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Heterogeneous reactions of ozone with commonly used pesticides adsorbed on silica particles

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HIGHLIGHTS

- The ozonolysis constants and the lifetimes of 8 commonly used pesticides are assessed.
- The experimental data are described by both L–R and L–H kinetic mechanism.
- Adsorbed pesticides react slowly towards ozone in the atmosphere.

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ABSTRACT

There is an increasing concern about the pesticides spread in the atmosphere. They can be found in the gas-phase but because of their physico-chemical properties they mostly remain adsorbed on the surface of the atmospheric particles. The kinetic data of the adsorbed pesticides towards atmospheric oxidants such as ozone and hydroxyl radicals are very scarce.

Here we present the kinetic data set for the heterogeneous reactions of gas-phase ozone and eight commonly used pesticides adsorbed on silica particles. The obtained rate constants are described by both kinetic patterns, i.e., Langmuir–Rideal (L–R) and Langmuir–Hinshelwood (L–H) mechanisms. Concerning the L–R mechanism the rate constants range between $3.4 \cdot 10^{-19}$ cm^3 molecules^{-1} s^{-1} and $8.8 \cdot 10^{-19}$ cm^3 molecules^{-1} s^{-1}. With respect to the L–H mechanism, the values of air–silica partitioning coefficient ($K_{(O_3)}$) vary between $21 \cdot 10^{-16}$ cm^3 molecules^{-1} and $358 \cdot 10^{-16}$ cm^3 molecules^{-1}. The maximum rate constants range between $0.4 \cdot 10^{-4}$ and $1.7 \cdot 10^{-4}$ s^{-1}. The estimated lifetimes of the selected pesticides according to both L–R and L–H mechanism span from 8 to >33 days, demonstrating that these species are very persistent with respect to ozone reactivity in the atmosphere.

The results obtained in this study can contribute to better describe the atmospheric fate of pesticides in the particulate phase.

1. Introduction

Pesticides are used worldwide to control pests in agricultural production and in many non-agricultural settings (e.g., home, public spaces, gardens and parks, industrial areas). The important increase in their utilization and their potentially adverse human health effects (Inserm, 2013) make their environmental fate a hot topic and a recurring study. The use of pesticides is even becoming increasingly controversial and represents a subject to strict regulation (Regulation (EC), 2009; Directive 98/8/EC). A wide variety of pesticides, more specifically insecticides, herbicides, and fungicides, have been detected in the atmosphere throughout the world (see for instance Sarigiannis et al., 2013; Shunthirasingham et al., 2010). The quantity of emitted pesticides in the atmosphere depends on many factors such as the mode of application (e.g., spray-drift (Guicherit et al., 1999; Van den Berg et al., 1999)), the geographical location (Sanusi et al., 2000) as well as the meteorological conditions (e.g., volatilization (Guicherit et al., 1999; Van den Berg et al., 1999), wind erosion (Glotfelty et al., 1989), rain (Sauret et al., 2009)). Once the pesticides reach the atmosphere, they may undergo different transport and transformation processes resulting in the generation of secondary products that could be more hazardous than the primary pesticides (Segal-Rosenheimer and Dubowski, 2007; Vera et al., 2011). It is therefore necessary to study the atmospheric fate of pesticides for comprehensive understanding of their environmental and health impacts.

The partitioning of pesticides between the gas and particulate phases (Sanusi et al., 1999) influences the atmospheric fate of these compounds such as their direct and indirect photo-chemical degradation. Because of their usually low volatility, pesticides

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currently used are semi-volatile compounds and are often associated with atmospheric particles (Sanusi et al., 2000; Sauret et al., 2008; Yao et al., 2008). Therefore, beside the photo induced degradation of pesticides, their atmospheric fate and lifetime is mostly determined by the heterogeneous reactions with atmospheric oxidants such as ozone (O_3) and hydroxyl radicals (OH) (Atkinson et al., 1999). Yet, there are many uncertainties concerning the behavior of the pesticides in the atmosphere. Especially, there is a gap of knowledge regarding the degradation of pesticides induced by heterogeneous reactions. Indeed, there is a lack of kinetic data with respect to the particulate phase of pesticides. As a result, only the gas-phase reactivity of pesticides has been considered for the estimation of their atmospheric lifetimes. In order to understand their fate and predict their atmospheric behavior, the degradation of pesticides induced by heterogeneous processing must be further investigated.

The aim of the present work is to study the ozonolysis kinetics and the lifetimes of eight commonly used pesticides adsorbed on silica model particles. These eight compounds are representative of major applications, i.e., insecticides, herbicides, and fungicides, and were chosen for their worldwide utilization but also for their physico-chemical properties (i.e., vapor pressure, Henry's constant) and the availability of their toxicological data (i.e., acceptable daily intake, which is based on ingestion, exposure but to the best of author's knowledge there is no information in the literature regarding inhalation exposure). The obtained results may help policy makers to give the recommendations in order to reduce population exposure to the pesticide plume and will contribute to better describe and understand the atmospheric behavior of these compounds.

2. Experimental method

2.1. Chemicals

Cyprodinil (purity 99.8%), deltamethrin (99.7%), difenoconazole (97.0%), fipronil (97.5%), oxadiazon (99.9%), pendimethalin (98.8%), permethrin (98.3%), and tetraconazole (99.0%) were purchased from Sigma–Aldrich (PESTANAL®, analytical standard) and were used as received. The chemical structures of the pesticides under study are depicted in Figure S1 and their physico-chemical properties are given in Table S1.

