

ABSTRACT

Snow is a very good scavenger of atmospheric pollutants, which can be deposited on the ground and accumulated in the seasonal snowpack. In the polar regions, solar irradiation of the organic or inorganic constituents of snow can have an impact upon the composition of the lower atmosphere and in the snowpack. Chemicals and photoproducts can enter the atmosphere or be released *via* melt water into the environment during the periods of temporal warming. Our knowledge concerning the photodegradation processes of chemicals in matrices of ice and snow is still very limited. Laboratory experiments are important for better understanding the behavior of organic compounds in pristine arctic environments.

Organophosphorus pesticides are widely used throughout the world, which mitigates the use of more toxic organochlorine pesticides. Fenitrothion and methyl-parathion (with very similar structures) are among the organophosphates that can absorb directly ultraviolet (UV) light and undergo transformations in liquid solutions and in ice. In this thesis, the main photoproducts in ice and water found were oxons, nitrophenols and denitration product in the case of fenitrothion. Oxons can also photodegrade in the environment or can be responsible for causing toxicological effects, such as the inhibition of acetylcholine esterase. Comparison of the photodegradation of both compounds (fenitrothion and methyl-parathion) in water and in ice can then be used to predict their subsequent fate in the environment.

Artificial snow is a reaction matrix, in which many photochemical studies can be conducted. In this thesis, contaminated snow samples prepared by different methods were investigated. Aqueous solutions were sprayed into liquid nitrogen ($-196\text{ }^{\circ}\text{C}$) or inside a walk-in-chamber at ($-35\text{ }^{\circ}\text{C}$). The specific surface area of artificial snow was measured to make up $\sim 400\text{ cm}^2\text{ g}^{-1}$ based on the photodegradation of valerophenone and surface coverage by hydrophobic compound. The diffusion and restrictions of benzyl radicals were explored based on the bimolecular reaction known as the Norrish type I process of 4-methyldibenzyl ketone. The temperature dependent cage effect (probability of radical recombination) of such a reaction in artificial snow was investigated. Limited mobility of radicals was found to occur at higher temperatures than previously measured in frozen solutions. Density functional theory calculations supported the observation that molecules are self-associated, which is in contrast to frozen solutions.