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Photochemical transformation of atrazine and formation of photointermediates under conditions relevant to sunlit surface waters: Laboratory measures and modelling

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ABSTRACT

By combination of laboratory experiments and modelling, we show here that the main photochemical pathways leading to the transformation of atrazine (ATZ, 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) in surface waters would be direct photolysis, reaction with $\cdot\text{OH}$ and with the triplet states of chromophoric dissolved organic matter ($^3\text{CDOM}^*$). Reaction with $^3\text{CDOM}^*$ would be favoured by elevated water depth and dissolved organic carbon content, while opposite conditions would favour direct photolysis and $\cdot\text{OH}$ reaction. Desethylatrazine (DEA, 4-amino-2-chloro-6-isopropylamino-1,3,5-triazine) was the main detected intermediate of ATZ phototransformation. Its formation yield from ATZ (ratio of DEA formation to ATZ transformation rate) would be 0.93 ± 0.14 for $\cdot\text{OH}$, 0.55 ± 0.05 for $^3\text{CDOM}^*$, and 0.20 ± 0.02 for direct photolysis. Direct photolysis and $\cdot\text{OH}$ reaction also yielded 4-amino-2-hydroxy-6-isopropylamino-1,3,5-triazine (DEAOH) and 6-amino-2-chloro-4-ethylamino-1,3,5-triazine (DIA). Reaction with excited triplet states also produced 2-hydroxy-4,6-diamino-1,3,5-triazine (AN) and 2-chloro-4,6-diamino-1,3,5-triazine (CAAT). Therefore, if biological processes can be neglected and if the low formation yields do not prevent detection, DEAOH and DIA could be used as markers of ATZ direct photolysis and $\cdot\text{OH}$ reaction, while AN and CAAT could be markers of ATZ reaction with $^3\text{CDOM}^*$. Model predictions concerning ATZ phototransformation were compared with available field data from the literature. When sufficiently detailed field information was provided, good agreement was found with the model.

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1. Introduction

Atrazine (ATZ) is a triazine herbicide that is mainly intended to control broadleaf and some grassy weeds. For this reason it is extensively used in agricultural applications to corn and rice, but substantial use is also made in the case of sorghum and sugarcane. Moreover, ATZ is widely applied on non-agricultural sites such as lawns and turf. As far as the mode of action is concerned, ATZ blocks electron transport in chloroplast's photosystem II complex, thereby preventing CO₂ fixation and subsequent energy production. Plant death occurs mostly by desiccation following membrane damage, because of formation of reactive species (¹O₂ and triplet-state chlorophyll) that trigger a chain reaction of lipid peroxidation (Brassard et al., 2003).

The quite high water solubility of ATZ (33 mg L⁻¹; Mudhoo and Garg, 2011) favours the occurrence of this compound in surface and ground water, where it often exceeds the 10 µg L⁻¹ level of concern for aquatic ecosystems (USEPA, 2012). ATZ is moderately to slightly toxic to many fish species, and somewhat less toxic to aquatic invertebrates (Brassard et al., 2003; USEPA, 2012). Due to its intended use as an herbicide, ATZ is understandably highly toxic to aquatic vascular plants and algae (USEPA, 2012). As far as human health is concerned, the main risk related to ATZ exposure is connected to its endocrine-disruption capabilities (USEPA, 2012; Forgacs et al., 2012).

Although presently forbidden in the European Union, ATZ is still detected in EU countries (Silva et al., 2012; Bono-Blay and Guart, 2012), probably because of persistence in ground water that may act as source for surface water and soil. Moreover, some illegal ATZ use cannot be excluded. More importantly, ATZ is extensively applied worldwide in both developed and developing countries (Bhullar et al., 2012; Reilly et al., 2012; Wang et al., 2012; Zhang et al., 2012).

Biotransformation and phototransformation are the main known pathways of ATZ removal from the environment. They produce a number of transformation intermediates such as desethylatrazine (DEA), desisopropylatrazine (DIA), chlorodiaminotriazine (CAAT), ammeline (AN), hydroxyatrazine (ATOH) and cyanuric acid (CYA) (Torrents et al., 1997; Larson et al., 2004; Mudhoo and Garg, 2011; see Table 1 for the structure of the cited compounds). Among photochemical pathways, direct photolysis and [•]OH reaction have received most attention to date (Torrents et al., 1997; Acero et al., 2000; Balci et al., 2009).

