



# Surface photochemistry of pesticides containing 4-chlorophenoxy chromophore

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## ABSTRACT

The surface photochemistry of pesticides containing 4-chlorophenoxy chromophore was accessed on the model surfaces cellulose and silica, using diffuse reflectance and chromatographic techniques. 4-Chloroanisole was chosen as the model compound and its phototransformation was followed under lamp (254 nm) and sunlight irradiation. The photodegradation rates are faster on cellulose than on silica. The main photodegradation products on cellulose are anisole and dimerization compounds while on silica the formation of 4-hydroxyanisole and dimerization are the main reaction pathways. Transient absorption studies showed the formation of the 4-methoxyphenylperoxy radical only on cellulose and in the presence of oxygen. The homolytic cleavage of the C–Cl bond, and consequent formation of a triplet radical pair, is the main primary reaction step on both surfaces. The radical pair then diffuses apart or undergoes electron transfer to form phenyl radicals and phenyl cations, respectively. These two reaction intermediates account for reduction, addition, and formation of bonded residues, the main reactions observed on the studied surfaces and also expected to prevail under natural conditions.

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## 1. Introduction

The photochemical transformation is one of the main dissipation processes of pesticides and other xenobiotics under natural conditions [1]. Since most part of these compounds is localized at the solid/gas interface [2], any description of their behavior in the environment requires a detailed study of these systems. Natural environmental surfaces are however very complex and usually do not allow for conventional photochemical experiments. Surface photochemistry studies under controlled conditions on models of natural surfaces are therefore very important before the final experiments under environmental conditions. Diffuse reflectance and chromatography techniques have been used to study the surface photochemistry of several pollutants adsorbed on model surfaces [3–6]. Cellulose is one of the main structural components of vegetal cells and silica is one of the major constituents of soil surfaces. Microcrystalline cellulose and silica have been widely used as solid powdered supports to study the photophysics and the photochemistry of several organic compounds. Therefore these supports can be used to access the photochemical behavior of pollutants on leaf and soil surfaces.

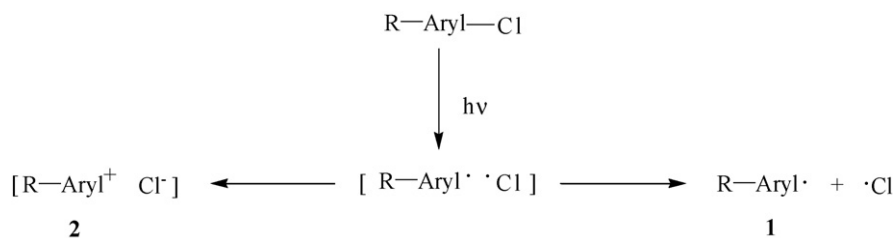
Pesticides are an extremely heterogeneous group of chemical compounds in many cases, with two or more functional groups. Given the multiplicity of pesticide chemical structures and the complexity of the environmental surfaces, the prevision and the generalization of the behavior for pesticides and surfaces based on the photochemical results obtained for a specific compound and conditions is difficult. Therefore, a reasonable approach is to study the photochemistry of a chromophoric chemical group common to several pesticides, adsorbed on model environmental surfaces. The knowledge of the final photoproducts and transients involved in the photoreaction of a chromophoric group adsorbed on model solid supports can be used to predict the photoproducts on other surfaces and the main primary photochemical processes for other pesticides containing the same group.

The 4-chlorophenoxy group is an important chromophore shared by several pesticides. The photodegradation of these compounds in solution and on the solid/gas interface is mainly due or related to this chromophoric system [4–7]. The detailed knowledge of the surface photochemistry of this group, namely the final photoproducts and intermediates formed after irradiation, can be used to understand and predict the photochemistry of other 4-chlorophenoxy pesticides. Monochlorophenols are the simplest group of compounds containing this chromophore. They are environmental important on their own right but show a very specific photochemical behavior [5,8]. It has been proposed that the main primary photoreaction step of chlorophenoxy compounds in polar environments is the heterolytic cleavage of the C–Cl bond and the formation of the correspondent phenyl cation. In the case of

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**Scheme 1.** Main primary photochemical steps of aryl chlorides.

