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# **Photolytic degradation of *N,N*-diethyl-*m*-toluamide in ice and water: implications in its environmental fate**

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## **Abstract**

The photochemical transformation of *N,N*-diethyl-*m*-toluamide (DEET), one of the most widespread and efficient mosquito repellents, has been investigated. Initially, photoinduced DEET degradation was investigated in liquid samples, at 20 °C and 0 °C, and in ice (-15 °C), aimed to simulate all possible photoinduced processes occurring in water and in cold environments. Under UV-illumination, DEET degradation was more efficient in ice than in water. The evaluation of transformation products (TPs) formed during the photolysis in solution and in ice evidences mostly the same degradation products, but with different concentration ratio and some peculiar differences. An hypothesis about what kind of processes may play a role is reported. In solution, the oxidative process mostly involved were (poly)hydroxylation or oxidation of the hydroxyl groups, while in ice *N*-dealkylation and monohydroxylation prevail. Finally, DEET and its TPs were searched out in snow and river water in wintertime.

**Keywords:** DEET, ice, photolysis, HRMS, transformation products

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## 1. Introduction

*N,N*-diethyl-m-toluamide (DEET) is one of the most widespread and efficient mosquito repellents diffused worldwide, included in Pharmaceuticals and Personal Care Products (PPCPs) list and in some emerging contaminant list [1]. This mosquito repellent is widely used in Europe and in America, where a consumption of 1800 tonnes per year is estimated. It can be considered as an emerging contaminant of environmental concern because of its continuous release into the aquatic environment, its persistence and evidences of ecotoxicological effects [2].

Only 20% of DEET is absorbed by skin, metabolized and excreted; mostly will then be washed away entering in the aquatic system [3]. Its wide use and high stability have led it to become a ubiquitous pollutant; it was found worldwide in aquatic environment (i.e. Australia, Germany, Holland, Norway, Italy, USA [4] to a level ranging from  $0.1 \text{ ng L}^{-1}$  to up  $1.1 \mu\text{g L}^{-1}$  [5] in surface waters, groundwater and waters for human consumption [4, 6-11].

Earlier studies were concerned with simulation by  $\text{TiO}_2$ -mediated photolysis of *N,N*-diethyl-*m*-toluamide [12], where a total of 51 unknown DEET degradation products (TPs) were identified and characterized by multiple stage mass spectrometry, and focused on their identification in Po River water (North Italy [13]). In the latter case, all the possible main and secondary transformation products (TPs) were searched in natural samples. Fifteen TPs were identified in Po river waters and four different transformation routes were proposed; within this framework, the fate of DEET in the river water was clarified.

The identification of *N,N*-diethyl-*m*-toluamide, in aerosols was recently documented [14] and this prompt us to extend the investigation on the fate of this pollutant to other environmental compartments, e.g. snow, with particular focus on cold environments. The role of snow in the distribution and the fate of organic contaminants [15-16] as well as in hosting possible (photo)chemical transformations in regions of high altitude and latitude [17-19] has received growing attention. While photochemical processes in aqueous media have been extensively investigated, significantly fewer published studies regarded photochemical transformations of anthropogenic organic contaminants in ice. Most of the available studies investigated direct photochemical processes under controlled laboratory conditions [20-25] and indicated efficient photochemical reaction for several species. In cold environments, snow and ice exhibit a marked influence on the photochemical transformation of semi-volatile organic contaminants [17-18]. Hydrophobic or hydrophilic solute molecules are known to become spontaneously segregated at grain boundaries of ice during the freezing process. As ice forms from freezing water, pure water crystallizes first, and solutes are excluded from the bulk and concentrated at the surface [26]. This results in a chemically enriched liquid-like layers at the surface, grain boundaries and interstitial pores of snow and ice, which can affect the type and rates of chemistry that may occur. Such a solute-concentration enhancing effect may cause the solute organic molecules to self-organize and their chemical reactivity is significantly altered [27-28].

