# Flux of volatile organic carbons in the sub-arctic northwestern North Pacific in winter

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#### Introduction.

Volatile organic carbons (VOCs) are major reactive gases in the atmosphere, and the global budged of them have been studied for several decades investigating their role on atmospheric chemistry. Long-lived (lifetime is over 0.5 year) halocarbons and short-lived (lifetime is below 0.5 year) halocarbons destruct ozone in the stratosphere and the troposphere (and lower stratosphere), respectively. Water surface, mainly sea-surface, is an important source as well as a sink of some kinds of halocarbons in the atmosphere. Iodinated and brominated halocarbons are known to be produced by macro-algae and phytoplankton in the ocean. The oceanic source accounts for the large fraction of the total global flux of short-lived halocabons. Few studies have measured fluxes of halocarbons between the ocean and the air especially in winter. It is necessary to understand a role of the ocean as a regional source or sink of halocabons during winter when the biological activity is low. We focused on the production and destruction of halocarbons in the coastal area and the open ocean in the sub-arctic northwestern North Pacific.

#### Method.

A ship observation was conducted by the Hokkko-maru cruise (Fisheries Research Agency) over the Oyashio region in January 2008. Surface seawater pumped from the bottom of the ship was continuously supplied to a silicone membrane tube equilibrator at a rate of 20 L/min. The silicone membrane tube equilibrator has produced the air that has reached a state of equilibrium of VOC with surface seawater. Air sample was continuously collected from the upper deck of the ship at a rate of 30 L/min, and introduced to the analytical system. Partial pressures of VOCs (CH<sub>3</sub>Cl, CCl<sub>3</sub>F (CFC-11), CHClF<sub>2</sub> (HCFC-22), CH<sub>2</sub>Br<sub>2</sub>, CHCl<sub>3</sub>, C<sub>2</sub>Cl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CHBrCl<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>I, CH<sub>3</sub>I, CHBr<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>S (DMS), CH<sub>3</sub>Br, CH<sub>2</sub>FCH<sub>3</sub> (R-134a), C<sub>2</sub>H6S<sub>2</sub>, COS, CS<sub>2</sub>, and CH<sub>2</sub>ClI) in the surface seawater and the air were alternately measured by an automatic pre-concentration & gas chromatography / mass spectrometry at 70 min interval.

### Results and Discussion.

HCFC-22 in surface seawater was highly correlated with R-134a (R = 0.93), and those components were undersaturated to the air (Saturation anomaly (S) = -7%). The partial pressure of HCFC-22 and R-134a in surface seawater would depend on the physical processes (air-sea gas exchange, mixing, and temperature dependent solubility). On the other hand, bromomethane and chloromethane in surface seawater were undersaturated to the air (S = - 30% and - 41 %, respectively) during the cruise, and correlated with each other (R = 0.78). Biological activity would have decomposed those components in the ocean. Iodemethane in surface seawater was highly super-saturated in the open ocean (S = 280%) and near the shore (S = 900%). The average concentration of iodemethane in the open ocean (approximately 2 pM) was consistent with published concentrations for the open ocean in the Atlantic and the Southern Ocean (Chuck et al., 2005). Other short-lived halocarbons except for tetrachloroethylene and dichloromethane were super-saturated in surface seawater. We found that the sub-arctic western North Pacific is a source of many kinds of short-lived halocarbons in winter.

Reference

Chuck et al., J. Geophys. Res., Vol. 110, doi:10.1029/2004JC002741, 2005