



An analytical method for measuring specific endocrine disruptors in activated sludge (biosolids) using solid phase microextraction-gas chromatography



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ABSTRACT

Occurrence of emerging contaminants in the environment reveals a growing problem, attributed to uncontrolled disposal or insufficient elimination of those pollutants during wastewater treatment. The possession of efficient and competent analytical tools is important in order to examine the root of this problem. In the present study, an analytical method was developed for the determination of selected endocrine disruptors and pharmaceutical compounds in activated sludge (biosolids). The following ten compounds, triclosan, 2,4-dichlorophenol, 2,3,4-trichlorophenol, bisphenol A, estrone, 17-beta-estradiol, 17-alpha-ethinylestradiol, androsterone, 5 α -androstane-17 β -ol-3-one and 19-norethindrone were examined and finally included in the analytical method described. Target compounds were isolated from sludge by ultrasound extraction followed by solid-phase microextraction (SPME). The desorption of the analytes from the SPME fiber was carried out by gas chromatography, while identification and quantitation was achieved with mass spectroscopy. For the development and validation of the method, sludge standards were created by spiking target compounds in dewatered sludge. The metabolic activity of activated sludge was interrupted without changing the structure of the biomass, in order to imitate real sorption conditions that exist in wastewater treatment plants (WWTPs). Concerning the optimization of the extraction process, several parameters were investigated, including the type of organic solvent used, duration of the ultrasound extraction, purification of the extract. The limits of detection for examined compounds ranged between 4 and 50 ng g⁻¹ (biomass, dry weight). The method was applied for the determination of the selected compounds in sludge samples collected from large scale municipal on the island of Crete (Greece).

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1. Introduction

Concern is growing, regarding the presence of endocrine disrupting compounds (EDCs) and other chemicals existing in personal care products in the environment. Even if they are present in small concentrations, these compounds can affect and disturb normal activities of living organisms [1]. Their toxicity is not direct but is expressed as a biological disruption, affecting the endocrine system and the development of organisms [2]. The main pathway for these compounds to enter into the environment is through municipal wastewater treatment plants (WWTPs). Even though a large part of these compounds can be eliminated during treatment,

they are detected both in effluent wastewater and in excess sludge. Since their detection is a challenge, due to low concentrations and due to the large number of existing compounds, most studies focus on the analysis of wastewater and water samples for the detection of these compounds in the dissolved phase [2–5]. Research in this field focuses on improving the detection limits and the number of chemical compounds per analysis in the water phase, but at the same time effort is made to simplify the analytical methodology used. On the other hand, less work has been done on the detection and quantification of these compounds in the solid phase. This could be explained due to i) the complexity this matrix presents, which may increase difficulties during analysis, and ii) underestimation of the ramifications that could occur due to accumulation of EDCs in the solid phase.

In order to provide information on the distribution of EDCs between the solid and dissolved phase some researchers

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calculated solid–water distribution coefficients, K_d ($L\text{ kg}^{-1}$) for a variety of pharmaceuticals by determining the quantity of compounds encountered both in the solid and the dissolved phase [6–8]. Carballa et al. [6] studied the solid–water distribution coefficients, K_d ($L\text{ kg}^{-1}$) for a variety of pharmaceuticals, estrogens and musks in digested sludge, Stasinakis et al. [7] calculated the same coefficient for endocrine disruptors, pharmaceuticals, benzothiazoles, benzotriazoles and perfluorinated compounds in primary and secondary sludge, while Ternes et al. [8] proposed a method for calculating distribution coefficients for pharmaceuticals and musk fragrances in primary and secondary sludge. On the other hand, Andersen et al. [9] described the distribution of steroid estrogens between water and sludge, by analysing the dissolved phase. However, prediction of the presence of micropollutants in biosolids by calculations based on their concentration in the dissolved phase cannot substitute particulate matter sample analysis. Therefore appropriate analytical tools and methodology for the determination of compounds in the particulate phase still need to be developed and optimized [10].

Concerning existing methods, some researchers have presented results for the quantification, in sludge samples, of many compounds (up to 148) at the same time and with good detection limits (method limits of detection; MLODs lower than 10 ng g^{-1} d. w. for most compounds) [11]. In general, some of the more frequently examined compounds are: Triclosan (TCS; up to $17,500\text{ ng g}^{-1}$ in secondary sludge, $133,000\text{ ng g}^{-1}$ in treated sludge and 949 ng g^{-1} in soil) [12], Bisphenol A (BPA), Estrone (E1), 17-beta-estradiol (E2), and 17-alpha-ethinylestradiol (EE2) and others. Detection limits for the identification of these compounds vary but are scarcely higher than 10 ng g^{-1} (Table 1). Most methods use Solid Phase Extraction (SPE) [10,11,13–17] for the pretreatment of samples, a method that requires significant amounts of organic solvents, specific type of cartridges and a long procedure concerning sample preparation prior to analysis. Only few alternatives exist for analysis of sludge samples for the determination of micropollutants without using SPE [18,19]. Furthermore, in many cases, the standard addition method is being used [9,17], resulting in a time-consuming method not suited for a large number of samples, while another point observed in most of the analytical methods applied so far is the use of a calibration curve developed with standards in the water phase and not in the sludge matrix [8,10].