The formation of photoproducts may be of toxicological relevance if they are formed in ice and subsequently released with spring melt [25]. As an example, the photodegradation of chlorobenzenes or chlorophenols in ice can give rise to more persistent polychlorinated biphenyls or chlorohydroxybiphenyls [22, 29]. Pollutants could be incorporated to snow by wet or dry deposition processes [30]. If they do not absorb solar radiation, they may still react with other reactive photochemically produced species, such as hydroxyl radicals [31-32]. The reaction with hydroxyl radicals is often the dominant removal pathway for organic pollutants in natural waters [33]. However, when aromatics are present at the surface of frozen water (ice), this reaction pathway may

not occur: recent studies have shown that at air-ice interfaces hydroxyl radicals do not react to an appreciable extent with aromatic compounds, including benzene, whereas in aqueous solution these reactions occur at near diffusion-limited rates [34-36].

In an attempt to clarify the fate of DEET in cold environments, we have performed a laboratory investigation on DEET photolysis in both water and ice; the degradation photokinetics was evaluated and main TPs were identified in water and ice phases. The same TPs were then searched out in river water and snow.

## **2. Experimental section**

### **2.1. Materials and reagents**

*N,N*-diethyl-*meta*-toluamide (DEET) (purity 97%), isoxsuprine hydrochloride were from Sigma Aldrich. Formic acid (99%) was from Merck (Milan, Italy). HPLC grade water was obtained from MilliQ System (Millipore, Milan, Italy). HPLC grade acetonitrile (BDH) was filtered through a 0.45 µm filter before use.

### **2.2. Procedures for irradiation**

Photolysis experiments were carried out in quartz cells containing DEET at 10, 20 or 40 mg L<sup>-1</sup> (52, 104 or 208 µM) and illumination was provided by a Philips Ultraviolet Light Bulb 15 Watt TUV G15 T8 lamp with emission maximum at 254 nm. Temperature within the cell was controlled by a thermostatic bath and fixed at +20 °C, 0 °C or -15 °C. In the case of photolysis in ice, DEET solutions were frozen overnight at -15 °C before illumination.

### **2.3. Sampling procedure**

Snow samples were collected in Coazze, a town located at 750 m above sea level, 40 km west of Turin, Italy, in a huge area far from streets. It can be considered countryside, with a limited contribution of anthropic contamination. Snow sampling was performed at three different points, all located in Coazze. At each point 10 l of melted water was sampled.

River water samples were collected in a sampling campaign performed in Turin at three sampling points, all located close to the city centre and before the town wastewater treatment plant. Late winter samples were collected from February 1, 2009 to March 8, 2009 and repeated in March 2010. Summer samples were sampled from 1 to 4 July 2008 and repeated on July 2009 with the procedure described elsewhere [13]. Samples were collected 2 m far from the river border using brown glass bottles; samples are then kept in the dark and promptly analysed.

#### **2.4. Extraction procedures**

River water and snow samples were extracted by adopting the more appropriate procedure. All samples were acidified at pH 2 with HCl 37%, concentrated on SPE cartridge and analyzed by HPLC/HRMS.

Strata X solid phase extraction (SPE) cartridges (Phenomenex, Bologna, Italy) were used for extracting snow and river water samples. Samples were spiked with 10 µL isoxsuprine (1 mg L<sup>-1</sup>, 3.3 µM) used as recovery standard. Elution was performed with 2 mL CH<sub>3</sub>OH and 2 ml of 2 % ammonia in CH<sub>3</sub>OH. Eluted solutions were dried under nitrogen flux and then reconstituted with 200 µL 0.05% (10 mM) formic acid and directly injected into HPLC/MS. Quantitative data were obtained through an external calibration after normalization on isoxsuprine signal. Limit of detection (LOD) for DEET after concentration on SPE cartridges was 0.5 ng L<sup>-1</sup> (2.6 pM). With this method, DEET and all formed TPs showed a recovery percentage > 90%.

