



Evaluation of nitrate effects in the aqueous photodegradability of selected phenolic pollutants



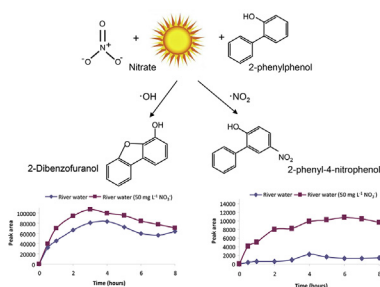
G. Castro, I. Rodríguez*, M. Ramil, R. Cela

Departamento de Química Analítica, Nutrición y Bromatología, Instituto de Investigación y Análisis Alimentario (IIAA), Universidad de Santiago de Compostela, Santiago de Compostela 15782, Spain

HIGHLIGHTS

- Assessment of nitrate effects in the photodegradability of phenolic pollutants.
- Half-lives determination and transformation products elucidation by LC-QTOF-MS.
- Enhanced UV and solar photodegradability in presence of nitrate anions.
- Identification of nitro addition and cleavage transformation products.
- Favourable formation of stable nitro derivatives of *o*-phenylphenol.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of nitrate in the aqueous photodegradation of five phenolic environmental pollutants (*ortho*-phenylphenol, OPP; methyl paraben, MeP; propyl paraben, PrP; Triclosan, TCS and bisphenol A, BPA) is evaluated. Time-course of precursor compounds and formation of transformation products (TPs) were investigated by liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QTOF-MS). Nitrate showed a positive effect in the removal of pollutants. Observed TPs resulted from hydroxylation, aromatic nitration (with or without molecule cleavage) and nitro dehalogenation processes. The above reactions involved the participation of $\cdot\text{OH}$ and $\cdot\text{NO}_2$ radicals arising from photolysis of nitrate. Nitro TPs were produced in a different extent depending on the structure of the precursor pollutant, nitrate concentration, light source (254 nm UV and solar light) and water matrix (ultrapure, surface and urban wastewater). Some of these nitro TPs were also observed during UV irradiation of untreated and unbuffered wastewater, either naturally polluted with parent phenolic compounds or spiked with these species at the sub $\mu\text{g L}^{-1}$ level. Nitration reactions were particularly favourable for OPP with the generated nitro TPs displaying a higher stability than the precursor molecule and the hydroxylated TPs of the same compound.

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1. Introduction

Attention paid to the determination of emerging pollutants in the aquatic environment has increased exponentially in the last two decades. On the other hand, data for their transformation products (TPs), generated through chemical, photochemical and

* Corresponding author.

E-mail address: isaac.rodriguez@usc.es (I. Rodríguez).

microbial processes, are still limited (Blestou et al., 2015; Aguera et al., 2013). Quite often, TPs show relevant structural changes in comparison to precursor pollutants; thus, their further fate and potential environmental risks merit to be assessed.

Nitration reactions are recognized as potential sources of concerning TPs in water (Chiron et al., 2009), sludge (Chiron et al., 2010; Osorio et al., 2016) and atmospheric compartments (Takayuki, 2011). Aromatic pollutants, particularly phenolic compounds, are prone to interact with nitrogen reactive species. In this vein, it has been recently reported the formation of nitro derivatives of bisphenol A (BPA), and other alkylphenols, during activated sludge treatment of urban wastewater (Sun et al., 2012). The source of these TPs was the reaction between parent pollutants and nitrite, which is generated from microbial oxidation of ammonia during wastewater treatment. Additional studies have demonstrated the formation of nitro and/or nitroso TPs from other aromatic pollutants during biological treatments at sewage treatment plants (STPs) (Jewell et al., 2014; Nödler et al., 2012).

Nitration reactions can be also photochemically promoted. As example, formation of nitrophenols has been noticed in agriculture fields treated with phenoxyacid herbicides (Chiron et al., 2009). Nitrate anions, existing in irrigation water, produce $\cdot\text{NO}_2$ radicals through solar photodecomposition. These radicals further react with the intermediate degradation products of phenoxyacid herbicides (phenols) to generate toxic and stable nitrophenols (Chiron et al., 2009). Thorough studies on the molecular mechanisms and the kinetics of the different processes involved in the formation of nitro derivatives from phenol and chlorophenols have been widely investigated in the literature (Vione et al., 2007; Bedini et al., 2012). Parameters such as the water pH, the concentration of dissolved natural organic matter and the presence of inorganic anions exert complex effects in the yield of the above reactions for phenols, affecting the kinetics of direct photolysis and indirect reactions involving nitro radicals (Vione and Chiron, 2014). In addition to phenolic species, the existence of photonitration reactions has been also described for phenyl urea and aniline pyrimidine pesticides (Shankar et al., 2007; Rodríguez-Cabo et al., 2016). The photochemical decomposition of nitrates generates not only $\cdot\text{NO}_2$, but also $\cdot\text{OH}$ radicals (eq. (1)), which are involved in the transformation and/or the mineralization of any organic compound (Vione et al., 2014).



