



Multiclass method for the determination of pharmaceuticals and personal care products in compost from sewage sludge using ultrasound and salt-assisted liquid–liquid extraction followed by ultrahigh performance liquid chromatography–tandem mass spectrometry analysis



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ABSTRACT

An analytical method for the analysis of 16 pharmaceuticals and personal care products in compost from sewage sludge is successfully validated. Ultrasound assisted extraction with a mixture of acetonitrile:ethyl acetate (1:1, v/v) containing 10% (v/v) of acetic acid was carried out. Two cycles of extraction of 10 min were applied. A clean-up of the extracts using salt-assisted liquid–liquid extraction (SALLE) was also included. Experimental design was used for the optimization of the main parameters involved in the extraction and cleaned-up steps. The chromatographic separation was carried out by ultrahigh performance liquid chromatography using a mobile phase gradient mixture of a 13 mM buffer ammonium formate solution (pH 9.25) (solvent A) and methanol (solvent B). An ACQUITY UPLC® BEH C18 column (1.7 μm; 2.1 × 50 mm) column was used. Analytes were separated in less than 11 min. The compounds were detected and quantified using single reaction monitoring electrospray tandem mass spectrometry. The limits of detection calculated ranged from 0.5 to 4 ng g⁻¹ d.w., and the limits of quantification from 2 to 13 ng g⁻¹ d.w. Recoveries from 93% to 111%, with relative standard deviations lower than 11% in all cases, were obtained. The method was applied to natural compost samples. High concentrations of some analytes were found. Ketoprofen (510 ng g⁻¹ d.w.), methylparaben (240 ng g⁻¹ d.w.), diclofenac (175 ng g⁻¹ d.w.) and flufenamic acid (128 ng g⁻¹ d.w.) were the most abundant.

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1. Introduction

Contamination by pharmaceuticals and personal care products (PPCPs) is an environmental issue great of concern, as stated in the EU Directive 2013/39/EU19 on priority substances in the field of water policy [1]. PPCPs have been detected in water bodies throughout the world, even in Antarctic waters [2]. In Europe, the rate of increase in the consumption and production of PPCPs has grown markedly in the last 20 years. Most PPCPs, up to 90% in the case of pharmaceuticals, enter the environment [3] through human consumption and excretion in the domestic wastewater stream. PPCPs are often filtered ineffectively by wastewater treatment plants (WWTPs) which are not designed to manage them. Another impor-

tant sources are improper disposal of unused medicines (e.g. by flushing them down the sink or toilet) an release of active pharmaceutical ingredients by manufacturers [3]. These compounds enter the aquatic environments through the effluents from WWTPs and hospitals and enter systems through treated sewage sludge (biosolids) intended for agricultural use and reclaimed wastewater irrigation.

For more than one decade, many papers have reported on the harmful health effects of exposure and bioaccumulation of PPCPs on living organisms. Most studies were conducted on freshwater [4–6] and saltwater (marine) [7] organisms. Diclofenac has been detected in brown trout [6] and mussels [7]; antidepressants and antiepileptic, in fish in rivers of the United States [5]; gemfibrozil, in goldfish [4]; and benzophenone uv-filters in fish in Spanish rivers [8,9]. Terrestrial fauna can also be exposed to PPCPs. Some studies show that overuse of diclofenac in livestock and inefficient disposal of dead livestock resulted in the death of vultures that feed on carcasses of

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dead animals treated with diclofenac [10]. This drug was approved for veterinary use in Spain in 2013 [11]. Moreover, parabens and their metabolites were detected in black bears and in some birds such as bald eagles and albatrosses [12].

The reason why these substances accumulate in the ecosystem is their biodegradation rate is lower than their emission rate. For this reason, traditional techniques used in WWTPs for PPCPs removal need to be improved. More advanced technologies such as advanced oxidation processes (AOPs), UV-photolysis and ozonation, are already used in some countries [13,14]. But even these new technologies cannot eliminate completely very persistent compounds such as diclofenac, while others such as ketoprofen and naproxen are rapidly degraded [15,16]. More recently, composting of the sewage sludge (biosolids), a by-product of wastewater treatment has been proposed as a good alternative for recycling sludge in many countries [17,18]. PPCPs amounts are greatly diminished after composting, but these compounds can still be detected in the final compost [19,20]. Also, fly larvae composting has been used to remove pharmaceuticals and pesticides with excellent results [21]. Crop uptake of PPCPs from reclaimed wastewater and biosolids and the effect of these compounds on the microbial communities in soil [22] have been reported by several authors. This warrants the need to remove completely PPCPs from compost [23–28].

While there is much literature on the determination of PPCPs in sewage sludge and wastewater, there is little information available on the analysis of composted sewage sludge [29–38]. In addition, the most commonly analyzed group of substances is antibiotics, followed by the rest of pharmaceutical products and, to a lesser extent, preservatives and other additives with demonstrated endocrine activity used in personal care products [39,40]. The published methods involve an endless number of techniques such as ultrasound-assisted extraction (UAE), Soxhlet extraction, pressurized-liquid extraction (PLE), supercritical fluid extraction (SFE), microwave-assisted extraction (MAE) or solid-phase extraction (SPE). One of the newest extraction techniques applied is QuEChERS (quick, easy, cheap, effective, rugged, and safe) [41–44], which is based on salting-out-assisted liquid–liquid extraction (SALLE) followed by a cleanup step with SPE sorbent. However, for cleanup QuEChERS has not been as widely applied as SPE, that is a more time-consuming and costly technique [45].

