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Degradation study of the aerosol-borne insecticides Dicofol and DDT in an aerosol smog chamber facility by OH radicals in relation to the POPs convention

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The Stockholm Convention is a global treaty to protect human health and the environment from persistent organic pollutants (POPs). POPs are chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife. POPs circulate globally (see UNEP POPs programme at www.pops.int)..., mainly through the atmosphere. All of the restricted and banned POPs (DDT, Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene, Mirex, Toxaphene, Polychlorinated Biphenyls, -Dioxins and -Furans) are semivolatile chlorinated compounds, where aerosol-borne transport plays a vital role.

The insecticide Dicofol is still in use, though it has a structure quite similar to DDT. Degradation by reaction with OH is a major loss process, limiting atmospheric long-range transport. We present the first experimental study of the reaction of OH radicals with DDT and Dicofol in the aerosol-borne state.

For comparison, Dicofol and DDT have been studied in an aerosol smog chamber facility (1700 l) that can be cooled in order to overcome loss of the compounds from the particles by volatilisation during the experiment. A temperature of 7 °C turned out to be sufficient to lower the loss rate constant of an initial coating of 1% w/w from fused silica particles (Aerosil 380, Degussa) of both compounds below 10^{-4} s^{-1}. This enabled us to observe a significant increase of the loss of the compounds upon OH-exposure of up to $\int[OH]dt = 4.5 \times 10^{11}$ molecules cm^{-3} s within 5 h. Initial levels up to $[OH]_0 = 10^9$ molecules cm^{-3}, three orders of magnitude above atmospheric levels, were obtained by photochemical degradation of methyl nitrite by a solar simulator consisting of 16 fluorescent lamps (Osram Eversun, 80 W each). The rapid photolysis of methyl nitrite enables us to separate volatilisation from OH-reaction of DDT within the same run, since the disappearance rate follows the concomitant rapid decrease of OH level. Using the dark reaction of hydrazine with ozone as a source of OH and employing rapidly increasing levels of OH, a similar separation of volatilisation and OH-reaction can be demonstrated for Dicofol.

Three experiments with methyl nitrite photolysis (two of them with DDT admixed at 1% w/w to Diofol at 1%w/w can be combined to deliver a rate constant of $3x10^{-12}$ cm^3s^{-1}; two experiments with hydrazine are combined to deliver a rate constant of $1.7x10^{-12}cm^3s^{-1}$. Combining all five experiments delivered a final value of $2x10^{-12}$ cm^3s^{-1} for the reaction of Dicofol with OH radicals. Using an atmospheric concentration of $[OH]=5x10^5$molecules cm^{-3} as a global average, this rate constant leads to an atmospheric half-life of 8 days, well above the threshold of 2 days of the POPs convention defined for the potential for long-range environmental transport.

The degradation of DDT alone delivered a rate constant of $5x10^{-13}cm^3s^{-1}$ (corresponding to an atmospheric lifetime of almost 4 months) but the degradation of DDT ceased in the presence of Dicofol (1% w/w). This indicates an interaction of the two compounds, where Dicofol may enclose and cover the DDT, impeding the access of OH to DDT. In a mixture with other compounds (Terbuthylazine, di-(2-ethylhexyl-)-phthalate, α- and γ-hexachlorocyclohexane (1% w/w each), DDT exhibited a much higher OH-reactivity of $5x10^{-12}$ cm^3s^{-1}, an order of magnitude larger than DDT alone – though still above the atmospheric persistence threshold of the Stockholm convention.

Such interactions of POPs and other compounds with aerosol constituents should be considered since they may enhance persistence and thus promote atmospheric long-range transport.

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