4-chlorophenols the phenyl cation undergoes deprotonation and leads to the formation of the correspondent carbene. The main reaction pathway in these cases can be accounted for by the phenyl cation and/or by the carbene. Since the replacement of the hydroxyl group by an ether group dramatically changes the primary photochemical processes of chlorophenoxy pesticides, another model molecule is needed.

We proposed recently [9] a general mechanism for the phototransformation of aryl chlorides in solution. The main primary photochemical reaction step is the homolytic cleavage of the C–Cl bond to produce a triplet radical pair in the solvent cage (Scheme 1). In non-polar solvents hydrogen abstraction, after radical diffusion, leads to reduction. In polar solvents, in addition to H-abstraction, electron transfer within the caged radical pair occurs and leads to an ion pair (phenyl cation + Cl<sup>-</sup>).

In this work 4-chloroanisole was chosen as model for 4-chlorophenoxy compounds, other than chlorophenols. The photochemistry of this compound was studied in detail on silica and cellulose surfaces. The photodegradation kinetics was assessed, the final degradation products and transients identified and a reaction scheme is proposed.

## 2. Experimental

### 2.1. Materials

4-Chloroanisole, anisole, 4-chlorophenol (Riedel-de Haën); phenol, 4-methoxyphenol (Aldrich); cellulose DSO (Fluka); silica (60 Å) (Merck); methanol and acetonitrile (Merck Lichrosolv) were used without further treatment. Water was deionized and distilled.

### 2.2. Sample preparation

Samples of 4-chloroanisole on cellulose were initially prepared using the solvent evaporation method, as described in previous works [4–6]. The final concentration of 4-chloroanisole was determined by extracting the samples with methanol (a known weight of sample in a known volume of solvent) followed by centrifugation and analysis by HPLC. 4-Chloroanisole was lost by volatilization during the sample preparation process. Therefore all samples on silica and cellulose (10, 20, 50, 100 and 400 μg<sup>-1</sup>) were prepared by mechanical mixture. This was achieved by adding directly the probe to the correspondent amount of solid support, followed by magnetic stirring during 3 days. The final concentration of 4-chloroanisole was determined by HPLC.

### 2.3. Methods

#### 2.3.1. Diffuse reflectance ground state absorption spectra

Ground state absorption spectra of the solid powdered samples were recorded using a Cintra 40 GCB Scientific Equipment spectrophotometer, with a diffuse reflectance attachment. The measured reflectance, *R*, was used to calculate the remission func-

tion *F*(*R*) using the Kubelka–Munk equation defined by

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{K}{S}$$

where *K* and *S* are the absorption and scattering coefficients, respectively. The Kubelka–Munk equation was applied to optically thick samples, i.e., those where any further increase in the thickness does not affect the experimentally determined reflectance. For an ideal diffuser, where the radiation has the same intensity in all directions, *K* = 2ε*C*, where ε is the Napierian absorption coefficient and *C* is the concentration. Since the substrate usually absorbs at the excitation wavelength, *F*(*R*)<sub>probe</sub> = *F*(*R*)<sub>substrate</sub> = Σ<sub>i</sub> 2ε<sub>i</sub>*C*<sub>i</sub>/*S*, where *F*(*R*)<sub>substrate</sub> is the blank obtained with a cell containing only substrate. Whenever the probe is only in the form of monomer, this equation predicts a linear relationship for the remission function of the probe as function of the concentration (for a constant scattering coefficient) [10].

#### 2.3.2. Irradiation conditions

Photolysis studies were conducted in a system previously used to study 4-chlorophenol and pesticides [4–6]. The 254 nm radiation was obtained using a 16 W low-pressure mercury lamp (Applied Photophysics) without filters and without refrigeration. The photodegradation kinetics and product formation studies, under lamp and sunlight irradiation, were made using samples prepared by spreading the solid powder on glass microscope slides (~50 mg spread on ~10 cm<sup>2</sup>) covered with quartz slides. The edges of the slides were then sealed with parafilm to prevent the losses by volatilization. The samples used for the volatilization studies were prepared in the same way but were kept opened (without the cover slide) in the dark. All the experiments were repeated three times.

