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DETERMINATION OF THE CONTENT OF 4-NONYLPHENOLS AND THEIR ETHOXYLATES IN SEWAGE SLUDGE FROM POLISH MUNICIPAL WASTEWATER TREATMENT PLANTS

The aim of the present study was to examine the content, and its change with time, of 4-nonylphenol and nonylphenol ethoxylates in sewage sludge from Polish municipal wastewater treatment plants. The sludge samples from twelve wastewater treatment plants were examined for three consecutive years (2005–2007). The content of 4-NP was determined only in one set of samples from 2005 and in those from 2007. In none of them it exceeded 1 mg/kg. The content of NPEOs in the samples examined decreased with time, from more than 200 mg/kg in 2005 to 10–30 mg/kg at the end of the study; in most of the samples it proved to be below 50 mg/kg – the new threshold value proposed by the EU.

1. INTRODUCTION

Nonylphenol ethoxylates (NPEO) are a class of non-ionic surfactants that for many years were widely used as the components of various household and industrial products.

Their molecules are composed of a phenyl ring to which two groups are attached: a linear or branched nine-carbon alkyl chain and, usually in position *para* to it, a polyethoxylate chain comprised of 1 to 20 ethoxy units.

NPEO were used as dispersing agents in paper and pulp industry, emulsifying agents in latex, paints and pesticide formulations, floating agents as well as components of various household and, mainly, industrial cleansers.

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These compounds reach the environment mainly with wastewaters, untreated and, to a lesser extent, treated, and with sewage sludge, the main by-product of wastewater treatment process. Their main degradation products are nonylphenol (NP), which is also their precursor, nonylphenol monoethoxylate (NP_1EO) and nonylphenol diethoxylate (NP_2EO) (YING et al. 2002; CORVINI et al. 2006). These compounds are classified not only as persistent in the environment (POPs) but also potentially harmful for both wildlife and humans due to their stated endocrine disrupting activity (EU, 2002; SERVOS et al. 2003; STAPLES et al. 2004; GOKSOYR, 2006).

Henceforth in many countries, including Poland, the use of nonylphenol ethoxylates in various products was either totally banned or severely restricted.

In the EU several legal measures were adopted in order to minimise the impact of NPEO's on the environment and human health. These comprise the limitations imposed by the Directive 2000/60/EC which establishes a framework for community action in field of water policy (EU, 2000), as well as the threshold values for the content of these substances in sewage sludge intended for use on soil (50 mg/kg), set within the proposal of the new Directive on the Sewage Sludge (EU, 2000).

Independently, many EU Member States set their own threshold values on the content of nonylphenol and nonylphenol ethoxylates in water, wastewater sewage sludge and chemicals intended for use in the environment, in order to protect human health and wildlife (such actions were undertaken for example by the Scandinavian countries) (EU, 2001). Simultaneously many countries undertake the studies focused on the monitoring of the content of nonylphenol ethoxylates in various matrices, such as soil, water, sediments and sludge. In some countries such extensive studies have been carried out for many years, starting from 1980s.

In Poland the restrictions on the use of nonylphenol and nonylphenol ethoxylates in various chemical products have been introduced via the Decree of the Minister of Economy (Minister of Economy of the Republic of Poland, 2004). Very little, however, is known on the content of these compounds in wastewater and, especially, sewage sludge prior to and after the above mentioned regulations have entered into force.

This paper presents the results of the research, carried out in the years 2005–2007, on the content of 4-nonylphenol (branched) and its ethoxylates in sewage sludge from selected Polish wastewater treatment plants. The main task of this study was to assess the content of nonylphenol and nonylphenol ethoxylates in processed sewage sludge from twelve Polish wastewater treatment plants, and its changes with time over 3-years period. We also wanted to check how the characteristics of wastewater reaching a given wastewater treatment plant (% of the industrial wastewaters reaching a given plant) may influence the content of 4-nonylphenol and nonylphenol ethoxylates in produced sewage sludge. Finally we wanted to examine whether and how the introduction of the new law, strongly limiting the use of 4-nonylphenol and nonylphenol ethoxylates, would influence the content of these compounds in sewage sludge shortly after its adoption as well as after a longer period of time.

