



Formation of halogenated acetones in the lower troposphere

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Western Australia is a semi-/arid region that is heavily influenced by climate change and agricultural land use. The area is known for its saline lakes with a wide range of hydrogeochemical parameters and consists of ephemeral saline and saline groundwater fed lakes with a pH range from 2.5 to 7.1.

In 2012 a novel PTFE-chamber was setup directly on the lakes. The 1.5 m³ cubic chamber was made of UV transparent PTFE foil to permit photochemistry while preventing dilution of the air due to lateral wind transport. This experimental setup allows linking measured data directly to the chemistry of and above the salt lakes.

Air samples were taken using stainless steel canisters and measured by GC-MS/ECD. Sediment, crust and water samples were taken for investigation of potential VOC and VOX emissions in the laboratory using GC-MS. Several lakes were investigated and canister samples were taken over the day to see diurnal variations. The first samples were collected at 6 a.m. and from this time every 2 hours a canister was filled with chamber air.

Concentrations of chloroacetone up to 15 ppb and of bromoacetone up to 40 ppb in the air samples were detected. The concentrations vary over the day and display their highest values around noon.

Soil and water samples showed a variety of highly volatile and semi-volatile VOC/VOX but no halogenated acetones. An abiotic formation of these VOC/VOX seems conclusive due to iron-catalysed reactions below the salt crust [1]. The salt crust is the interface through which VOC/VOX pass from soil/groundwater to the atmosphere where they were photochemically altered. This explains the finding of halo acetones only in the air samples and not in water and soil samples measured in the laboratory.

The main forming pathway for these haloacetones is the direct halogenation due to atomic chlorine and bromine above the salt lakes [2]. A minor pathway is the atmospheric degradation of chloropropane and bromopropane [3]. These halopropanes were found in minor concentrations in soil and water samples (maximum of 8.8 ng/g in soil and 0,012 ng/ml in water).

[1] Huber et al., 2009, Environ.Sci.Technol., 43 (13), 4934-4939

[2] Wittmer et al., 2014, J. Phys. Chem. A, DOI: 10.1021/jp508006s

[3] Burkholder et al., 2002, Geophysical Research Letters, 29 (17)