The sunlight irradiation studies were performed in Algarve (South Portugal, latitude: 37° N, longitude: 8° W) in July and August. After irradiation the 4-chloroanisole residue and its photoproducts were extracted as described in Section 2.2. The solar radiation was monitored using an International Light IL 700 A Research Radiometer, equipped with a SEE240 #3358 detector, a W # 6237 diffuser and a UVB #12813 filter.

#### 2.3.3. Photodegradation kinetics and product analysis

The 4-chloroanisole volatilization and photodegradation losses were followed by HPLC using a Merck-Hitachi 655A-11 chromatograph equipped with a 655A-22 UV detector. A column LiChroCART 125 (RP-18, 5 μm) Merck was used and the runs were performed using mixtures water/acetonitrile as the eluent. Analyses were also conducted on control samples kept in the dark during irradiation.

The photoproducts were studied by GC–MS and LC–MS. GC–MS analyses were performed using a Hewlett Packard 5890 Series II gas chromatograph with a 5971 series mass selective detector (E.I. 70 eV). A CP-WAX 58CB capillary column with 25 m length, 0.25 mm I.D. and 0.25 μm film thickness (Chrompack) and a DB-35MS capillary column with 30 m length, 0.25 mm I.D. and 0.25 μm film thickness (J&W Scientific) were used. The initial temperature 70 °C was maintained during 5 min and then a rate of 5 °C/min was

used until a final temperature of 250 °C was reached. The LC–MS system is an Agilent Technologies 1200 Series LC coupled to a Bruker Daltonics HCT ultra (ion trap detector). The ionization was made by electro-spray in the positive polarity. A Purospher STAR (Merck) LiChroCART 125-2 (12.5 cm length, 2 mm internal diameter, RP-18, 5 μm) column stabilized at 30 °C was used. Analyses of the main photoproducts were conducted at conversions ~2%.

### 2.3.4. Diffuse reflectance laser flash photolysis system

Laser flash photolysis experiments were carried out with the system described in reference [10], using the diffuse reflectance geometry. The transient absorption data are reported as percentage of absorption (%Abs) defined as  $100\Delta J_t/J_0 = (1 - J_t/J_0)100$ , where  $J_0$  and  $J_t$  are the diffuse reflected light before exposure to the laser pulse and at time  $t$  after excitation, respectively.

## 3. Results and discussion

### 3.1. Ground state absorption

The diffuse reflectance ground state absorption spectra of 4-chloroanisole showed the expected  $\pi\pi^*$  absorption band between 250 and 300 nm (see Figure S1, Electronic Supplementary Data), similar to the observed in solution [11]. The absorption reaches a maximum near 280 nm and then decreases with the wavelength until 300 nm. The difference in the absorption maximum indicates that 4-chloroanisole interacts differently with silica and cellulose surfaces.

Under natural conditions only the solar radiation above 290 nm arrives to the earth surface [1]. Low overlap with the absorption of 4-chloroanisole in both solid supports occurs and therefore low direct photodegradation rates are expected under solar irradiation. However, it was shown that compounds with similar absorption spectra undergo direct photodegradation at the solid/gas interface under solar irradiation [5,6]. This is a very important result for stable compounds where photodegradation, although taking place at low rates, is the only dissipation pathway. From the ground state absorbance results it is therefore expected direct degradation of 4-chloroanisole under sunlight irradiation, on the studied solid supports.

### 3.2. Photodegradation kinetics

The photodegradation of 4-chloroanisole adsorbed on cellulose and silica was studied under lamp (Hg, 254 nm) and solar irradiation (see Table 1). The volatilization was also measured under the same conditions but in the dark. The obtained standard deviations indicate that the solid samples were well homogenized and that the irradiation conditions are reproducible. 4-Chloroanisole is liquid at room temperature and therefore the volatilization losses are expected to be significant. In fact, after 1.5 h 4-chloroanisole decays to 66% and to 22% of its initial concentration on silica and cellulose, respectively ( $24 \pm 1$  °C). These differences in the volatilization rates suggest a weaker adsorption interaction of the probe with cellulose. The evaluation of the photodegradation rates was therefore made using closed samples. The losses by photodegradation are lower than by volatilization. After 4 h of irradiation 17% is lost on silica while on cellulose 44% of 4-chloroanisole is decomposed, indicating that the photodegradation is also slower on silica than on cellulose. The formation of photoproducts under sunlight confirms that 4-chloroanisole undergoes photodegradation under natural conditions. In fact the same main photoproducts were detected under these irradiation conditions.

