Formation of Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans and Their Precursors in Fires of Pyrethroid Pesticide Alpha-Cypermethrin

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ABSTRACT

This study reports the results of the gas phase oxidation of alpha-cypermethrin, a common insecticide, elucidating the decomposition pathways and formation of toxic species such as polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) and their precursors. Conditions investigated are similar to those encountered in post combustion and cooling-down zones of forest, agricultural and wild fires, as well as in burning of biomass contaminated or treated with pesticides. The experiments were conducted under fuel lean conditions in a tubular reactor housed in a three-zone heating furnace and operated with a dilute stream of alpha-cypermethrin in ultra high purity nitrogen and oxygen. PCDD/F were identified and quantified by high resolution gas chromatography (HRGC)-ion trap mass spectrometry (ITMS). We detected mono to hepta chlorinated dibenzo-*p*-dioxins and dibenzofurans with maximum emission factors of 141 μg g^{-1} and 384 pg ΣTEQ-WHO_{2005} g^{-1} of alpha-cypermethrin. 1-monochlorodibenzofuran was ranked as the most abundant congener. We also conducted the analyses of volatile organic compounds (VOC) attempting to identify the PCDD/F precursors by means of HRGC-quadrupole mass spectrometry (QMS). The results of VOC revealed chlorobenzene, diphenyl ether, benzaldehyde, chlorotoluene, dichlorotoluene as important PCDD/F precursors.

KEYWORDS: toxicity, polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, wildfires, emission factors.

INTRODUCTION

Belonging to the pyrethroid group of insecticides, alpha-cypermethrin is used for a wide range of domestic and agricultural applications such as sprays and insect coils. In general, the pyrethroids have been developed synthetically from the naturally occurring compound pyrethrum to preserve the toxicity of the natural species and to enhance their stability in sunlight. Their recent increase in popularity can be attributed to their effectiveness and potency in combating Lyctine borers and termites at low concentrations [1–3]. Alpha-cypermethrin is a highly active broad-spectrum insecticide, effective by contact and ingestion against target pests. It is widely used for protection of agricultural crops, forests, and in domestic applications due to its short field life.

Owing to their substantial use, pyrethroids are frequently handled in large quantities during production and storage, with pesticide fires reported to occur during these activities. The fires result in the release of significant amounts of toxic pollutants such as polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF); in combination these chemicals are denoted as PCDD/F or dioxins. PCDD/F exhibit similar chemical properties and are primarily formed as unwanted pollutant by-products in many thermal processes. PCDD/F are of great concern due to their environmental persistence, toxicity and bioaccumulation through the food chain. Taking into consideration these criteria, we selected alpha-cypermethrin, with rapidly growing production and use in the pyrethroids market, to investigate its behaviour in fires; especially, its propensity to form precursors that act to produce PCDD/F in fires.

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