



## **The formation of trichloroacetic acid and its input into the vegetation of various climatic zones in Russia**

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Halogen compounds can be found in the troposphere due to the chemical degradation of halogenated organic substances originating from various natural and anthropogenic sources. Industrial solvents and degreasing agents represent a major anthropogenic source for volatile halogen compounds and some of them are also released from sea salt aerosols and by biomass burning.

Some of these high-volatile organic chemicals such as C<sub>2</sub>-chlorohydrocarbons are transported over long distances through the atmosphere. As these substances pass through the air, they are exposed to oxidative, photolytic and hydrolytic processes which alter their original structure and hence both their physicochemical properties and their potential biological effects. These processes can e.g. result in conversion products with lower or higher phytotoxicity. An outstanding example is the formation of Trichloroacetic acid (TCA) in the atmosphere, in plants and in the soils as a result of oxidative reactions of the high-volatile C<sub>2</sub> chlorohydrocarbons.

TCA has been detected in many different compartments of the environment, e.g., precipitation, mist and dew, soil water as well as conifer needles. Photochemical decomposition of short-chain chlorinated hydrocarbons from anthropogenic sources has been proposed as the principal atmospheric source of TCA. Precursors include methyl chloroform, (MC, CH<sub>3</sub>CCl<sub>3</sub>), and Perchloroethene, (PER, C<sub>2</sub>Cl<sub>4</sub>). Evaporation and subsequent atmospheric photooxidation of these compounds causes the presence of TCA in air and precipitation. Due to its high solubility in water, TCA is washed out from the gas phase by precipitation as well as by mist and dew formation and is then

taken up by the vegetation from the soil via the roots. However there are indications that TCA may also be formed naturally in the soil and in microorganisms and plant cells as a result of enzymatic processes. Tri- and perchloroethene are believed to be converted to TCA by organisms. Another process of natural TCA formation in the soil is proposed by Neidleman and Geigert (1986). Finally TCA formation can be expected for all combustion processes because all types of oxidised chlorinated organic compounds can be formed in the presence of chlorine.

The ongoing industrialisation of Russia and Asia means the use of PER as solvents in the metal and textile industries of these regions can be expected to rise. The increasing emissions of this substance – together with the rise in the atmospheric oxidation potential caused by urban activities, slash and burn agriculture and forest fires could lead to a greater input/formation of TCA in the vegetation located in the lee of these emission sources. By means of biomonitoring studies, the input/formation of TCA in vegetation was detected at various locations in Russia.

Varying amounts of TCA depending on the prevailing climatic conditions were detected in pine needles from locations in southern (Caucasus, Kalmykia), western (Moscow) and northern (Kola Peninsula) Russia. Given TCA's phytotoxic properties, especially in connection with long-term effects, it poses – even in low concentrations – a potential risk for sensitive ecosystems such as grassy steppes, savannahs, mountain pastures and woods/forests on all continents. These properties could exacerbate the dry stress suffered by semiarid and arid climatic zones and thus lead to the further destabilisation of local vegetation – in turn accelerating the desertification already observed in such areas.

PER is by far the most important contributor to the calculated TCA concentration in precipitation. Over the year nearly 89% of the TCA calculated for Kalmykia and 97% for the Kola Peninsula are produced via the hydrolyse of TCAC ( $\text{CCl}_3\text{COCl}$ ), a by-product of the Cl-atom initiated reaction chain of PER. The rest is contributed by MC since the gas-phase production of TCA with less than 0.1% contribution can be neglected. A rather strong seasonal variation of TCA production [g/season] was found with high levels in spring and summer and minima in winter and autumn. A seasonal variation of TCA concentration [ng/l] in precipitation was also elaborated. High uncertainties mainly due to bad knowledge of the atmospheric Cl-atom distribution had to be taken into account to elaborate this investigation, so that the calculated concentrations may just be seen as a possible “basic level” of TCA in precipitation in the two investigated regions.

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