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Investigation of nonylphenol and nonylphenol ethoxylates in sewage sludge samples from a metropolitan wastewater treatment plant in Turkey

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ABSTRACT

Nonylphenol ethoxylates (NPEOs) have drawn significant attention within the last decade for both scientific and legislative reasons. In Turkey, the *Regulation Regarding the Use of Domestic and Urban Sludges on Land* states a limit value for the sum of nonylphenol (NP), nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO) as NPE (NPE=NP+NP1EO+NP2EO). Unfortunately a standard method for the determination of these chemicals has not been yet set by the authorities and no data exists about the concentrations of NP and NPEOs in sewage sludge in Turkey. The aim of this study is to propose simple and easily applicable extraction and measurement techniques for 4-*n*-nonylphenol (4-*n*-NP), NP, NP1EO and NP2EO in sewage sludge samples and investigate the year round concentrations in a Metropolitan Wastewater Treatment Plant (WWTP) in Turkey.

Different extraction techniques and GC/MS methods for sewage sludge were tested. The best extraction method for these compounds was found to be ultrasonication (5 min) using acetone as the solvent with acceptable recovery of analytes suggested by USEPA and other studies. The optimized extraction method showed good repeatability with relative standard deviations (RSDs) less than 6%. The recovery of analytes were within acceptable limits suggested by USEPA and other studies. The limits of detection (LODs) were 6 μg kg^{-1} for NP and NP1EO, 12 μg kg^{-1} for NP2EO and 0.03 μg kg^{-1} for 4-*n*-NP. The developed method was applied to sewage sludge samples obtained from the Central WWTP in Ankara, Turkey. The sum NPE (NP+NP1EO+NP2EO) was found to be in between 5.5 μg kg^{-1} and 19.5 μg kg^{-1}, values which are in compliance with Turkish and European regulations.

1. Introduction

Alkylphenols are synthetic organic chemicals with wide industrial and domestic uses. Nonylphenol ethoxylates (NPEOs) represent approximately 80% of all alkylphenols produced [1]. Due to their surface active properties, NPEOs have extensive industrial (especially in pulp and paper and textile), commercial and domestic uses (as surface cleaners, lubricants, shampoos, detergents, and other products) [2]. Following use and disposal, they often reach wastewater treatment systems and consequently the receiving environments [3]. The nonyl group (C_9H_{19}) attached to the phenol ring is mostly branched. Due to this property the chemical can be formulated in a number of different isomeric forms. Industrial and household chemicals include a mixture of branched NP isomers, rather than the linear molecule. For this reason, the chemicals observed in wastewaters and sewage sludge are mainly composed of these isomeric mixtures.

Biodegradation of NPEOs is possible and occurs by the elimination of ethoxy chains. Biodegradation of NPEOs in aerobic environments leads mainly to the formation of nonylphenol polyethoxy carboxylates (NPECs) and carboxyalkylphenol ethoxy carboxylates (CAPECs), whereas in anaerobic environments, the final metabolite is nonylphenol (NP) following degradation of nonylphenol diethoxylate (NP2EO) and nonylphenol monoethoxylate (NP1EO) [2,4].

The fate and behavior of NP and NPEO compounds in different environmental systems such as sediment, soil, surface waters and biota depend on their physico-chemical properties [5–7] and their molecular structure (Fig. 1(i)–(iii)). NP and NPEOs are known to be toxic to most organisms and carcinogenic to humans [8,9]. As illustrated in Fig. 2, the branched carbon chains on the NP molecule are similar to the 17-β-estradiol structurally [10,11].

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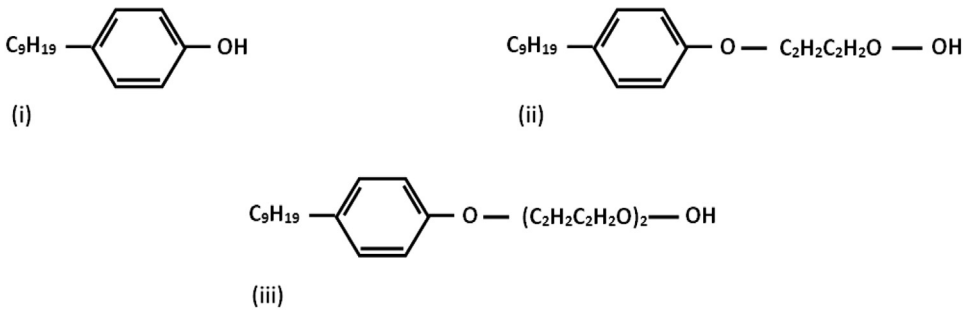

Fig. 1. Molecular structures of (i) NP (ii) NP1EO and (iii) NP2EO.

