

SEASONAL MONITORING OF NONYLPHENOL COMPOUNDS IN SEWAGE SLUDGE

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ABSTRACT

Nonylphenol compounds (NPnEO) enter wastewater treatment systems from a number of different sources, including domestic and industrial. These compounds start losing their ethoxy groups during treatment processes and eventually form nonylphenol diethoxylate (NP2EO), nonylphenol monoethoxylate (NP1EO) and nonylphenol (NP) as final products with higher toxic properties. Even though they are removed during wastewater treatment to a certain extent, an important fraction heavily concentrate on solids due to their hydrophobic nature. Due to their toxicity and endocrine disrupting ability, these compounds create concern about land application of sludge. Many countries in Europe including Turkey set the limit value for NPE (NP+NP1EO+NP2EO) as 50 mg/kg dm. Although Turkey set a limit value for these chemicals, no method was suggested for their quantification in related regulations. The determination and monitoring of NP, NP1EO and NP2EO compounds in sewage sludge prior to use for agricultural purposes is critical. Therefore, the aim of the study was to determine the concentrations of NP, NP1EO and NP2EO and monitor the seasonal changes in their concentrations in dewatered sewage sludge samples obtained monthly from Central Wastewater Treatment Plant, Ankara for a year. In order to identify and quantify NP compounds in sludge samples a GC/MS was used. Results showed that the compounds of interest were detected in sludge samples, however, all values measured were lower than the limit required by the regulation.

Keywords: Endocrine disrupting compounds, hydrophobicity, land application, nonylphenol compounds, sewage sludge

1. Introduction

Nonylphenolpolyethoxylates (NPnEO) are widely used in household and industrial activities due to their surface active properties (Diaz and Ventura 2002, Soares *et al.*, 2008). These compounds reach surface waters at high concentrations by direct discharge or through effluents of wastewater treatment plants. Biological degradation of nonylphenol polyethoxylates is possible; it starts at the hydrophilic chain by losing ethoxy groups and leads to the formation of more toxic and persistent metabolites: nonylphenol (NP), nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), more water-soluble nonylphenoxy acetic acid (NP1EC) and nonylphenoxyethoxy acetic acid (NP2EC) (Ahet *et al.*, 1994; Birkett and Lester, 2003).

Previous studies showed that NPnEOs have toxic, carcinogenic and estrogenic effects (Soto *et al.*, 1991; Cox, 1996). Because of the structural similarities between nonylphenol and natural estrogens, they mimic these hormones and compete for the estrogen binding receptors in vertebrates (Jobling *et al.*, 1993; Rodgers-Gray *et al.*, 2001). Due to their hydrophobicity and lipophilicity, nonylphenol compounds accumulate in cells, tissues and on solid surfaces; they have been detected at large concentrations in river sediments and sewage sludge (Marcomini *et al.*, 2000).

Due to environmental and health concerns related to these compounds, some European countries like United Kingdom and Germany have banned the use of alkylphenol ethoxylates

(including NPnEOs) in household cleaning products in 1995 and also regulated their industrial applications for cleaning purpose in 2000 (Renner, 1997). Also, Nonylphenol (NP) is listed as a priority hazardous substance under the Water Framework Directive (WFD, 2000/60/EC) due to its potential impact on the aquatic environment. The awareness of adverse effects of NP compounds has led to increase in concerns about the application of sludge for agricultural purposes, therefore, European Union proposed a limit value in "Working Document on Sludge-3rd Draft (2000) for NPEs (sum of NP, NP1EO, and NP2EO) as 50 mg/kg dry solids. Turkey also set the same limit value in a regulation named as "Regulation on the Use of Municipal and Urban Sludge on Land" in 2010. Despite the fact that a limit value was set for NPEs, a standard method for determination of these chemicals has not been announced and no data monitoring their concentrations in sewage sludge samples have not been reported yet by the authorities. Therefore, this study aimed the determination and seasonal monitoring of NP, NP1EO and NP2EO compounds in dewatered sewage sludge samples taken from the central wastewater treatment plant in Ankara in 2012.

2. Materials and methods

2.1. Sludge Samples

Dewatered sludge samples were supplied from Central Wastewater Treatment Plant, Ankara monthly between February 2012 and December 2012. The treatment plant is the biggest treatment plant in Ankara and the second biggest in Turkey with a current flow rate of 765,000 m³/day (ASKI, 2015).