A proper modelling of pollutant photochemical fate in surface waters requires a quantitative assessment of additional pathways, such as reaction with CO₃⁻, ¹O₂ and most notably the triplet states of chromophoric dissolved organic matter (³CDOM*) (Latch et al., 2003; Canonica et al., 2005, 2006; Halladja et al., 2007). Humic acids (HAs) have been shown to enhance or inhibit ATZ phototransformation (Minero et al., 1992; Prosen and Zupancic-Kralj, 2005; Garbin et al., 2007; Ou et al., 2009; Sun et al., 2011). This may happen because HAs compete with ATZ for irradiance, thereby inhibiting direct photolysis, and scavenge photogenerated transients such as [•]OH. However, HAs might also photosensitize ATZ degradation through the reaction of their triplet states (Hartenbach et al., 2008). Quantitative reactivity data are needed to assess the actual environmental importance of ATZ transformation

by natural sensitizers. Moreover, formation yields are required to model the photochemical production of transformation intermediates under environmental conditions (De Laurentiis et al., 2012). In the case of ATZ, such a task can be greatly favoured by the commercial availability of many known or potential phototransformation intermediates, which allows easy measurement of formation yields.

The present work has the purpose of modelling the photochemical fate of ATZ in surface waters. Reaction kinetic parameters were experimentally determined together with yields of major intermediates, which are formed via the main pathways of ATZ photoinduced transformation. The goal was to identify conditions that would favour or hamper ATZ phototransformation and intermediate formation, as well as to compare model predictions with field data.

2. Experimental

2.1. Reagents and materials

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, ATZ), 2-chloro-4,6-diamino-1,3,5-triazine (CAAT), 2-hydroxy-4,6-diamino-1,3,5-triazine (ammelina, AN), 6-amino-4-ethylamino-2-hydroxy-1,3,5-triazine (DIAOH), 4-amino-2-hydroxy-6-isopropylamino-1,3,5-triazine (DEAOH), 6-amino-2-chloro-4-ethylamino-1,3,5-triazine (DIA), 4-amino-2-chloro-6-isopropylamino-1,3,5-triazine (DEA) and 4-ethylamino-2-hydroxy-6-isopropylamino-1,3,5-triazine (ATOH) were all Pestanal grade from Aldrich. Cyanuric acid (2,4,6-trihydroxy-1,3,5-triazine, CYA, purity grade 98%), antraquinone-2-sulphonic acid sodium salt (AQ2S, 97%), sodium hexanesulphonate (>99%) and H₃PO₄ (85%) were purchased from Aldrich, H₂O₂ (30%), NaNO₃ (>99.5%) and NaHCO₃ (99%) from VWR Int., methanol (gradient grade) from Carlo Erba (Rodano, Italy), Rose Bengal from Alfa Aesar. Water used was of Milli-Q quality.

2.2. Irradiation experiments

Irradiation experiments were carried out on synthetic solutions prepared by dissolving the relevant compounds in Milli-Q water. The stock ATZ solution (0.1 mM) was prepared by dissolving the solid in water, without use of organic solvents that could introduce a bias in irradiation experiments in the presence of photoreactive transients. Solutions to be irradiated (5 mL volume) were placed inside cylindrical Pyrex glass cells (4.0 cm diameter, 2.5 cm height) having a lateral neck tightly closed with a screw cap. Cells were magnetically stirred during illumination, which took place mainly from the top. The direct photolysis of 20 µM ATZ was studied upon ultraviolet-B (UVB, 290–320 nm) irradiation under a 20 W Philips TL 01 RS lamp (emission maximum at 313 nm). The incident irradiance over the solutions was $9.8 \pm 0.2 \text{ W m}^{-2}$ between 290 and 400 nm, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter. The incident photon flux into irradiated solutions was $(6.4 \pm 0.1) \cdot 10^{-6} \text{ E L}^{-1} \text{ s}^{-1}$. It was actinometrically determined using the ferrioxalate method (Kuhn et al., 2004), taking into account the wavelength-dependent

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