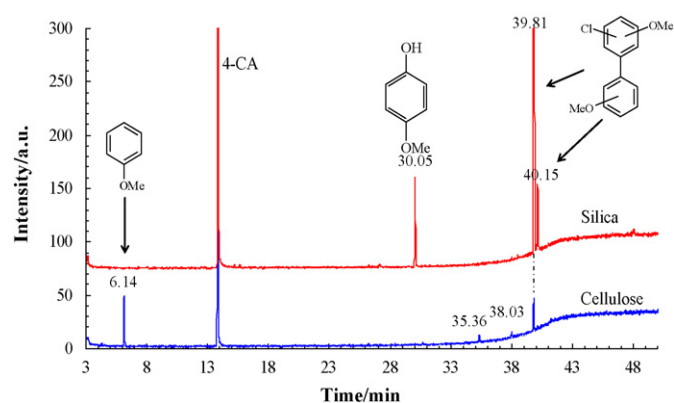


Fig. 1. GC–MS traces of the extracts of irradiated samples of 4-chloroanisole on cellulose and on silica. Peaks with retention time 35.36 and 38.03 were assigned to dimethoxybiphenyls.

### 3.3. Photodegradation products

All the samples used in the photochemical studies were first analysed by HPLC to verify the stability of 4-chloroanisole and to determine its concentration ( $\mu\text{mol g}^{-1}$ ). Fig. 1 presents the GC–MS traces of the extract of irradiated 4-chloroanisole (254 nm) on cellulose and silica under air.

The main photoproducts on cellulose are anisole (retention time (rt)=6.14 min), chlorodimethoxybiphenyls (rt=39.81 and 40.15) and dimethoxybiphenyls (rt=35.36 and 38.03). On silica 4-chloroanisole forms chlorodimethoxybiphenyls and 4-hydroxyanisole (rt=30.05). Anisole is not formed on silica surface. LC–MS analyses of the extracts confirmed the assignments.

The results indicate that the photoproduct distribution depends on the solid support and the major differences are the formation of anisole only on cellulose and the formation of 4-methoxyphenol only on silica.

### 3.4. Transient absorption

Transient absorption of 4-chloroanisole adsorbed on cellulose was first studied under air equilibrated conditions in order to obtain the spectra in conditions similar to those of the environment. The spectrum obtained 25 ns after the laser pulse shows an absorption maximum at 312 nm, an absorption band between 360 and 400 nm and a broad absorption above 450 nm that extends up to 650 nm (see Fig. 2). In the microsecond time scale only the former band persists.

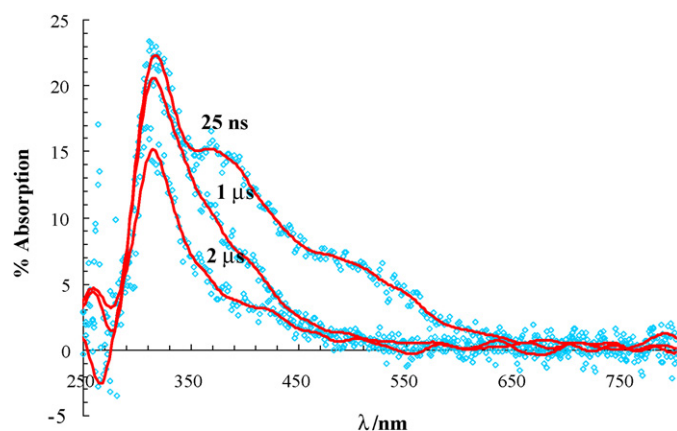


Fig. 2. Time resolved absorption spectra of 4-chloroanisole on cellulose under air equilibrated conditions (266 nm; ~20 mJ/pulse, ~50 μmol g<sup>-1</sup>).

**Table 1**  
Results and correspondent standard deviations of the dissipation of 4-chloroanisole on silica and cellulose under controlled (Hg lamp irradiation, 254 nm, 24 ± 1 °C) and natural conditions (sunlight irradiation, clear sky, Summer, 23–35 °C).

