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Session 3) Isotopologues in Atmosphere: CH_4, CO and CO_2

Tropospheric chlorine from mineral dust and sea spray aerosol measured using δ^{13}C-CO shifts understanding of methane sources

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Methane is a well-mixed greenhouse gas responsible for >1/3 of global warming since pre-industrial times whose atmospheric burden continues to increase with a new record set in 2022. Active chlorine in the atmosphere is poorly constrained and so is its role in the oxidation of Methane. This uncertainty propagates into methane source budgets through isotope-constrained top-down models, in which the observed abundance of ^{13}C in tropospheric methane (commonly expressed as δ^{13}C-CH_4) is used to constrain the sources of methane using their characteristic δ^{13}C-CH_4 values. These models need to account for the change in the observed δ^{13}C-CH_4 by the Cl and OH sinks, which shift the observed isotope towards higher δ^{13}C-CH_4 values of fossil fuel sources, and away from ^{13}C depleted biological sources. The ISAMO project focuses on the hypothesis that Cl atoms are produced naturally by the action of sunlight on particles containing iron and chloride and these chlorine atoms oxidize atmospheric methane. To study this, we use the sensitive and selective indirect quantification of the concentration of atomic Cl through the strong carbon kinetic isotope effect (KIE) in the CH_4 + Cl reaction, which leaves the remaining CH_4 enriched in ^{13}C, and producing extremely ^{13}C-depleted CO. We will present field and laboratory observations and global modelling, including CO isotope measurement from flasks samples across the North Atlantic. We show how this mechanism affects ^{13}C depletion in atmospheric CO and how the corresponding ^{13}C enrichment in CH_4 affects global methane emission estimates.