## **2.5. Analytical techniques**

### **2.5.1. HPLC-HRMS**

The chromatographic separations followed by a MS detector were run on a C18 column Phenomenex Luna, 150 × 2.0 mm, thermostated at 30°C using an Ultimate 3000 HPLC instrument (Dionex). Injection volume was 20 µL and flow rate 200 µL/min. Gradient mobile phase composition was adopted: 5/100 formic acid 0.05%/acetonitrile in 0/35 min. A LTQ Orbitrap mass spectrometer (Thermo Scientific, Bremen, Germany) equipped with an atmospheric pressure interface and an ESI ion source was used as detector. The LC column effluent was delivered into the ion source using nitrogen as sheath and auxiliary gas. The source voltage was set at 4.5 kV. The heated capillary was maintained at 265°C. The acquisition method used was previously optimized in the tuning sections for the parent compound (capillary, magnetic lenses and collimating octopoles voltages) in order to achieve the maximum of sensitivity. The tuning parameters adopted for ESI source have been the following: capillary voltage 7.00 V, tube lens 55 V. Mass accuracy of recorded ions (vs calculated) was ± 5 millimass units (mmu) (without internal calibration).

## **3. Results and discussion**

### **3.1. UV-photolysis in water and ice**

#### *3.1.1. DEET degradation*

DEET degradation under UV light as a function of irradiation time in water, melted water and ice is plotted in Figure 1. While DEET disappearance rate at 20 and 0 °C are very similar, its photodegradation takes place faster in ice than in the solution. Quicker photolysis on ice could be attributed to different reasons. Although light scattering and reflection lower the quantum yields of the photo-processes occurring in ice or snow [37], the increased rate could be attributed to an enhanced local concentration of the pollutant at the grain boundaries of the ice crystals; the specific

concentration effect [37-38] then increases the probability of intermolecular reactions. DEET absorption spectrum is shown in Figure S1 as supplementary material. Even if DEET spectrum does not overlap that of the solar radiation, recent studies point out that the absorption spectra of aromatic compounds, e.g. phenol derivatives, exhibit significant bathochromic shifts to wavelengths overlapping those of solar radiation at an air-ice interface [24, 34, 36], so suggesting that direct photolysis could be an important removal pathway in cold regions [39].

### 3.1.2. DEET transformation products

Along with DEET degradation, several TPs were formed and detected by LC-HRMS. Their evolution profiles as a function of irradiation time are plotted in Figures 2-4. All these TPs are well-matched with DEET TPs formed in laboratory simulations and were previously characterized [13]; the proposed structures are collected in Table S1 as supplementary material.

Figure 2 reports the temporal profiles of TPs produced during photolysis experiments in water (20 °C) and include three compounds with  $m/z$  208 (attributed to *N,N*-diethyl-4-hydroxy-3-methylphenylamide, *N,N*-diethyl-2-hydroxy-3-methylphenylamide (**208-B** and **C**) or *N,N*-diethyl-3-hydroxymethylphenylamide (**208-A**)), a compound labelled **164** and attributed to *N*-ethyl-3-methylphenylamide, *N*-ethyl-4-hydroxy-3-methylphenylamide (**180**), *N*, *N*-diethyl-3-hydroxymethylphenylamide (namely **194**) *N,N*-diethyl-oxo-3-methylphenylamide (**206**), *N,N*-diethyl-trihydroxy-3-methylphenylamide (**240**)), *N,N*-diethyl-oxo-dihydroxy-3-methylphenylamide (**222**). It comes up that main TPs formed through photolysis in aqueous phase are monohydroxy derivatives (**208**), while dealkylation product (**164** and **180**) are formed in minor amount. The formation of hydroxy- or peroxosubstituted photoproduct should be attributed to the presence of oxygen in liquid water as a biradical species [40].

Different kinetics of TPs formation lead us to assume a different attack of hydroxyl radical. Indeed, an initial resistance to de-ethylation was observed, because only the demethylened/hydroxylated TP

(namely **194**) and monohydroxylated compounds (**208**) formation was detected. Then, after 2 h of irradiation, hydroxylated /demethylated product (**180**) and poly-hydroxylated TPs (**240** and **222**) were formed.

Photolysis at 0 °C (see Figure 3) evidences the formation of almost the same TPs already discussed at 20 °C, formed at similar relative ratio, even if at lower amount. The only difference stands on the lack of polyhydroxylated compounds, e.g. **222** and **240** and the formation of TPs *N,N*-diethyl-oxo-trihydroxy-3-methylphenylamide (**238**) and *N,N*-diethyl-tetrahydroxy-3-methylphenylamide (**244**).

