THE USE OF EUPHORE FACILITY FOR STUDYING THE ATMOSPHERIC FATE OF PESTICIDES.

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ABSTRACT

The atmospheric fate of pesticides can be studied at the large outdoor European simulation chamber (EUPHORE) in Valencia, Spain. The reactions that can be carried out at EUPHORE (European PHotoREactor) include photolysis using natural sunlight, OH, NO3 and ozone initiated oxidation reactions.

The EUPHORE facility is up to the moment, one of the best equipped outdoor photoreactor worldwide. The installation consists of two half-spherical photoreactors made of FEP-foil (Teflon®) transparent to sunlight (also UV), each with a volume of 200 m³ approximately. For the detection of the compounds, the chambers are equipped with a wide number of sophisticated analytical techniques, ranging from monitor type instrumentation, chromatographic techniques and particle measurement as well as in-situ optical measurements in addition to the important physical parameters.

KEY WORDS: pesticide, outdoor photoreactor, atmospheric fate, air, atmospheric reactions.

INTRODUCTION

Pesticides are widely used in agricultural and gardening operations and together with the increase in their applications and uses, the concerns about risks to human health have been increased. (Konradsen et al 2003; Gupta et al 2004).

Once the pesticide is applied, it can be partitioned into the soil, water and atmosphere. (Kwok et al 1992, Woodrow et al 1983). The knowledge of the fate of pesticides in the environment and their adverse effect is very important for assessing the potential risks for the health of humans and animals during and after their release (Floesser-Muller et al 2001).

It has been recently recognised that the atmosphere is a major transport medium and reservoir for pesticides and their residues (Woodrow et al 1983, Bidleman 1988, Tsal et al 1991, Wania et al 1996, Muir et al 2004). Pesticides can enter the atmosphere through spray drift, post-application volatilisation and wind erosion of treated soil, in function of their properties and the manner of the application. Once in the air, these compounds can be distributed between the gas, particle and aqueous phases depending on their physicochemical properties (equilibrium constant, Henry’s law constant...) as well as on the environmental conditions (Tsal et al. 1991, Le Person et al 2006, Atkinson et al 1999). The main route to the removal of the pesticides in air is wet and/or dry deposition; however, it is of importance to consider the chemical reactions that can occur into the atmosphere. The chemical changes do not always result in a detoxification of the compounds.

In the atmosphere, oxidants as ozone and hydroxyl radicals (OH) as well as reactive intermediates as NOx enhance the photochemical conversion of pesticides, together with their direct photolysis reactions. (Atkinson et al 1999, 1994. Woodrow et al 1983, Finlayson-Pitts et al 1986, Seinfeld, 1986). The rates at which the pesticides react are a direct measure of their atmospheric persistence; hence, their rates of reaction are needed to develop exposure assessments and the ozone depletion potential for some of them. While a number of studies have
been conducted so far on the degradation of pesticides on aerosols, in soils and water, there is only a limited number of data on their atmospheric fate in the gas phase (e.g; Woodrow et al. 1983, Atkinson et al. 1999, Palm et al 1997, Krüger et al 2001, Palm et al 1998).

Determining the oxidation capacity of the atmosphere in real air masses requires a system that is able to isolate the chemical processes from the meteorological processes while maintaining the original air composition. Smog chambers have been used during the last decades to mimic the atmospheric chemistry isolated from transport and meteorology processes. Among the large smog chambers available worldwide, the EUPHORE facility is one of the most sophisticated ones.

The main limiting factor for studying the gas phase degradation processes of the pesticides is their very low vapour pressure. This limitation requires high volume chambers coupled to very sensitive analytical techniques. Giving the characteristics of Euphore, the pesticides that could be investigated should have a vapour pressure higher than 3 mPa to assure the presence of the compound in the gas-phase. Taking this into account, almost all kind of pesticides can be studied at the EUPHORE chambers regardless of their chemical family or type of use. Up to now the pesticides that have been investigated are: Trifluralin -dinitroaniline herbicide- (Le Person et al. 2007), Dichlorvos - organophosphate insecticide- (Feigenbrugel et al. 2006), chloropicrin – fungicide- (Vera et al 2006), diazinon -organothiophosphate insecticide- fenpropidin- piperidine fungicide-, hymexazol -oxazol insecticide-, propachlor -chloroacetanilide insecticide-, etc.

These pesticides are extensively used in agriculture, gardening, household insecticides, etc. They are sufficiently volatile as to be eventually emitted into the atmosphere. The experimentally obtained kinetic values of the atmospheric degradation of the studied pesticides can be compared with those derived using the structure activity relationships (SAR) developed by Atkinson and co-workers (see for example: http://www.syrres.com/esc/physprop.htm).

