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Occurrence and analysis of parabens in municipal sewage sludge from wastewater treatment plants in Madrid (Spain)

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HIGHLIGHTS

- Analysis of emerging contaminants, seven parabens and two by-products, in sludge.
- Paraben levels in sewage sludge from 19 WWTPs located in the region of Madrid.
- Methylparaben and propylparaben were the main parabens detected in sludge.
- Occurrence and time-course of parabens in samples from WWTPs during four years.

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ABSTRACT

A rapid method for determination of seven parabens and two chlorinated by-products in sewage sludge was developed based on matrix solid-phase dispersion and gas chromatography–tandem mass spectrometry. The analytical procedure showed good recoveries that ranged from 80 to 125%, with relative standard deviations lower than 12% and low detection limits, ranging from 0.1 to 2.0 ng g^{-1} dry weight. The developed method was applied to the analysis of sewage sludge collected during 2010 in 19 wastewater treatment plants (WWTPs) located in various urban, industrial or rural zones in Madrid (Spain). Methylparaben was found in most of the WWTPs sampled (95%) at levels between 5.1 and 26.2 ng g^{-1} dry weight and propylparaben was detected in 74% of the WWTPs at levels up to 44.1 ng g^{-1} dry weight. In order to study the temporal variation of parabens and two chlorinated parabens during a four-year period, sludge samples were collected from 3 selected WWTPs. The levels of methylparaben encountered were rather constant throughout the sampling period whereas propylparaben levels slightly increased. In one of the WWTPs monitored, isopropylparaben was found at the beginning of the sampling period but its content decreased and was not detected in the 2010 sampling.

1. Introduction

Pharmaceutical and personal care products, widely used around the world, are continuously released through wastewater and transported to wastewater treatment plants (WWTPs) where they can escape conventional treatment processes. Thus, these emerging contaminants have been found in treated water and sewage sludge, although in low amounts (ppm or ppb) [1,2].

The use of advanced technologies in secondary and tertiary wastewater treatment processes, such as membrane filtration, powdered activated carbon or ozonation are effective at removing these products [3,4]. Nevertheless, most WWTPs still use conventional treatment processes and it is important to know the occurrence and removal of emerging contaminants after WWTP treatment processes.

Parabens are hydroxybenzoate esters widely used as preservatives in pharmaceutical, personal care and food products. In the European Union (EU), the use of parabens in cosmetics is limited to a maximum concentration of 0.4% (w/w) for one type of parabens and of 0.8% (w/w), expressed as p-hydroxybenzoic acid for paraben mixtures [5]. Although these compounds are readily biodegradable under aerobic conditions, they could be considered “pseudo persistent” contaminants due to the high consumption and continuous introduction into the environment. Hardly any data are

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Abbreviations: BSTFA, N,O-bis(trimethylsilyl)trifluoroacetamide; BuP, butylparaben; BzP, benzylparaben; EI, electron impact; EtClP, ethylchloroparaben; EtP, ethylparaben; GC–MS/MS, gas chromatography–tandem mass spectrometry; iBuP, isobutylparaben; iPrP, isopropylparaben; LC–MS/MS, liquid chromatography–tandem mass spectrometry; LOD, limit of detection; LOQ, limit of quantification; MDL, method detection limit; MeClP, methylchloroparaben; MeP, methylparaben; MRM, multiple reaction monitoring; MSPD, matrix solid-phase dispersion; MTBSTFA, N-methyl-N-tert-butyldimethylsilyl-trifluoacetamide; PLE, pressurized liquid extraction; PrP, propylparaben; RSD, relative standard deviation; SMEs, small–medium enterprises; TMCS, trimethylchlorosilane; TS, time segment; UAE, ultrasonic assisted extraction; WWTPs, wastewater treatment plants.

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available on the environmental occurrence of parabens. Regarding their toxicological effects, these compounds have shown estrogenic activity and are potentially toxic for certain aquatic organisms [6]. Parabens, which contain a phenolic hydroxyl group, may produce chlorinated degradation by-products when they come in contact with chlorinated water as in tap and swimming pool water. In a recent study, chlorinated parabens were detected and quantified in swimming pool water, and it was suggested that these by-products were originated when personal care products containing parabens reached chlorinated water. Tesaraki and Makino [7] indicated that the chlorinated derivatives were considerably more toxic for aquatic organisms, such as *Daphnia magna*, than the corresponding parent compounds.

Different methods have been reported for the determination of parabens in environmental samples, such as water [8–10], sewage influents and effluents [11], dust [12,13] and soil [14–16], however, hardly any data are available on the environmental occurrence of parabens or some of their chlorinated by-products in sewage sludge [2]. This could be due to the high complexity of the matrix, which requires very selective analytical techniques such as liquid or gas chromatography coupled to tandem mass spectrometry (LC–MS/MS or GC–MS/MS).