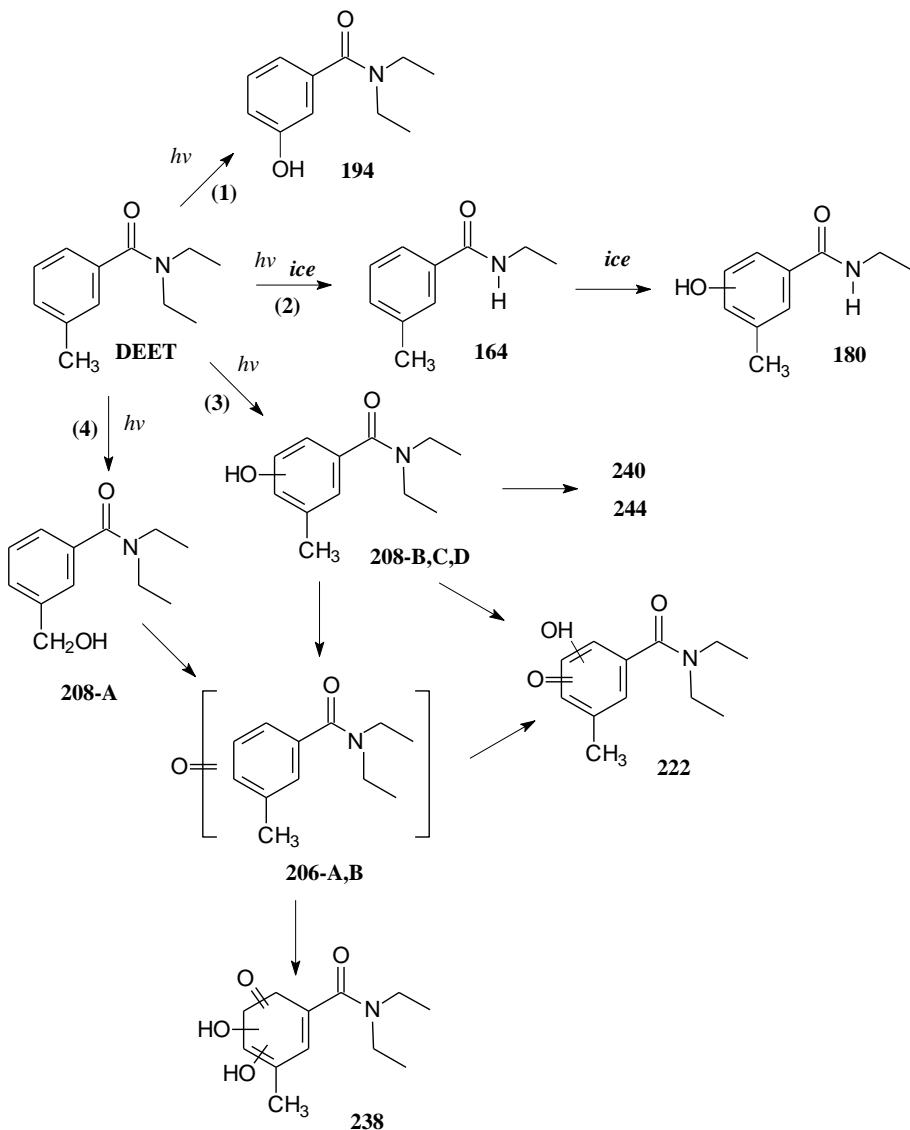
Looking closer to ice photolysis TPs (Figure 4), a monotonic increase of products is obtained like that found in water solution with almost the same time window, although with some peculiarities. In ice phase dealkylation, and particularly *N*-dealkylation, is the favoured reaction. Formation of TP **164** (*N*-dealkylated DEET) is strongly favoured and it becomes the main TP. Additionally, compared to the other conditions, formation of TP **180** becomes favoured too. TPs temporal profiles evidence a fast production of compound **164**, formed through *N*-dealkylation, followed later by hydroxylation with subsequent formation of TP **180**. Dealkylation occurring in frozen aqueous solutions, could involve oxygen; singlet oxygen formed by sensitization of  $^3\text{O}_2$  by triplet excited species may be a reactant [22]. Besides, the formation of dihydroxy derivatives is prevented in ice.