Following sampling, sludge samples were freeze-dried to remove moisture and sieved through 1 mm sieve to obtain homogenous samples.

2.2. Chemicals

The standard solutions of NP, NP1EO and NP2EO (analytical standard, 5µg/L in acetone) were supplied from Fluka (Sigma Aldrich Co. LLC, USA). The standard solution of 4-n-NP (10 ng/µL in cyclohexane) was purchased from Dr. Ehrenstorfer (Augsburg, Germany) and used as surrogate in extraction studies.

BSTFA (N,O bis(trimethylsilyl)trifluoroacetamide) + TMCS (trimethylchlorosilane), (99:1), kit was obtained from Supelco Analytical (Sigma Aldrich Co. LLC, USA). Sodium sulfate, fine powder copper and solvents (acetone, methanol, hexane and dichloromethane, all GC-MS grade) were supplied from Merck KGaA, Germany.

2.3. Extraction

Extraction of NP compounds from sludge samples was carried out by sonication-assisted extraction method. The details of developed method can be seen in *Ömeroglu et al.*, (2015). Acetone was used as an extraction solvent. Freeze-dried and sieved dewatered sludge samples (0.5 g) were placed into 12 mL amber vials and then 10 mL of acetone was added into each vial. The vials were placed into sonication bath (Ultrasonic, Falc, USA) and sonicated for 5 min. Following sonication, the vials were centrifuged at 2500 rpm for 10 min. The obtained extract (in acetone) was passed through sodium sulfate column for removal of moisture. If necessary, after making required dilutions, the extract was injected into GC/MS following derivatization.

2.4. Derivatization

Silylation was used for derivatization of extracted NP compounds from dewatered sludge samples. BSTFA and TMCS were chosen as a derivatizing agent and catalyst, respectively.

1 mL sample was taken and evaporated under gentle nitrogen stream until dryness. 100 µL BSTFA-1%TMCS reagent was added and vials are capped. Following vortexing for 1 min, the vials were placed into oven at 70°C for 30 min. After 30 min, they were cooled at room temperature. They were vortexed for 1 min. Each sample was transferred into injection vial and then sample was injected to GC/MS.

2.5. GC/MS analysis

In order to identify and quantify NP compounds in sludge samples a GC/MS (7890A Agilent gas chromatograph coupled to a 5975C Agilent mass spectrometer with Triple-Axis) instrument was used. The column used was HP-5MS 5% phenyl methyl siloxane (30 mx0.25mmx0.25 μ m) with helium as carrier gas (constant flow 1.0 mL/min). An amount of 1 μ l of the sample was injected in the splitless mode to GC/MS. The oven program used was as follows: 100 °C for 5 min, 25°C/min to 160°C, 10°C/min to 260°C, 260°C for 5 min, 35°C/min to 285°C and 285°C for 7 min. The temperatures of MS interphase, MS source and quadrupole were kept at 280°C, 230°C and 150°C, respectively.

GC/MS analysis was carried out using selective ion monitoring (SIM) mode and the m/z values for the derivatized compounds were: for 4-n-NP 73, 179 and 292; for NP 107, 135, 150, 179, 193, 207, 235, 277 and 292; for NP1EO 237, 251, 265, 279, 293 and 307; for NP2EO 281, 295, 309 and 323.

3. Results

With proposed regulation, in European countries, the dewatered sludges have to be checked for the sum of NP, NP1EO and NP2EO prior to land application and have to maintain the value of less than 50 mg/kg-dm (10 mg/kg-dm for Denmark). Similarly, Turkey has the same limit value for NPEs and dewatered sludges prior to land application have to meet the expectation of <50 mg/kg-dm. In order to monitor NPEs in dewatered sewage sludge samples, monthly sampling was carried out from the central wastewater treatment plant in Ankara for a year (except for January) and measured concentrations are illustrated in Figure 1.