It should be clarified here, that, according to already cited European Union Assessment Report on 4-nonylphenol (branched) and nonylphenol (EU, 2002), "the term "nonylphenol" can apply to a large number of isomeric compounds of general formula $C_6H_4(OH)C_9H_{19}$". The difference between these various form may consist on "the substitution position of the nonyl group on the phenol molecule" as well as the structure of the nonyl group itself (it can be either linear or branched). As a result there exist about 200 isomers known under one generic name "nonylphenol". As commercially produced nonylphenols, and hence the compounds of concern, are predominantly 4-nonylphenol molecules with a varied and undefined degree of branching in the alkyl group, the generic name for them is 4-nonylphenol (branched). This is also reflected in single CAS and EINECS numbers this class of compounds is bearing (the whole issue is discussed in detail on page 7 of the cited above report). Therefore, as our paper refers to regulatory issues for 4-nonylphenol and its ethoxylates and since in many legal documents (as well as in some scientific papers) these compounds are presented under their generic name "4-nonylphenol", for the reasons of consistency we decided to maintain this name. This has been done even though, from the scientific point of view, it would be more correct to use the name "4-nonylphenols". Additionally, as show the results of many research projects on the nonylphenols and their ethoxylates, it is virtually impossible, using standard HPLC analysis, to separate and determine individually each nonylphenol isomer.

Therefore, whenever further down this text the term "4-nonylphenol" is used it should be read as "a sum of the isomers of 4-nonylphenol".

2. METHODS

2.1. CHEMICALS

Analytical standard of technical 4-NP with 99.9% purity was purchased from Riedel-de-Haen. Analytical standards of NP_1EO with 99% purity and NP_2EO with 99% purity were purchased from Dr Ehrenstorfer GmbH. Stock standard solutions of 4-NP and NPEO were prepared in acetonitrile for liquid chromatography.

Organic solvents – hexane, dichloromethane, methanol and acetonitrile as well as sorbent for column chromatography – were purchased from J.T. Baker.

2.2. SAMPLING

For the purpose of this study twelve Polish municipal wastewater treatment plants, labelled WWTP 1 –WWTP 12, were chosen. Short characteristics of each plant is given in Table 1.

The samples of the treated sludge obtained from the examined plants were collected 7 times – three times in 2005 (in March, June and September), two times in 2006 (in March and June) and twice in 2007 (in June and September). Of the examined plants the six, codenamed WWTP 3 – WWTP 8, were examined for the content of nonylphenol and nonylphenol ethoxylates during the whole research period (2005–2007), two of them (WWTP 1 and WWTP 2) only in 2005 and 2006, while the remaining four (WWTP 9 – WWTP 12) solely in 2007. Samples were transferred to the Laboratory of Environmental Monitoring of the Institute of Environmental Protection. The results of this analysis are presented in Table 4.

2.3. CHEMICAL ANALYSIS

The sludge samples were analysed for the content of nonylphenol and nonylphenyl ethoxylates using the method developed by Ahel and Giger (AHEL and GIGER 1985; AHEL et al. 1994), further modified and verified in the Laboratory of Environmental Monitoring of the IEP.

About 1 gram of each sample of dry sewage sludge was extracted for 4 hours with dichloromethane in Soxtec® extractor in 90 °C. Obtained extracts were evaporated under reduced pressure, redissolved in n-hexane and purified on glass columns filled with neutral aluminium oxide. The columns were eluted with hexane (F1), mixture hexane-dichloromethane 3:1 (F2), mixture of hexane and dichloromethane 1:1 (F3) and mixture dichloromethane-methanol 100:1 (F4). Fractions F3 and F4 were collected, evaporated to dryness under the nitrogen, redissolved in 1 cm^3 of acetonitrile and analysed using HPLC.

Determination of nonylphenol and nonylphenol ethoxylates was carried out on Waters HPLC-UV chromatograph. The analysed samples were separated by Spherisorb ODS –2 column, 250*4.6 mm, 5 μm (Waters). The chromatographic analyses were carried out with acetonitryle (A) and water (B) in gradient mode. The elution programme used here is presented below in Table 2.