In attempt to clarify the mechanism involved in the **164** and **180** species, experiments were repeated in ice and water (20 °C) with different DEET concentrations (10 or 20 mgL<sup>-1</sup>) and the intermediates profiles are plotted in Figure S2-S7 as supplementary material. By changing the initial DEET concentration, remarkably changes in the **164** concentrations are observed, so that it could be proposed the **164** formation in ice through an intermolecular electron transfer from N-atom of DEET to the phenylcarbonyl group of DEET, via a common photoinduced process [41], and subsequent dark transformations. It is a concentration dependent process and should be more

pronounced in ice, due to the concentration effect, so accounting for the increased concentration of **164**.

All TPs recognized during photolysis experiments may be linked through the transformation pathways summarized in Scheme 1.

A comparison of TPs formed during the photolysis in solution (Figure 2) and in ice (Figure 4) evidence the occurrence of two main pathways, namely hydroxylation (to form **208**) and dealkylation (to obtain **164**) occurring in the two phases, while the formation of TP **222**, **240** and **244** takes only place in solution or in melted water. Key differences between the two system clearly arise when comparing the main TPs relative ratios detected in ice or water, as shown in Figure 5. From the graph it can be clearly seen that the formation of compound **164** and, at longer irradiation time, **180** mostly occurs by photolysis in ice phase. TP **208** is similarly formed in both matrices, with **208-D** only exception. However, the relative TPs ratio **164/208** overtakes from 0.25 (in solution) to 0.35 (melted water) and 13 (in ice), while **180/208** increases from  $2.5 \times 10^{-3}$  (ice) to  $2.8 \times 10^{-3}$  (melted water) and 0.27 (water), so providing a discriminating item helpful in the attribution of the DEET sources.



**Scheme 1.** Proposed DEET's transformation pathways under UV irradiation.

The overall presented data permits to identify path 2 (see Scheme 1) as a peculiar transformation route occurring in ice, while paths 1,3 and 4 should be ascribed to photolysis in solution. TPs **164** and **180-B** could be therefore utilized as a marker of cold environment photolysis. By evaluating the relative ratio among this compound and other TPs formed in river water through abiotic degradation (path 2 and 3), discrimination on the DEET sources could be conceivable.

### 3.3. In field analysis

In field analysis were performed in snow and river samples. A broad-spectrum of qualitative analysis was executed on all samples, aimed to be aware of the overall organic matter and pollutants content (data not shown). Quantification of DEET was carried out on all samples and data are collected in Table 1; snow and river water samples highlighted the presence of DEET, whose concentrations depend on diverse seasons and matrices. As expected, in river water DEET concentration is maxima in summertime (average concentration 97 ppt), but its presence is evidenced also in winter samples (12 ppt). Interestingly, DEET was also detected in snow samples, at a concentration level higher in fresh snow (42 ppt) rather than in snow subjected to solar light exposure (21 ppt).

DEET's TPs were also searched for in all samples. In wintertime, no TPs were recognized neither in snow or in river water, reasonably due to the lower DEET concentration and to the scarce occurrence of photolysis process.

In summertime key TPs were identified in river water, i.e. the hydroxyl-derivative and oxo-derivatives, whose formation was mainly attributed to indirect photolysis processes [13]; for TPs analytical standard were not available and a quantitative analysis cannot be performed. TPs **222-B** and **222-C** (hydroxylation and oxidation) were formed as main products, while several other TPs (**208-A** and **B**, **164**, **180**, **210-A**, **210-B** and **210-C**) were detected at lower amount [13]. This is well matched with data obtained under UV irradiation at 20 °C, where the key pathway passes through the polyhydroxylation/oxidation processes; the predominance of pathway 3 (see Scheme 1) in summertime underlines the importance of photolysis processes.

## Conclusions

Through the different photolysis tests and the use of a high-resolution MS technology, the different paths of transformation occurring in aqueous and solid phase have been clarified.

