

Stable Isotopic Studies of Carbon Monoxide in western North Pacific Ocean

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The oceans act as a source of atmospheric CO, since the concentration of CO dissolved in oceanic surface waters is supersaturated with respect to the equilibrium value in the troposphere. Oceanic CO is believed to be produced mainly by photochemical oxidation of dissolved organic matter (DOM) and to be removed by two processes; in situ microbial oxidation and an air-sea exchange. These production and removal processes result in diurnal variations of CO concentration in surface seawater. Since estimations of the total source strength of CO flux from the oceans show wide variation, ranging from 10 to 245 Tg/yr, more investigations of the oceanic CO flux and of the mechanisms of production and consumption of CO within seawater are required. Stable isotope compositions have become an important tool in the study of the mechanisms and pathways of production and consumption of trace gases, such as methane and nitrous oxide. Here, we present the results of the first isotopic studies on seawater-dissolved CO in the open ocean.

Seawater sampling was carried out at two stations in the western North Pacific (St.1: 28.34N, 140.38E; St.2: 33.05N, 139.46E), on the R/V Kairei (JAMSTEC) during the KR01-15 cruise. Surface seawater (0.5 m) was sampled approximately every 1 to 3h, using a tube pump. We also used 12 L Niskin bottles in order to determine the vertical profile (depths of 0.5 m to 2000 m) of dissolved CO. Seawater samples were transferred into ca 3 L dark-glass bottles. The concentration of CO and the stable carbon and oxygen isotopic compositions were measured by using continuous-flow isotope mass spectrometry.

The concentration of dissolved CO in surface waters was always above saturation but showed large diurnal variations, ranging from 0.4 nmol/kg to 12.2 nmol/kg at St.1 and from 0.4 nmol/kg to 8.4 nmol/kg at St.2. The maximum CO concentration appeared in the early afternoon, and minimum values were found in the early morning. Diurnal variations were also observed in the stable isotope ratios of CO at both stations. The variations are in proportion to marked diurnal variations in its concentration, due to the combination of isotopically light CO production in seawater and enrichment of heavy isotopes during consumption of CO by microbial action. Compared with the isotopic compositions of dissolved organic matter (DOM), from which most of the oceanic CO is derived, isotopic compositions of the CO produced from it agree well for ^{18}O , but are depleted in ^{13}C by more than 20 permil. We also observed a large degree of carbon isotope fractionation ($\delta^{13}\text{C}$: 30 permil) in laboratory photochemical CO formation from formic acid and acetic acid, indicating large fractionation processes for the carbon isotopes during the photochemical production of CO from DOM. There were time lag of several hours between the maximum solar radiation and the maximum CO concentration. The accumulation of isotopically depleted CO in the morning suggests bacterial oxidation is inactive relative to photochemical CO production at the time. In the early afternoon, the isotopic composition of CO becomes enriched in heavy isotopes, probably due to increases in the microbial CO consumption rate and the large isotopic effect during this oxidation. Even at this time, however, the CO concentration still increases, because the solar radiation is enough to produce more CO than is being consumed. Around midday to late afternoon, the increasing CO oxidation rate finally overtakes the decreasing photochemical CO production rate and predominates thereafter. The mean isotopic compositions of CO emitted from the oceans have been estimated using the data from the surface seawater in the western North Pacific. Oceanic CO can be an important source of isotopically light CO relative to fossil fuel combustion and biomass burning, which is valuable when calculating the global CO budget using isotopic tracers.