Initial concentration (μmol g <sup>-1</sup> )	Silica					Cellulose				
	246 ± 3		241 ± 4			167 ± 4		297 ± 6		
Conditions	Volatilization	Lamp	Lamp	Dark	Sun	Volatilization	Lamp	Lamp	Dark	Sun
Time	1.5 h	4 h	5 min	2.5 days	2.5 days	1.5 h	4 h	5 min	2.5 days	2.5 days
Final concentration (μmol g <sup>-1</sup> )	163 ± 13	204 ± 8	232 ± 3	202 ± 4	201 ± 5	36 ± 2	93 ± 8	147 ± 5	19 ± 3	21 ± 3

The longer wavelength absorption was already observed after the phototransformation of 4-chloroanisole in solution under air equilibrated and oxygen saturated conditions [9]. On cellulose surface this absorption is absent under argon atmosphere. We therefore assign this band to 4-methoxyphenylperoxyl radicals.

Transient absorption of higher concentration samples (~400 μmol g<sup>-1</sup>) of 4-chloroanisole on cellulose also showed the absorption of the peroxy radical under air equilibrated conditions but the absorption intensity of the band between 360 and 400 nm increases relatively to that of the this radical. The absorption in this region was also observed in solution and has been ascribed to transient species whose formation involves the reaction of a primary intermediates with a ground state 4-chloroanisole molecule [12,13]. The absorption between 360 and 400 nm was therefore assigned to the precursors of chlorodimethoxybiphenyls. The lower absorption band can be due to phenyl radicals [14].

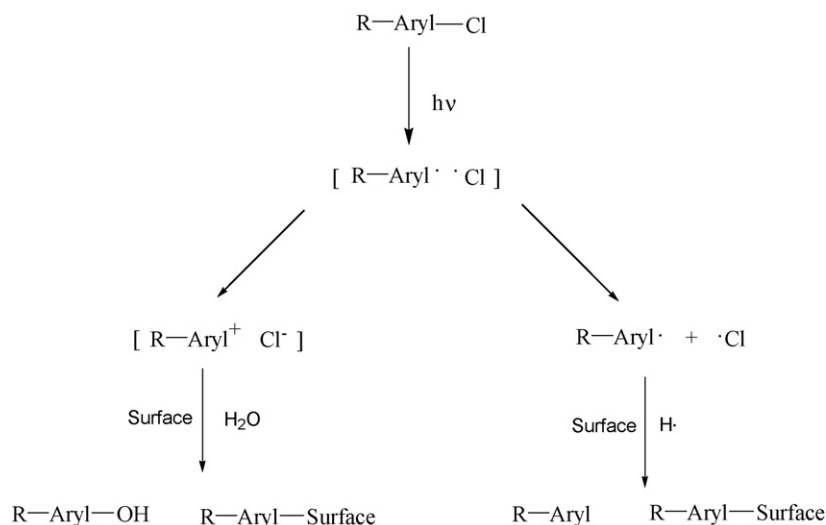
The transient absorption spectra on silica are broader than on cellulose (see Figure S2, Electronic Supplementary Data). The spectra indicate the formation of the precursors of chlorodimethoxybiphenyls, in agreement with the product distributions. The absorption due to phenylperoxyl radicals was not clearly observed.

### 3.5. Photodegradation pathways of 4-chloroanisole on cellulose and silica

Previous studies in solution indicated that the main primary photochemical reaction step is the homolytic cleavage of the C–Cl bond to produce a triplet radical pair in the solvent cage (Scheme 1) [9]. In non-polar solvents hydrogen abstraction, after radical diffusion, leads to reduction. In polar solvents, in addition to H-abstraction, electron transfer within the caged radical pair occurs and leads to an ion pair (phenyl cation + Cl<sup>-</sup>). The formation of radical cations of 4-chloroanisole has also been observed in acetonitrile [9].