This study evidences the potential for abiotic processes to differently contribute to DEET transformation in temperate or cold environments. Identification of degradation products can provide information about which type of process took place for DEET transformation. *N*-dealkylated TPs could be used as a marker of a photolysis process occurring in frozen phase. This raises the issue that these compounds are likely to be formed in sunlit snow and ice, complimenting other formation routes in the environment, such as photo-oxidation in the atmosphere and surface waters. The combined effects of prolonged sunlight exposure during spring/summer and the potential for enhanced reactivity on snow and ice could make photochemical degradation of DEET in snow-covered environments an important transformation route.

Conversely, in aqueous phase hydroxylation and oxidation processes prevail and became the main transformation route occurring in summertime in temperate climate.

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**Table 1:** DEET concentration in the different environmental samples.

Sample	DEET (ng l <sup>-1</sup> )
Snow	<b>42 ± 4</b>
Snow after sunny day	<b>21± 4</b>
River water (summer)	<b>97.6± 4</b>
River water (winter)	<b>12± 2</b>

## Figure captions

**Figure 1.** DEET ( $40 \text{ mgL}^{-1}$ ) degradation in ice (-15 °C), m.p. water (0 °C) and water (20 °C) under UV-illumination.

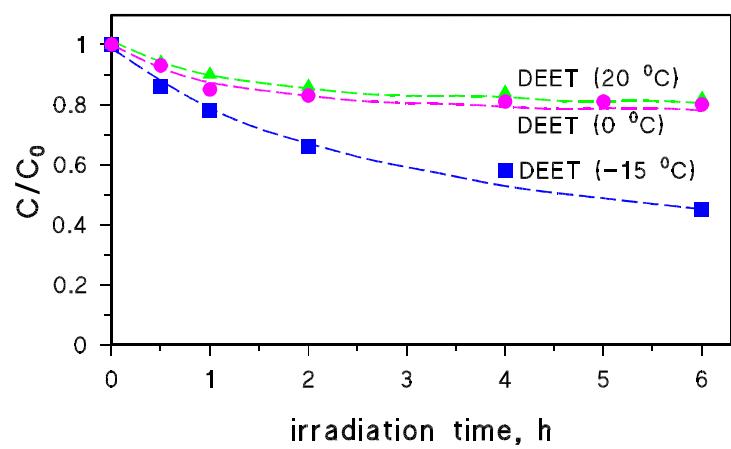
**Figure 2:** TPs formed under DEET ( $40 \text{ mgL}^{-1}$ ) irradiation at 20 °C in water: top) main TPs; bottom) secondary TPs.

**Figure 3:** TPs formed under DEET ( $40 \text{ mgL}^{-1}$ ) irradiation at 0 °C: top) main TPs; bottom) secondary TPs.

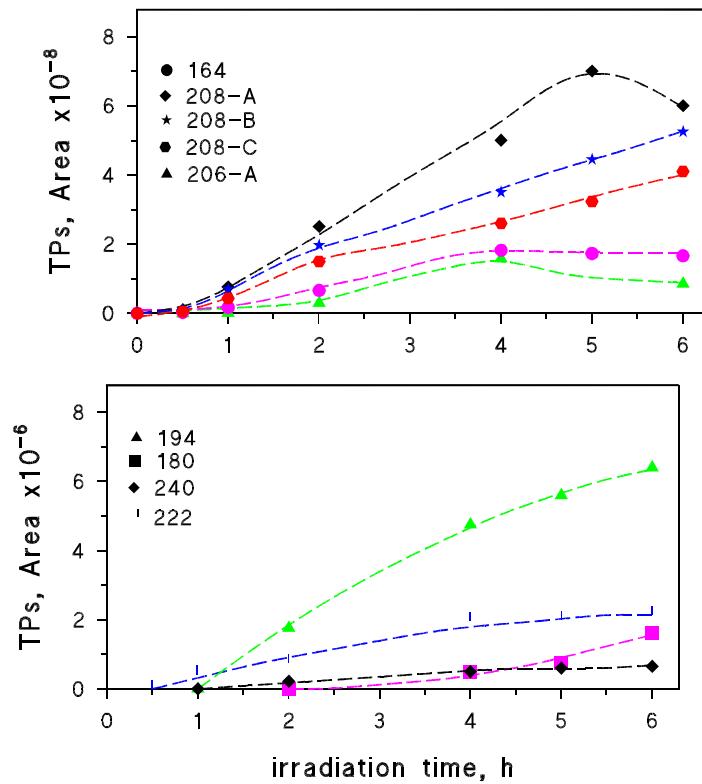
**Figure 4:** TPs formed under DEET ( $40 \text{ mgL}^{-1}$ ) irradiation at -15 °C in ice: top) main TPs; bottom) secondary TPs.