Based on the above, the objectives of this work were to develop a practical and easy to adopt analytical method for the determination of specific EDCs and micropollutants occurring from personal care products in biosolids. The method included extraction of target compounds from sludge with ultrasound, appropriate handling, isolation and analysis by means of Solid

Phase Micro-Extraction coupled with Gas Chromatography-Mass Spectroscopy (SPME/GC–MS), presenting an alternative way to quantify EDCs, without the use of SPE. The substances investigated in this work were the antibacterial and antifungal agent TCS and its derivatives 2,4-dichlorophenol (PH24) and 2,3,4-trichlorophenol (PH234), as well as BPA that is found in plastics and epoxy resins. These four compounds are frequently detected both in influent and effluent wastewater but less information is available on their presence in sludge. Furthermore, the hormones E1, E2, EE2, androsterone (A), 5α -androstan-17 β -ol-3-one (DHT) and 19-norethindrone (NE) were also included in the method, as they are the hormones that are found in higher concentration in wastewater. The development of the method was based on a previously developed method for the measurement of EDCs in the water phase [23] and more steps were investigated and added for the expansion of this method to sludge samples. The calibration curve was created with dewatered sludge samples where the target compounds were spiked with an aquatic solution, in order to allow sorption to occur as in WWTPs. Finally, for the first time, a short sampling campaign took place in two municipal WWTPs of Crete in order to determine concentration of target compounds in the solid phase.

2. Material and methods

2.1. Reagents and standards

Concerning standard compounds, 2,4-dichlorophenol (CAS 120-83-2) and 2,3,4-trichlorophenol (CAS 15950-66-0) were purchased from Supelco. Triclosan (CAS 3380-34-5), bisphenol A (CAS 80-05-7), estrone (CAS 53-16-7), 17-beta-estradiol (CAS 50-28-2) and 17-alpha-ethinylestradiol (CAS 57-63-6) were purchased from Dr. Ehrenstorfer. Androsterone (CAS 53-41-8), 5α -androstan-17 β -ol-3-one (CAS 521-18-6) and 19-norethindrone (CAS 68-22-4) were purchased from Sigma Aldrich. NaCl was purchased from Merck (Germany). Methanol, acetone, acetonitrile and methylene chloride, all pestanal grade, were purchased from Fluka (Germany). Sodium azide (NaN_3) was purchased from Sigma-Aldrich (Germany). The hormone (estrone, 17-beta-estradiol, 17-alpha-ethinylestradiol, androsterone, 5α -androstan-17 β -ol-3-one and 19-norethindrone) standards and spiking solutions were prepared by dissolving the neat compounds in acetonitrile, while the rest of standard solutions were prepared in methanol.

2.2. Calibration curve and calibration standard preparation

In order to plot the instrumental response to the concentration of each analyte, a calibration curve was created. The basis for accurate quantification is an appropriately fitted calibration curve, which should be created with calibration standards in the same matrix of the samples that are going to be analyzed [24]. Therefore, in this current study, dewatered and appropriately deactivated sludge was used as a matrix for the creation of the calibration standards and therefore the calibration curve.

For calibration standard preparation, activated sludge was collected from the municipal WWTP of Chania. After collection, the sludge was left for one day without any treatment, in order to stabilize biological activity of the microorganisms and degrade EDCs that could be present in sludge. After 24 h a sample of sludge was analyzed in order to ensure that none of the target compounds were present. Preparation of sludge included dewatering by centrifugation at 4000 rpm (Thermo-scientific CL10) as a first step. Afterwards, the appropriate amount of sludge (corresponding to 1 g of dry solids) was added into an amber vial (capacity of 40 ml). Before spiking target compounds and in order to ensure that no biological activity would be present, sodium azide was

Table 1
Detection limits referred in other analytical methods.

Compounds investigated	LODs (ng g^{-1})	Reference
E1	2	[20]
E2	2	
EE2	4	
E1	10	[21]
E2	5	
EE2	5	
E1	1–2	[22]
E2	1–2	
EE2	1–3	
TCS	15	[7]
BPA	33	

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