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Degradation of indomethacin in river water under stress and non-stress laboratory conditions: Degradation products, long-term evolution and adsorption to sediment

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ABSTRACT

The pharmaceutical compound indomethacin is not totally removed in wastewater treatment plants, whose effluents flow into aquatic environments; concentrations in the 0.1–100 ng/L range are commonly found in surface waters, and its fate is unknown. Here, biological, photochemical and thermal degradation assays were conducted under stress and non-stress conditions to estimate its degradation rate in river water and establish its degradation products over time. The results revealed that direct sunlight irradiation promoted the complete degradation of indomethacin (2 μg/L) in less than 6 hr, but indomethacin was detected over a period of 4 months when water was kept under the natural day–night cycle and the exposure to sunlight was partially limited, as occurs inside a body of water. The biological degradation in water was negligible, while the hydrolysis at pH 7.8 was slow. Residues were monitored by ultra-pressure liquid chromatography/quadrupole time-of-flight/mass spectrometry after solid-phase extraction, and six degradation products were found; their structures were proposed based on the molecular formulae and fragmentation observed in high-resolution tandem mass spectra. 4-Chlorobenzoic and 2-acetamido-5-methoxybenzoic acids were the long-term transformation products, persisting for at least 30 weeks in water kept under non-stress conditions. Furthermore, the degradation in the presence of sediment was also monitored over time, with some differences being noted. The adsorption coefficients of indomethacin and degradation products on river sediment were calculated; long-term degradation products did not have significant adsorption to sediment.

Introduction

The presence of pharmaceutical compounds in the environment is a matter of increasing concern because they impact negatively on the environment. The effluents discharged from wastewater treatment plants (WWTPs) are the main introduction source of pharmaceuticals in surface waters. These compounds are found in the influents of the WWTPs mainly as a result of the inappropriate domestic disposal of unused medicinal products. Indomethacin (INDO) is a non-steroid

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anti-inflammatory drug detected in the primary influents that reach the WWTPs in concentrations, generally, of 20–100 ng/L, although concentrations of about 1 μg/L have also been reported (Sui et al., 2009; Radjenovic et al., 2009). Concentrations of about 10–20 ng/L have been found in depurated effluents (Zhou et al., 2009). In river water, INDO concentrations between 0.1 and 100 ng/L are frequent (Kim et al., 2009; Lewandowski et al., 2011; Yamamoto et al., 2009; Zhou et al., 2009). Concerning the efficiency of WWTPs at removing INDO, there are contradictory data; some authors have concluded that its removal in the global process is non-existent or slight (Radjenovic et al., 2009; Rosal et al., 2010; Sui et al., 2009; Tran et al., 2014), while other authors find that the removal rates are about 40%–100% (Huang et al., 2011; Matsuo et al., 2011; Zhou et al., 2009). Moreover, it has been stated that INDO infiltrates to subsurface waters (1 m depth) from surface waters, as has occurred for other pharmaceuticals (Lewandowski et al., 2011).

The frequent detection of INDO in surface waters and WWTP effluents discharged into rivers advises us not only to evaluate its persistence in the environment, but also to determine the possible transformation products in order to obtain an overall perspective and to assess possible risks, because the effects resulting from exposure to the parent pharmaceutical and the degradation products can be different (Celiz et al., 2009). So, INDO dissolved in different media has been subjected to degradation studies under stress conditions that indicate its photolability, and some degradation products generated in these conditions have been described (Temussi et al., 2011; Yamamoto et al., 2009), but there is no reliable information about its behavior in surface water and especially about its long-term fate in non-stress conditions.

