

A Revised Look at the Oceanic Sink for Atmospheric CCl₄

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Extensive negative saturation anomalies for carbon tetrachloride (CCl₄) from 16 cruises in the Pacific, Atlantic, and Southern Oceans from 1987 through 2010 confirm that atmospheric CCl₄ is consumed in large amounts by the ocean. Data support findings previously reported from four research cruises, all in the Pacific Ocean [JH Butler et al, EOS 78 (46):F105, 1997; SA Yvon-Lewis and JH Butler JGR 107 (D20):4414, 2002], with only slight quantitative change. All seasons in both hemispheres are captured in this record and some cruises are repeat transects separated by over a decade. Nearly continuous, in situ measurements were made by gas chromatography with electron capture and/or mass spectrometer detection on air and surface water samples. Surface water was equilibrated with a continuous flow equilibrator. Grab samples of air were collected to confirm in situ measurements with independent instruments on land and, on some cruises, supporting grab samples of surface water were analyzed on board ship. Net CCl₄ saturation anomalies, corrected for physical effects associated with radiative heat flux, mixing, and air injection, were commonly on the order of -5% to -10%. The atmospheric flux required to sustain these anomalies still implies that the ocean accounts for about 1/4-1/3 of the total sink of atmospheric CCl₄. Although CCl₄ hydrolyzes in seawater, currently published hydrolysis rates for this gas cannot support such large saturation anomalies and inferred losses, given our current understanding of air-sea exchange rates. Explanation of the measured, surface-water undersaturations requires higher hydrolysis rates, additional sink mechanisms, such as biological consumption in surface waters or at depth, lower rates of air-sea exchange, or some combination of these processes.

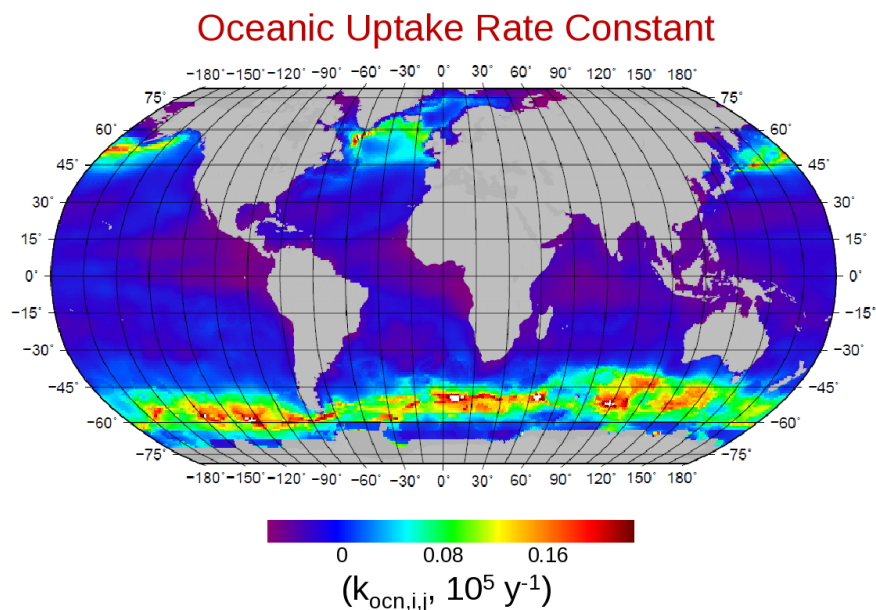


Figure 1. The distribution of oceanic uptake of atmospheric CCl₄ is a function of wind speed, sea-surface temperature, solubility, and aquatic removal rate.