**Degradation of pesticides in the atmosphere: direct photolysis, photo-oxidation and reaction with ozone**

Amalia Muñoz , Teresa. Vera, Esther Borrás, Milagros Ródenas, Tatiana Gómez

1 *Fundación CEAM. Parque Tecnológico.C/Charles R..Darwin 14 46980 Paterna (Valencia), Spain* amalia@ceam.es

Pesticides are the most widely used chemical compounds. Once a plant protection product is applied to the field, the active ingredient can be partitioned into the soil, water and the atmosphere. The active ingredient can be emitted into the atmosphere through either dispersion during spraying or post-application volatilization from ground or leaf surfaces. In the atmosphere, pesticides are distributed among the gas, particle and aqueous phases, depending on their physicochemical properties and environmental conditions.

As for other organic compounds, the gas phase degradation of pesticides in the atmosphere could be controlled by chemical reactions with ozone (O3), hydroxyl radicals (OH) and nitrate radicals (NO3). Pesticides, once released to the atmosphere, may be also subject to direct photolysis if its UV-visible absorption spectrum shows absorbance above 290 nm.

Studies of the gas-phase degradation of pesticides are in general problematic because of their low vapour pressures and usually, only theoretical information is used when it is necessary to know the degradation of the pesticides in the air compartment. Nevertheless, the theoretical values about lifetimes in the atmosphere provided by the SAR method, only contains information about OH radical reaction, and in most of the cases, the values differ highly from the experimental values since the database of rate constant data for the reactions of OH radicals with N, P, or S containing compounds is sparse. For this reason, obtaining experimental values becomes completely necessary. In addition, direct photolysis reactions could play an important role for some kind of compounds. Furthermore, only a few studies are available and, in some cases, results are inconsistent among them probably due to differences in the light sources employed being, in nearly all of the cases, artificial light.

In this work we present results about experimental atmospheric degradation of several types of pesticides including: halogenated, organophosphorous, acetanilides, and dinitroaniline pesticides carried out at the high volume outdoor European Photoreactor (EUPHORE). This simulation chamber enables the reactions to be carried out under realistic atmospheric concentrations and at solar wavelengths and intensities. Direct photolysis of pesticides was investigated under natural solar radiation, and the photolysis rate coefficient determined. The rate coefficients for the reactions of ozone in the dark and photo-oxidation with hydroxyl radicals were also measured under atmospheric conditions using absolute and relative rate techniques, respectively. Products of reaction were also determined by means of different analytical techniques, and degradation mechanisms were proposed. Knowledge of the specific degradation products, including the formation of secondary particulate matter, could complete the assessment of their potential impact. In fact, the fingerprint chemical composition analysis has indicated that they are a relevant source of multi-oxygenated molecules. The formation of those types of degradation products is important because they play a significant role in the atmospheric chemistry, global climate change, radiative force, and are related to health effects.

**Acknowledgements**

The research leading to these results received funding from the Spanish Ministry of Economy and Competitivity (project IMPLACAVELES: CGL2013-49093-C2-1-R) and, Generalitat Valenciana for the DESETRES-Prometeo II project