**MATERIAL AND METHODS**

The two EUPHORE simulation chambers, 200 m$^3$ volume each, are located in the Fundación CEAM building, in Valencia (Spain). The construction of the EUPHORE [Becker eds., 1996] simulation chambers was supported by the EU, the Valencian Community Regional Government and Spanish Ministry of Science and Education in order to give responses to some critical questions and gaps on atmospheric chemistry (for example, degradation of target compounds, photooxidation processes, etc). Indeed, these chambers have proven to be a very effective tool in many research projects performed within the European AIRES strategy. More and more, the scientific community is aware of the fact that it’s important to have a better understanding of the chemistry of the atmosphere due to its implication in health problems, greenhouse effect and in the air quality. On the other hand, modelers working on air pollution dynamics and on air quality
in general, realize that they also need more information about the chemical processes taking place in real conditions. This knowledge can be acquired in the simulation chambers of EUPHORE.

Both chambers are protected by steel covering which allows carrying out experiments in the dark. They can also be opened in order to conduct experiments under sunlight conditions since the FEP-foil (Teflon) is approx. 85% transparent to sunlight. This material is also transparent to UV light, allowing simulation of real conditions with a low ratio of wall-effects due to the shape and to the large volume of the chambers. A schematic representation of the simulation chamber is shown in Figure 1.

An air drying and purification system supplies the chambers with oil vapor, hydrocarbon and NO\textsubscript{x} free dry air. The dilution rate of the chamber due to small leaks is determined by measuring the decay of SF\textsubscript{6} added at the start of the experiments (monitored using its IR absorption). For the detection of the compounds, the chambers are equipped with a wide number of analytical techniques, ranging from different types of chromatographs, monitors and particles instrumentation to sophisticated in-situ optical devices. Therefore, wide number of species can be measured, e.g. Volatile Organic Compounds (VOCs), semi-VOCs, nitrates, ozone, NO\textsubscript{x}, particles (size distribution and chemical composition), OH and HO\textsubscript{2} radicals, solar radiation, etc. Among these instruments, some are on-line (e.g. FTIR, GC-MS (I), GC-FID/PID, monitors, DOAS, LIF, etc) and others as HPLC and LC-MS or GC-MS (II), are used off-line. In addition, physical parameters such as temperature, humidity, etc. are also monitored during the course of the experiments. Table 1 shows the list of the available permanent instrumentation at the EUPHORE chambers.
To perform a photolysis experiment the target chemicals are introduced inside the chamber together with the SF$_6$ and kept in the dark for a while to study the wall losses of the chemicals. The chamber is then opened and the gas mixture is exposed to the sunlight irradiation for several hours taking samples periodically with the available instrumentation. Combining the information obtained from different instruments it is then possible to calculate the photolysis rate, the half-life time and the products formed in the reaction. Those are important inputs to suggest reaction mechanisms. However, there are many compounds that may react with OH radicals and/or may be lost partially on the wall, in that case some corrections may be required:

$$\ln\left(\frac{\text{[compound int]}_0}{\text{[compound int]}_t}\right) = (J + k_{\text{OH}}[\text{OH}] + k_{\text{SF}_6} + k_{\text{wall}}) \times t$$  \hspace{1cm} (1)

Where $\text{[compound int]}_0$ and $\text{[compound int]}_t$ are the initial concentration of the introduced compound and that after a reaction time ($t$), respectively. $J$ is the photolysis rate coefficient, $k_{\text{OH}}$ the coefficient rate of the reaction with OH (in this case it is needed to consider a residual concentration value for the OH), $k_{\text{SF}_6}$ the decay of SF$_6$ and $k_{\text{wall}}$ the wall loss of the compound of interest.

Considering:

$$k_{\text{total}} = J + k_{\text{OH}}[\text{OH}] + k_{\text{SF}_6} + k_{\text{wall}}$$  \hspace{1cm} (2)

$k_{\text{total}}$ is derived from the slope of the representation of $\ln[\text{compound int}]_0/[\text{compound int}]_t$ versus photolysis time.