2.2. Silica particles coating

The atmospheric mineral aerosols can be mimicked with commercial silica particles such as AEROSIL R812 (Barbas et al., 1996; Net et al., 2009, 2010a, 2010b, 2010c, 2010d; Nieto-Gligorovski et al., 2010; Pflieger et al., 2009, 2011, 2012). In this study, the hydrophobic silica particles (AEROSIL R812, Degussa, purity SiO_2 content ≥99.8%, average primary particle size of 7 nm and specific surface area (BET) of 260 ± 30 $m^2\ g^{-1}$) were coated with the pesticides under study according to a liquid/solid adsorption. 5 mL of a pesticide solution at 20 mg L^{-1} in dichloromethane (for HPLC, ≥99.8%, Sigma–Aldrich) was mixed with 500 mg of silica particles in a Pyrex bulb of 500 cm^3 wrapped with aluminum foil to prevent any photo-degradation. This bulb was ultrasonicated for 15 min. Then, dichloromethane was evaporated by a rotary evaporator (Rotavapor R-114, Büchi) at 40 °C and 850 ± 85 mbar. The percentage of the coated aerosol surface was between 0.2 and 0.4% which is much less than a monolayer assuming a uniform particle surface coverage for the pesticide molecules and a spherical geometry for particles. The load of pesticides on silica particles was about 0.02% by weight (See calculation in Supplemental Information).

2.3. Ozonolysis experiments

About 500 mg of dried coated silica particles were placed in a Pyrex bulb of 500 cm^3 and wrapped with aluminum foil. The bulb was fixed at a modified rotary evaporator (Laborota 4000 efficient, Heidolph) and was placed in a thermostated water bath. A constant temperature was kept at (25 ± 1)°C (Fig. 1). This experimental setup was initially developed by Net et al. (2009) and an important number of ozone heterogeneous reactions have been studied (e.g., Net et al., 2010a, 2010b, 2010c, 2010d, 2011). Later on, Pflieger et al. have adapted to study the heterogeneous reactions of pesticides and successfully validated by intercomparison with the flowtube reactor with trifluralin, a dinitroaniline herbicide (Pflieger et al., 2011).

The rotation of the bulb ensured a homogeneous exposure of the particles during the experiment. Ozone was generated by passing a flow of purified air (zero air generator ZA-1500, F-DGS) through an ozone generator (UVP, LLC Upland, UK) with a constant flow of 250 mL min^{-1}. The basic principle of ozone generation is to expose air to ultraviolet (UV) radiation at 185 nm emitted by a mercury vapor pen lamp. Various ozone concentrations were obtained by exposing the air stream to various lengths of the mercury pen lamp. Silica particles coated with pesticides were exposed to different mixing ratios of ozone ranging from 215 ppb to 977 ppb, in order to be as close as possible to realistic atmospheric conditions. Each experiment was performed at constant ozone mixing ratios. Ozone mixing ratios were monitored on-line and continuously by a photometric ozone analyser (O_3 41M, Environnement S.A) as shown in Fig. 1. An additional flow of 800 mL min^{-1} was necessary because the required flow for the ozone analyser is 1300 mL min^{-1} and the maximum allowed gas flow in the reaction chamber is 500 mL min^{-1}. Ozone concentration inside the reaction chamber was calculated from the measured one by taking account the dilution. To avoid a loss of ozone due to its solubility in water, a separate humidified air flow at rate of 250 mL min^{-1} was necessary to keep the humidity constant at (55 ± 5) % for all the experiments. The relative humidity (RH) was measured throughout all experiments with a humidity probe (Hydrolog NT, Rotronic, USA).

The silica particles coated with pesticides were exposed during a period of 26 h.

2.4. Extraction and pesticide quantification

After ozone exposure, pesticides adsorbed on silica particles were extracted by accelerated solvent extraction (ASE 300, Dionex). Each 40 mg aliquot of particles was introduced in a 33 mL stainless-steel cell with an internal standard solution (Triphenyl phosphate, 99.9%, Sigma–Aldrich). The optimized extraction conditions were as follows: extraction solvent, dichloromethane; oven temperature, 100 °C; pressure, 100 bars; heat up time, 5 min; static time 6 min. The flush volume amounted to 70% of the extraction cell volume. The extracted analytes dissolved in dichloromethane were purged from the sample cell using pressurized nitrogen (100 bars) for 300 s. Four cycles per cell were done.

Afterwards, the extracts were concentrated under a nitrogen flow using a concentration workstation (TurboVap II, Biotage) with pressure 11 bars and a water bath at 40 °C, until a 500 μL extract was obtained.

The obtained solutions were analysed by gas chromatography coupled to tandem mass spectrometry (GC/MS–MS), with a Trace GC Ultra (Thermo Scientific) coupled to a TSQ Quantum™ Triple Quadrupole (Thermo Scientific) using electron impact ionisation (70 eV) according to the following parameters: column THERMO TG-5MS (internal diameter 0.25 mm, length 30 m, film thickness 0.25 μm), carrier gas: helium with 1 mL min^{-1} flow rate, split/