The present work describes a multiclass analytical method for the determination of parabens, benzophenone uv-filters, lipid regulators and non-steroidal anti-inflammatory drugs in sewage sludge compost at trace levels. Since the compounds belongs to different families, the physicochemical properties and, therefore, their behavior are different. However, the objective of the present work was to optimize and validate an analytical method to analyze PPCPs of great use worldwide. For example, PPCPs that not need medical prescription for use or related with common diseases such as obesity. The method involves UAE, followed by a cleanup step based on SALLE, used to reduce matrix effect. UHPLC–MS/MS was used to detect and quantify the selected analytes. The method was applied to samples of sewage sludge compost. This approach can be used for the development of more in-depth research on the occurrence and fate of these PPCPs during the composting process.

2. Experimental

2.1. Chemicals and reagents

Diclofenac sodium salt (DIC), naproxen sodium salt (NAP), methylparaben (MPB), ethylparaben (EPB), propylparaben (PPB), butylparaben (BPB) and benzophenone 6 (BP6) were purchased from Alfa-Aesar (Ward Hill, MA, USA). Flufenamic acid (FLU), ketoprofen (KET), bezafibrate (BEZ), fenofibrate (FEN),

gemfibrozil (GEM), 4-hydroxybenzophenone (4-OH-BP), benzophenone 1 (BP1), benzophenone 3 (BP3), benzophenone 8 (BP8); surrogates 2-((2-chlorobenzoyl)amino) benzoic acid (BEN), 2-(4-chloro-3-methyl-phenoxy)-2-methyl-propionic acid (MET) and ketoprofen- d_3 (KET- d_3) were obtained from Sigma-Aldrich (St. Louis, MO, USA) and ethyl- d_5 -paraben (EPB- d_5) from TRC Toronto (Toronto, ON, Canada). Individual standard solutions of compounds ($200 \mu\text{g mL}^{-1}$) were prepared in methanol, except for deuterated surrogates that were prepared in acetonitrile, and stored at -20°C . These solutions were prepared fresh every three months. Working standard mixtures were prepared by diluting the individual stock solution in acetonitrile. These solutions were stored at -20°C and prepared fresh monthly. Anhydrous magnesium sulphate and sodium chloride used for the SALLE cleanup procedures were provided by Panreac (Darmstadt, Germany). BAKERBOND[®] Octadecyl C18 and dispersive sorbents PSA were obtained from Avantar (Center Valley, PA; USA) and Sigma-Aldrich (St. Louis, MO, USA), respectively. Technical methanol (MeOH), acetonitrile (ACN), ethyl acetate (EtAc), acetone and glacial acetic acid used for the preparation of extraction solutions was purchased from VWR (Radnor, Pennsylvania, USA). LC–MS grade water, MeOH, ACN, ammonia ($\geq 25\%$) and formic acid ($\geq 98\%$) used for the preparation of standards, mobile phases and pH adjustments were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Instrumentation and software

UAE was performed with a 400W digital sonifier (Branson Ultrasonic Corporation, Danbury, CT, USA), with a 0.5 inch (12.7 mm) probe operating at a frequency of 20 kHz. UHPLC–MS/MS analyses were performed using a Waters Acquity UPLC[™] H–Class system (Waters, Manchester, UK). Separation of compounds was performed on ACQUITY UPLC[®] BEH C18 column ($1.7 \mu\text{m}$; $2.1 \times 50 \text{ mm}$) (Waters, Manchester, UK). A Xevo[™] TQS tandem quadrupole mass spectrometer (Waters) equipped with StepWave ion guide and an orthogonal Z–spray[™] electrospray ionization (ESI) source was used for mass analyses. Compost samples were freeze-dried using a SCANVAC CoolSafe[™] freeze dryer (Lyngø, Denmark). A digital pH-meter (EUTECH Instruments Ltd, Singapore), a vortex-mixer (IKA, Wilmington, NC, USA), a Hettich Universal 32 centrifuge (Tuttlingen, Germany), a Digicen 21 centrifuge (Orto Alresa, Madrid, Spain), a sample concentrator (Stuart, Staffordshire, UK) and an ultrasound bath (Selecta, Barcelona, Spain) were also used. Statgraphics, Minitab and Excel software were used for statistical treatment of data. MassLynx software 4.1 was used for UHPLC–MS/MS instrument control, peak detection and integration.

2.3. Sample collection and storage

Samples were obtained from different stores and composting plants located in Southern Spain. A total of 14 different samples were collected. In order to ensure the representativeness of bulk samples, a systematic sampling procedure was carried out. A geometric schedule was followed and portions of about 100 g of compost were taken from at least 15 sampling points of the composting pile (final sample weight 1.5 kg approximately). After collection, samples were freeze-dried, sieved through a mesh with $\leq 1.41 \text{ mm}$ pore size and stored in airtight bags in the dark at 4°C until analysis. In relation to the composition of the obtained material, since it is not a natural product, compost from sewage sludge does not have a defined chemical composition. However, the typical values of a generic compost are defined. Data are included as supplementary material (Table S1).

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