The aim of this research was to investigate whether nitrate, at concentrations in the range of values expected in surface and wastewater samples, affects the photodegradation kinetics of selected pollutants and/or leads to formation of nitro TPs, or not. Experiments were carried out with five phenolic species employed as preservatives and bactericides in personal care products: methyl paraben (MeP), propyl paraben (PrP) and Triclosan (TCS); household and hospital disinfection products, as well as in the fruit processing industry: *ortho*-phenylphenol (OPP); and monomers in the production of polymeric materials: bisphenol A (BPA). All of them are recognized as ubiquitous in different compartments of the aquatic environment (Lee et al., 2005; Yu et al., 2011). In addition to model experiments with ultrapure water, two different scenarios were considered: (1) UV irradiation of sewage water, and (2) surface water exposed to natural sunlight. Although previous data for the photo reactivity of some of the above pollutants in presence of nitrate are available (Sarakha et al., 1993), they correspond to assays carried out in ultrapure water solutions, with nitrate levels three orders of magnitude higher than those expected in any surface or urban wastewater sample. Efforts are focussed on the identification of TPs and on assessing their potential formation under real-life

situations.

Liquid chromatography (LC) separation followed by accurate mass spectrometry (MS) detection, based on a hybrid quadrupole time-of-flight (QTOF) MS system, was employed as analytical technique to follow the degradation kinetics of precursor pollutants, to detect possible TPs and to elucidate their structures from information contained in the accurate MS and the product ion (MS/MS) spectra (Blestou et al., 2015; Sancho et al., 2006). In-silico estimated toxicities, for some of the identified TPs, are also provided and compared to those assigned to the corresponding precursor species.

2. Material and methods

2.1. Standards, solvents and sorbents

OPP (99%), BPA (100%), MeP (99%), PrP (99%) and TCS (99%) were obtained from Sigma-Aldrich (Milwaukee, WI, USA). A standard of 4-phenylphenol was provided by the same supplier. Individual stock solutions of the above compounds were prepared in methanol and stored at 4 °C. Diluted solutions were made in the same solvent.

Methanol, HPLC-grade; ethyl acetate, trace analysis quality; and sodium nitrate were provided by Merck (Darmstadt, Germany). Ultrapure water was obtained from a Milli-Q system provided by Millipore (Billerica, MA, USA). OASIS HLB solid-phase extraction (SPE) cartridges (60 mg) were purchased from Waters (Milford, MA, USA).

Surface water was obtained from a small river in the Northwest of Spain. Grab samples of raw and treated wastewater were collected at the inlet and outlet streams of an urban STP equipped with primary and biological (activated sludge) treatment units. After reception, samples were passed through glass fibre and cellulose (0.45 μm pore size) filters, allowed to equilibrate at room temperature (20 ± 2 °C), and used in photodegradation experiments. Filtered samples were characterized in terms of dissolved organic carbon (DOC), nitrates and other anions. DOC values ranged between 1.4 and 5.6 mg L^{-1} , and nitrate varied from 4.7 to 36.3 mg L^{-1} . Further details about the composition of these samples are provided as supplementary information, Table S1. The pH of the river water was 6.8 and that of treated wastewater 7.1.

2.2. Phototransformation experiments

Photolysis was carried out using ultrapure, surface and wastewater matrices. Spiked water samples were directly prepared in the quartz tubes (o.d. 30 mm, 200 mm length, Afora, Barcelona, Spain) employed in the photolysis experiments. To this end, a methanolic standard solution (0.1–0.5 mL) of the investigated compound was poured into the tube, the organic solvent was evaporated with a gentle stream of nitrogen, and 20 mL of the selected water matrix (previously spiked with NaNO_3 , when required, and stabilized to 20 ± 2 °C) were added. Tubes were vortexed for 5 min and exposed to the considered light source. Unless otherwise stated, unbuffered water samples spiked with precursor compounds at 0.5 mg L^{-1} were used. In this series of photolysis experiments (considering high concentrations of precursor species) water aliquots (1 mL) were withdrawn at different times, transferred to 1 mL autosampler vials (containing 0.1 mL of methanol as quencher of reactive radical species), and injected in the LC-QTOF-MS system within the next 24 h.

Nitrate levels added to the water samples were in the range of 25–50 mg L^{-1} , equivalent to 50 and 100% the maximum allowable concentration of this anion in surface water intended for tap water production. UV irradiation experiments were carried out in a

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