Another type of experiments to get relevant information on the compound of interest are photooxidations. In this case, the production of the OH radical can be done by the photolysis of a precursor in the presence of NOx (e.g. addition of HONO) or without NOx (adding H$_2$O$_2$). The well-known relative method, i.e. using reference compounds (e.g. 1,3,5-trimethylbenzene or...
cyclohexane among the most used ones), is used to obtain the rate constant of OH with the key compound. Assuming that the OH reaction is the only significant loss process for the compounds of interest and the references, it can be shown that:

$$\ln\left[\frac{\text{compound int}}{0}\right] / \left[\frac{\text{compound int}}{t}\right] = \frac{k}{k_R} * \ln\left[\frac{\text{reference}_0}{\text{reference}_t}\right].$$  \hspace{1cm} (3)

Where the subscripts 0 and t indicate the concentrations at the beginning of the experiment and at time t, respectively, and $k_R$ is the $k_{OH}$ of the reference compound and $k$ is the $k_{OH}$ to obtain. After the corrections required (leakage and wall loss if necessary), the representation of $\ln\left[\frac{\text{compound int}}{0}\right] / \left[\frac{\text{compound int}}{t}\right]$ versus $\ln\left[\frac{\text{reference}_0}{\text{reference}_t}\right]$ should exhibit straight line where the slope is $k/k_R$. The $k_R$ of the reference compound is well-documented in literature, thus the rate coefficient of OH reaction with the compound of interest can be calculated according to the equation (3).

As well as the calculation of the OH constant of reaction, it is possible to study the product formation due to the photooxidation in the presence or in the absence of NO$_x$.

**EXAMPLES OF STUDIES CONDUCTED AT EUPHORE**

Among the studies on the atmospheric fate of pesticides conducted so far at the Euphore facility, we present below a brief summary of the data obtained on the degradation of three pesticides: dichlorvos, trifluralin and chloropicrin.

**Dichlorvos:**

The OH-initiated oxidation of dichlorvos has been investigated under atmospheric conditions. The rate constant of OH reaction with dichlorvos, $k$, was measured by using the conventional relative rate technique where 1,3,5-trimethylbenzene (TMB) and cyclohexane were taken as references. Using the rate constants of $5.67 \times 10^{-11}$ and of $6.97 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the reactions OH + TMB and OH + cyclohexane, respectively, the resulting value of the OH reaction rate constant with dichlorvos was derived to be $k = (2.6 \pm 0.3) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The tropospheric lifetime of dichlorvos with respect to reaction with OH radical has been estimated to be around 11 hours. The major carbon-containing products observed for the OH reaction with dichlorvos in air under sunlight condition were phosgene and carbon monoxide. Figure 2 shows an example of the concentration-time profiles of the reactant and products during the OH reaction with dichlorvos. The formation of a very stable toxic primary product such as phosgene associated to the relative short lifetime of dichlorvos may make the use of pesticide even more toxic for human when released into the atmosphere (Feigenbrugel et al 2006).
Figure 2: Concentration-time profiles of the reactant and products during the OH reaction with dichlorvos at EUPHORE (3rd June 2004). The initial concentrations were the following: $[\text{dichlorvos}]_0 = 184.2$ ppbv and $[\text{NO}]_0 = 75.2$ ppbv. CO has been quantified by FTIR between 2027 and 2241 cm$^{-1}$.

Trifluralin:

The gas phase atmospheric degradation of trifluralin has also been investigated at the EUPHORE facility. Its photolysis has been studied under sunlight conditions and its reaction rate constant with OH radicals was measured using the relative rate method. Using 1,3,5-trimethylbenzene as reference compound, the rate constant of OH-reaction with trifluralin was obtained to be $k_{\text{OH}} = (1.7 \pm 0.4) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at $(300 \pm 5)$ K and atmospheric pressure. The mean photolysis rate measured under solar radiation was $J_{\text{trifluralin}} = (1.2 \pm 0.5) \times 10^{-3}$ s$^{-1}$ ($J_{\text{NO}_2} = 8 \times 10^{-3}$ s$^{-1}$). The photolysis of trifluralin was found to generate organic aerosols with a yield of $(20 \pm 10)$ %. The data obtained enabled us to discuss the atmospheric fate of trifluralin in the gas phase (Le Person et al. 2007).

Figure 3: Time-Concentrations profiles of trifluralin, 1,3,5-Trimethylbenzene (TMB), aerosols and the product formed during a photolysis experiment (110703) of trifluralin.
Chloropicrin:

The photolysis of chloropicrin under atmospheric conditions using sunlight was studied. The obtained results that the photolysis lifetime determined is around 3 hours which confirms that the photolysis is the major degradation pathway for chloropicrin in the atmosphere. Figure 4, shows an example of the time-concentrations profiles obtained during a photolysis experiment.

![Figure 4: Time-Concentrations profiles of chloropicrin, its photolysis products and acetone (this later being produced through the oxidation of isopropanol used here as Cl-atoms scavenger).]

CONCLUSION

The results presented here show the usefulness of the EUPHORE facility as a sophisticated tool for studying the atmospheric fate of pesticides under controlled conditions. The data derived from such studies are of potential importance to assess the impact of these species on air quality and on human health.

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