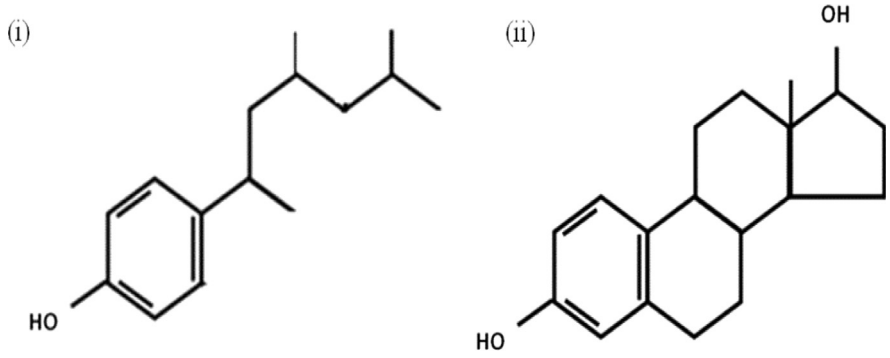

Fig. 2. Structural similarity between (i) NP and (ii) 17-β-estradiol.

Due to this structural similarity, NP is able to mimic estrogen hormone through a direct interaction with the estrogen receptor, blocking the action of the original hormone which can result in reproductive diseases. For this reason NP and some NPEOs are listed as endocrine disrupting chemicals (EDCs) and priority pollutants in the Water Framework Directive [12–14]. Also, due to their high K_{ow} values, NP and NPEO compounds tend to stay on surfaces like soil, sediment and sewage sludge. Persistence of these compounds in sewage sludge is an important issue since among other sludge handling methods, land application is the most favorable due to its low cost and beneficial recycle of nutrients. Since sewage sludge does not only contain nutrients but also contaminants such as NP and NPEO compounds; they must be monitored properly to judge about their suitability for land application [15]. Once sewage sludge containing NP and NPEOs are used for agricultural purposes, these compounds can build up along the food chain and accumulate in the fatty tissues of living organisms [3,9].

The increasing concerns on health and environmental effects of NP and NPEO compounds, it has become critical to determine the levels of these compounds in sewage sludge prior to disposal. Several methods have been suggested in the literature for the quantification of these compounds [16,17]. But, there is no consistency between methods in terms of extraction process (solvent, method and period), or analytical procedure (different instruments like GC/MS, GC/MS/MS, LC/MS/MS etc). The methods differ from each other even if the determination was carried out with the same type of instrument. For example, for solid samples like soil, sediment and sewage sludge, sonication-assisted extraction [18–20] combination of sonication and mechanical shaking assisted extraction [15,19], enhanced solvent extraction [21] and Soxhlet extraction [22] have been used for the analysis of NP, 4-*n*-NP, NP1EO and NP2EO. Among these methods, NP and NPEO compounds were analyzed using GC/MS [18,19] or LC/ESI/MS [23]. When extraction solvent is taken into consideration, dichloromethane:methanol (7:3) [19] acetone:methanol (1:1) [20] and hexane [24] have been used for sonication-assisted extraction from sewage sludge. In addition, some of these methods aimed at measuring only one NP or NPEO compound [23,25], whereas others more than one compound simultaneously [15,18].

As stated earlier, these compounds tend to accumulate on sewage sludge solids and can be carried along the food chain threatening human health and environment. Therefore, to test the suitability of sewage sludge for land application, limit values have been suggested by countries worldwide. For this reason, in agricultural use of sewage sludge, European Union suggested a limit value for the sum of NP, NP1EO and NP2EO (called as NPE) as 50 mg kg^{-1} dry mass (dm) in Working Document on Sludge, 3rd Draft [26].

In the EU accession period of Turkey, the limit value for NPE in sewage sludge was set as 50 mg kg^{-1}-dm in Regulation on the Land Use of Domestic and Urban Sludges [27]. However, a practical method for the qualitative and quantitative determination of NP and NPEO compounds has not been suggested for routine analysis in sewage sludge samples. With the need of a practicable and validated method for simultaneous quantification of all NP (NP+NPEO) compounds, this study aimed to come up with such a method and monitor NP, NP1EO and NP2EO concentrations in sewage sludge samples. The sludge samples obtained from Ankara Central WWTP were analyzed with the proposed sonication assisted-extraction method and the qualitative and quantitative determination of the chemicals were made using GC/MS.

2. Materials and methods

2.1. Chemicals and standards

Standard solutions of NP, NP1EO and NP2EO (analytical standard, 5 μg mL^{-1} in acetone) were supplied by Fluka, Sigma Aldrich, USA (Product# 32889, 32895, 32899, respectively). The standard solution of 4-*n*-NP (10 ng μL^{-1} in cyclohexane) (Product# L15630000CY) was purchased from Dr. Ehrenstorfer GmbH, Germany. Sodium sulfate, fine powder copper and GC/MS grade acetone (AC),