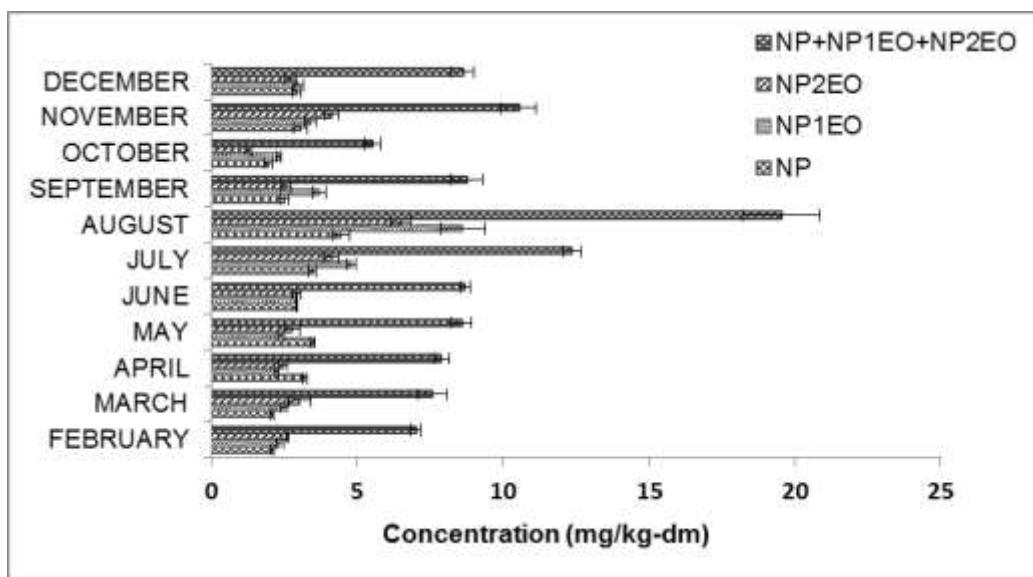


Figure 1: Concentrations of NP, NP1EO, NP2EO and sum of NPE in dewatered sludge samples

As can be seen from Figure 1, the results indicate that these compounds exist in sludge samples collected. From the three compounds tested, NP1EO or NP2EO had the highest concentration at one sampling time. The results also indicated a seasonal variation of the sum NPE concentrations, especially when cold season was compared with the warm one. In February, NPE concentration was determined as 6.99 ± 0.17 mg/kg-dm and during spring time it reached 8.58 ± 0.34 mg/kg-dm (in May). Results showed that in spring months, a slight change was observed in level of NPEs in dewatered sewage sludges. With start of summer season, an increase in concentration of NPE was started and continued over summer months. In June NPE concentration was determined as 8.69 ± 0.17 mg/kg-dm and then with a noteworthy increase it reached 12.36 ± 0.31 mg/kg-dm in July. In August, it came up to 19.53 ± 1.33 mg/kg-dm as the

highest level of NPEs measured in all year. In winter time, NPE concentrations were slightly fluctuated over time but exhibited much lower concentrations compared to summer season. High values during summer months are likely due to the combination of dry weather and increased washing and bathing frequencies. These two conditions likely lead to a rise in detergent use and introduction of more nonylphenol compounds into sewage system which in turn is receiving a lower volume of water input. Conversely, in winter and spring, the decrease in NPE compound concentrations can be attributed to snow and heavy rain regime which contribute to dilution of NP compounds present in the waste stream. During all months, total concentrations were consistently well below the 50 mg/kg-dm regulatory limit.

4. Conclusions

In 2010, for the EU harmonization process, Turkey set a limit value for NPEs (NP+NP1EO+NP2EO) as 50 mg/kg dry solids. Although a limit value has been set, any method or procedure has not been announced by authorities for detection and quantification of these compounds. Also, no study has been reported indicating the level of these compounds in Turkish dewatered sludge samples.

With this study, it has been aimed to draw attention of authorities and researchers to accumulation of NP compounds in Turkish dewatered sludge samples prior to land application. Ankara is a capital city with high population and less industrialization. NPE compounds concentration reached nearly 20 mg/kg-dm (in August) as the highest level measured in collected sludge samples. In highlight of these findings it can be pointed out environmental compartments of highly populated and industrialized cities can be polluted heavily with NPE compounds and it can lead to serious environmental and public health problems. Therefore, Turkey should start monitoring NPE concentrations in different environmental systems like lake, river, sediment, sludge (for land application) etc. of highly populated and industrialized cities and if necessary, the use of NPnEOs as surfactant in industrial applications should be limited or banned with regulations.

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