Due to the polar nature of these compounds, a derivatization step is highly recommended to improve their chromatographic response when gas chromatography is applied. To carry out this step, silylation using N-methyl-N-tert-butyldimethylsilyl-trifluoacetamide (MTBSTFA) [10] and acetylation using acetic anhydride [9] have been reported for the derivatization of parabens. Regarding the extraction of parabens from environmental solid samples, matrix solid-phase dispersion (MSPD), pressurized liquid extraction (PLE) and ultrasonic assisted extraction (UAE) have been applied [12–14]. PLE and UAE are two modern extraction techniques that provide a significant reduction in solvent consumption and are less time-consuming than traditional extraction procedures; although with complex matrices, as sewage sludge, the application of pressure or ultrasonic energy not only ensures a more efficient extraction of the target analytes, but also a possible increase in the extraction of potential interferences. In this way, MSPD is an extractive technique that allows the simultaneous extraction and clean-up of analytes with a significant reduction in solvent consumption, is easy and simple to use and does not require special expensive instrumentation. MSPD has been successfully applied in our previous works to the determination of some organic pollutants in sewage sludge [17,18].

The aim of this work was to develop a quick and selective analytical method to carry out the determination of seven parabens and two chlorinated by-products in sewage sludge by GC–MS/MS and to study their occurrence in sewage sludge collected during 2010 in 19 WWTPs located in Madrid with different characteristics according to their population and activities (industrial or rural). In addition, the temporal variation of these compounds in sewage sludge was also investigated by collecting samples from 3 selected WWTPs during a four-year period.

2. Experimental

2.1. Reagents and standards

Methylparaben (MeP) (CAS number: 99-76-3), ethylparaben (EtP) (CAS number: 120-47-8), isopropylparaben (iPrP) (CAS number: 4191-73-5), methylchloroparaben (MeClP) (CAS number: 3964-57-6), propylparaben (PrP) (CAS number: 94-13-3), ethylchloroparaben (EtClP) (CAS number: 16357-41-8), isobutylparaben (iBuP) (CAS number: 4247-02-3), butylparaben (BuP) (CAS number: 94-26-8) and benzylparaben (BzP) (CAS number: 94-18-8) were obtained from Sigma–Aldrich (St Louis, MO, USA). Deuterated parabens (MeP-d_4, EtP-d_4, PrP-d_4, iBuP-d_4 and BzP-d_4) were supplied by CDN Isotopes (Quebec, Canada).

Ethyl acetate, acetone, methanol, acetonitrile and n-hexane, residue analysis grade, were purchased from Scharlab (Barcelona, Spain). Florisil for chromatography, 150–250 μm (60–100 mesh), and anhydrous sodium sulfate, procured from Sigma–Aldrich (Steinheim, Germany), were heated for 24 h at 140 °C and then allowed to cool down in a desiccator before use. Alumina 90 standardized was obtained from Merck (Darmstadt, Germany). Bondesil-C_{18} and Bondesil-PSA, particle diameter of 40 μm, were purchased from Scharlab (Barcelona, Spain). A mixture of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) in a ratio of 99:1 (v/v) was acquired from Sigma–Aldrich (Steinheim, Germany) as silylation reagent.

Separate stock solutions of individual compounds were made up at 50 $\mu g\,ml^{-1}$ level in ethyl acetate and a stock solution containing all the compounds at 5 $\mu g\,ml^{-1}$ level was prepared in ethyl acetate. The working standard solutions for calibration and recovery spike were prepared by dilution of the stock solution. These working solutions contained all the target analytes and EtP-d_4 and PrP-d_4 were added as surrogate standards. All the standard solutions were stored in glass flasks at 4 °C prior to use. The internal standard solution, containing MeP-d_4, iBuP-d_4 and BzP-d_4, was prepared at 200 $ng\,ml^{-1}$ level in ethyl acetate and used to spike all the samples prior to the chromatographic analysis.

2.2. Samples

2.2.1. Sewage sludge collection and pre-treatment

Two sewage sludge samples from 19 WWTPs located in the province of Madrid (Spain) were collected in 2010. Composite samples of digested sewage sludge were withdrawn manually from the conveyor belt subsequent to dewatering and collected in 2-L glass jars with Teflon-lined lids. The WWTPs selected had a rather wide variation in capacity (12,000–2,000,000 person equivalents, PE). As supplementary material, Table S1 lists the characteristics (flow rate, type of treatment and PE) of the 19 WWTPs investigated.

These WWTPs are located in zones that were classified in four categories according to their population and activities as: urban (population >250 hab km^{-2}), urban with small-medium enterprises (SMEs), industrial or rural (population <250 hab km^{-2}) zones, see Fig. 1. Urban WWTPs receive mainly domestic effluents, while those located in industrial areas receive effluents from various types of industries arising from different activities, such as cosmetics, pharmaceuticals, textiles, tanneries and small to medium-sized chemical plants.

In addition, to study the temporal variation of parabens and two chlorinated parabens, two sludge samples were collected from 3 WWTPs located in urban zones with SMEs in autumn of 2006, 2007, 2008 and 2010.

Sludge samples were transported to the laboratory at 4 °C and then frozen at −80 °C before being lyophilized. After the lyophilization process, sludge samples were homogenized and stored at −20 °C until analysis.

2.2.2. Sludge sample preparation

In a glass mortar, 1 g of lyophilized sludge was mixed with C_{18} (2 g) and anhydrous sodium sulfate (1 g). The mixture was blended with a glass pestle to yield a homogeneous material. For recovery studies, sludge was previously spiked with a mixture of parabens, chloroparabens and the surrogate standards (EtP-d_4, PrP-d_4) to reach final concentrations of 100, 50 and 25 $ng\,g^{-1}$. The blended sample was then transferred to a 20 ml glass column (10 cm × 20 mm i.d., from Normax, Portugal) with two filter paper circles of 2 cm diameter at the end of the column that