While the radical cation is easily detected by flash photolysis, it absorbs appreciably in the visible region [9], both phenyl radicals and phenyl cations are expected to show weak absorbance above 300 nm [12–14]. However, phenyl radicals and phenyl cations can react with oxygen and ground state molecules, respectively, leading to transients that absorb above 300 nm [12,13]. The formation of methoxyphenylperoxyl radicals (precursors of phenyl radicals [9]) together with the formation of anisole indicates that the homolytic cleavage of the C–Cl bond is one of the main photodegradation pathways on cellulose. Many arylperoxyl radicals only decay by second order with the other peroxy radicals present, leading to an unstable tetroxide which then eliminates O<sub>2</sub> and forms two identical phenoxy radicals [15]. In the case for 4-chloroanisole, in a hydrogen donor support like cellulose, these phenoxy radicals would lead to 4-methoxyphenol. Only traces of this compound were detected on cellulose. Therefore after homolytic cleavage only the methoxyphenyl radical leads to net reaction. Back reaction to the phenyl radical and formation of anisole should be the main reaction process from peroxy radicals.

The formation of phenyl cations (2, Scheme 1) cannot be excluded on cellulose. The reactions expected for phenyl cations are the reaction with ground state molecules (addition to π nucleophiles [8]), which leads ultimately to chlorodimethoxybiphenyls, and reaction with the OH group of cellulose surface. While the former products and their precursors were clearly detected, suggesting their formation, the reaction with the solid support leads to non-extractable residues and therefore these final products can't be detected. The presence of phenyl cations is however clear on silica. The formation of 4-methoxyphenol is readily explained after reaction of the phenyl cations with the water molecules (addition to σ nucleophiles) adsorbed on silica surface [8]. The formation of chlorodimethoxybiphenyls is also in agreement with the formation of the phenyl cations [13].



**Scheme 2.** Main photodegradation pathways of pesticides containing 4-chlorophenoxy chromophore.



All data suggest that the phototransformation on silica and cellulose surface follows the main primary steps shown in Scheme 1. The main primary photochemical reaction step is the homolytic cleavage of the C–Cl bond to produce a triplet radical. On cellulose both, diffusion of the radical pair and electron transfer should occur, leading to phenyl radicals and phenyl cations, respectively. On silica the formation of the phenyl cation prevails.

### 3.6. Expected photodegradation pathways for chlorophenoxy pesticides adsorbed on natural surfaces

Most pesticides containing the chlorophenoxy chromophore are solid at room temperature and are therefore expected to show low mobility on solid surfaces. Considering also that the concentration of most organic pesticides is low in the environment, the formation of dimerization products is expected to be a minor process under these conditions.

Under natural conditions chlorophenoxy derivatives are expected to undergo homolytic cleavage as the primary photochemical step, which can then lead to both, phenyl radicals and phenyl cations (see Scheme 2).

On leaf surfaces phenyl radicals can lead to the correspondent reduction product after hydrogen abstraction from the surface or even react with the surface forming bonded residues. The phenyl cations can form the correspondent OH derivatives after reaction with water or add to  $\pi$  nucleophiles of the surface (if present), leading also to bounded residues. The photoreduction of chlorophenoxy pesticides (triadimenol), adsorbed on hydrogen donor surfaces was already reported [6]. No dimerization products were observed. Photoreduction was not observed for triadimefon due to the presence of the carbonyl chromophore, which strongly changes the photochemistry [6]. On natural soil surfaces possessing organic matter, similar processes are expected. On soils containing Lewis acid sites like clays, the radical cation formation can also be formed [3]. This intermediate also leads to the correspondent OH derivative. All the observed photodegradation pathways invariably lead to dechlorination, even in the presence of oxygen. This is very important since chloroaromatics are known to be stable to dissipation processes other than photodegradation, under natural conditions.

## 4. Conclusions

We propose an approach to evaluate the environmental photochemistry of pesticides. The absorption spectra, the degradation rates, the final photo-products and the main reaction intermediates of a chromophoric chemical group, in a given model matrix, can be used to predict the main photo-transformation processes in other matrices and for other pesticides containing the same group. This was demonstrated for the 4-chlorophenoxy chromophore on

the model surfaces silica and cellulose. Pesticides containing this chromophoric group are prone to direct photo-degradation under sunlight irradiation. The main reaction intermediates (phenyl radicals and phenyl cations) as well as the final products indicated that the main reaction pathways expected on natural surfaces are reduction, addition and formation of bound residues.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.02.077.

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