In this context, river water spiked with INDO at trace levels was subjected to degradation studies in this work to ascertain the importance of the chemical, photochemical and biological processes in its degradation in surface water. In addition to assays under stress conditions, non-stress conditions were also applied to INDO in aqueous solution in order to simulate its behavior inside a body of water. Water aliquots were analyzed by ultra-pressure liquid chromatography/quadrupole time-of-flight/mass spectrometry, and the structures of the degradation products found were tentatively elucidated from the molecular formulae and fragmentation observed in high-resolution tandem mass spectra. The evolution of the degradation products was also monitored over time to estimate their occurrence, and a degradation pathway was outlined. In addition, the adsorption capacity of sediment for INDO and its degradation products was evaluated by calculating the corresponding adsorption coefficients.

1. Experimental

1.1. Materials and reagents

Water samples were collected from the rivers Pisuerga (pH value 7.8, chemical oxygen demand value 4.6 mg/L), in the urban area of the city of Valladolid, and Tuerto (pH value 7.4, chemical oxygen demand value 3.9 mg/L), in the rural area of the La Bañeza, province of León; chemical oxygen demand was determined by the potassium dichromate method. A sediment sample (total organic carbon 1.2%; clay 11%, silt 44%, sand 45%) was collected from the river Pisuerga. Total organic carbon was measured by a combustion method with a LECO CS-225 elemental analyzer (St. Joseph, MI, USA). Sediment particle size analysis was based on the Bouyoucos hydrometer method; soil aggregates were dispersed by chemical means.

Cellulose nitrate disks from Sartorius (Barcelona, Spain) were used: river water was filtered through 0.2 μm pore-size disks for the estimation of adsorption coefficients, through 3 μm pore-size disks to carry out biodegradation experiments, and through 0.45 μm pore-size disks for other degradation experiments.

Indomethacin (99% purity) was obtained from Sigma-Aldrich (St. Louis, MO, USA). LC–MS grade methanol, acetonitrile and formic acid were supplied by Panreac (Barcelona, Spain) and ultrapure water was obtained from a Milli-Q plus apparatus (Millipore, Milford, MA, USA). Analysis-grade sodium hydroxide, potassium dihydrogen phosphate and sodium azide were purchased from Panreac. EBH cartridges (60 mg) for solid-phase extraction (SPE) and PTFE disposable syringe filter units, 0.20 μm pore size, were obtained from Scharlab (Barcelona, Spain). Tryptone soya broth (TSB), a highly nutrient liquid culture medium for general purpose use, was purchased from Scharlab; its composition can be seen in the supplementary material (Appendix A Table S1). A vacuum centrifuge evaporator, Myvac model, was provided by Genevac (Ipswich, UK), a PK120 centrifuge by ALC (Winchester, VA, USA) and a Promax 2020 reciprocating platform shaker by Heidolph (Germany).

1.2. Biological degradation

1.2.1. Aerobic degradation

Biological degradation assays were carried out with water from the river Pisuerga (pH 7.8) which was spiked with INDO to achieve a concentration of 2 μg/L. A volume of 50 mL of river water was transferred into a 100 mL Erlenmeyer flask, which was then coated with aluminum foil to avoid exposure to sunlight but allowing the exchange of air with the atmosphere. An INDO control solution was similarly prepared in ultrapure water (pH 7.8 adjusted with NaOH) containing 0.02% (W/V) sodium azide as a biocide. Water blanks were prepared as well. Samples were run in parallel; flasks were shaken in a reciprocating shaker at a rotation speed of 130 r/min for 5 weeks, within a temperature range of 18–21°C. Aliquots of 5 mL were collected each week and subjected to analysis. Evaporation water losses were periodically restored by addition of water of the same type. All biological experiments were carried out in duplicate.

1.2.2. Anaerobic degradation

River water (pH 7.8) spiked at 2 μg/L was placed in 15 mL vials, completely filled to avoid the presence of air in the headspace. The vials were closed, protected from light by coating them with aluminum foil and kept in a temperature range of 18–21°C during experimentation. Control solutions with INDO in ultrapure water (pH 7.8 adjusted) containing 0.02% sodium azide, and the corresponding blanks, were also run in parallel. A batch of vials was assembled to withdraw weekly samples over a period of 5 weeks; a volume of 5 mL from each withdrawn vial was collected for analysis.