code, animations.**
https://d-sandborn.github.io/other