**Figure 5:** Relative ratio among key TPs formed through photolysis in solution and ice.

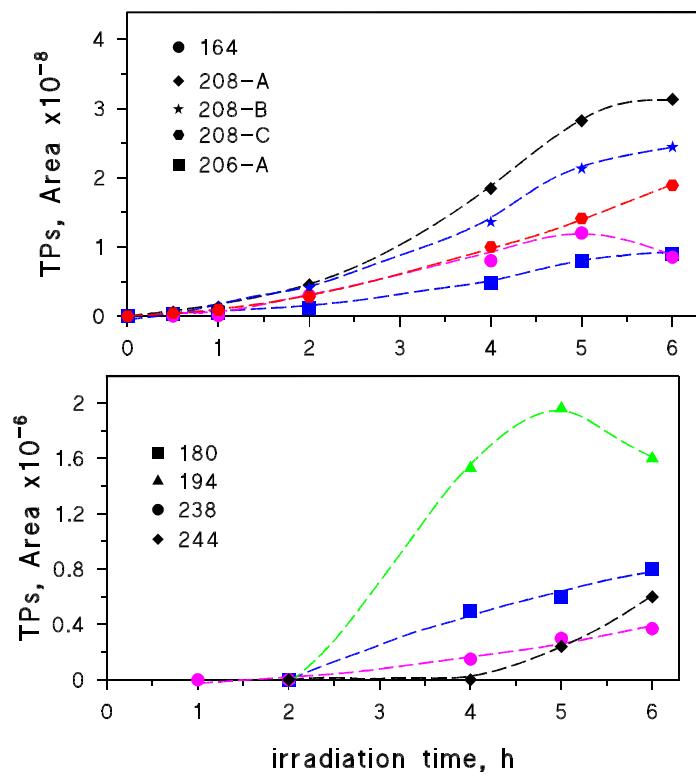
**Figure 1.**



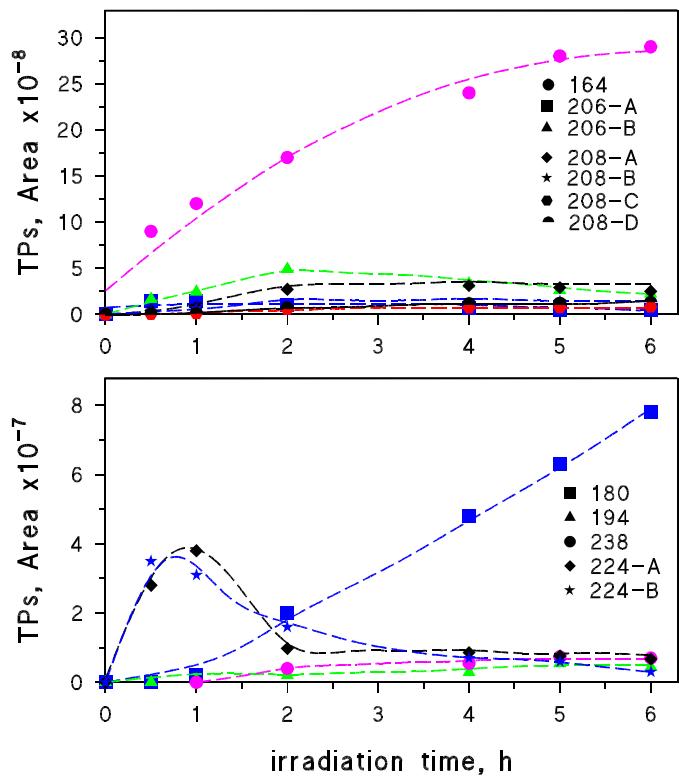
**Figure 2**



**Figure 3**



**Figure 4**



**Figure 5**