Table 2

The programme of the gradient elution used in the chromatographic analysis

T [min]	%A	%B
0	50	50
1	50	50
20	0	100
30	0	100
34	50	50
40	50	50

The detection of the analysed compounds was performed using two detectors: the PDA detector (Photo Diode Array detector) working within the wavelength range 220–300 nm and the FLSC detector working at $\lambda = 275$ nm for excitation and $\lambda = 300$ nm for emission.

The content of nonylphenol ethoxylates in each sludge sample was determined for the sum of them (there was no separation of the individual ethoxylates).

In order to limit the number of the repetitions made for each sludge sample the method was fully validated prior to analyses. The validation parameters are summarised in Table 2. Each sample of sewage sludge was extracted and analysed twice.

3. RESULTS AND DISCUSSION

3.1. VALIDATION OF THE METHOD

The Table 3 presents the results of validation of the analytical procedure used for the determination of the content of 4-nonylphenol and nonylphenol ethoxylates in examined sludge samples. The following parameters were determined:

– precision of the measurement expressed as the *SD*; determined for the standard's solution,

– precision of the method expressed as the *SD*; determined for the standard's solution,

– accuracy of the method expressed as *R* (analyte's recovery); determined for the standard's solution,

– accuracy of the method, expressed as *R*, determined for the spiked sewage sludge sample.

Table 3

Validation parameters for the analytical procedure used in the study

Compound	Precision			Accuracy (standard's solution)		Accuracy (spiked sludge sample)		
	Conc. [μg/ml]	*SD* (measurement)	*SD* (method)	Conc. [μg/ml]	*R* [%]	Anal. conc. [μg/g]	Bakcgr. conc. [μg/g]	*R* [%]
4-NP	1.0	0.0033	0.069	1.0	85	3.99	n. d.*)	53.88
Σ NPEO	3.5	0.057	0.094	3.5	98.85	13.99	328	124.23

*) not detected

Another important analytical parameter determined for the developed method was the limit of quantification (LOQ). For both 4-nonylphenol and the sum of nonylphenyl ethoxylates it was set for 0.01 mg/kg d. w.

3.2. BASIC CHARACTERISTICS OF THE EXAMINED SEWAGE SLUDGE SAMPLES

In the Table 4 are summarised some basic properties – pH, dry weight and the content of the organic matter, of the examined sewage sludge samples. The results are presented as year averages.

The presented above results reflect the conditions of the sewage sludge generation and treatment. As their year-to year variability is not significant it can be stated that the possible changes here should not be considered as one of the major factors influencing the changes in the concentrations of the examined compounds.

3.3. 4-NP AND NPEO CONTENT IN EXAMINED SLUDGE SAMPLES

Table 5 presents the results of the determination of the content of 4-NP in examined sewage sludge samples. The compound was quantified only in samples from seven wastewater treatment plants collected in March 2005 and in the year 2007. In all other samples the content of 4-NP was either below the quantification limit or even below the detection limit.

Table 5

The content of 4-NP in sewage sludge from the examined wastewater treatment plants

Plant/ symbol	Content of 4-NP [mg/kg d. w.] in sewage sludge sampled in:						
	2005			2006		2007	
	March	June	September	March	June	June	September
WWPT 1	0.32	<0.01	<0.01	<0.01	<0.01	n. e.*)	n. e.*)
WWPT 2	0.32	<0.01	<0.01	<0.01	<0.01	n. e.*)	n. e.*)
WWPT 3	0.24	<0.01	<0.01	<0.01	<0.01	0.07	0.09
WWPT 4	0.85	<0.01	<0.01	<0.01	<0.01	0.06	0.11
WWPT 5	0.05	<0.01	<0.01	<0.01	<0.01	0.08	0.12
WWPT 6	0.23	<0.01	<0.01	<0.01	<0.01	0.18	0.18
WWPT 7	0.27	<0.01	<0.01	<0.01	<0.01	0.09	0.10
WWPT 8	<0.01	<0.01	<0.01	<0.01	<0.01	0.11	0.17
WWPT 9	n. e.*)	n. e.*)	n. e.*)	n. e.*)	n. e.*)	0.05	<0.01
WWPT 10	n. e.*)	n. e.*)	n. e.*)	n. e.*)	n. e.*)	0.12	0.07
WWPT 11	n. e.*)	n. e.*)	n. e.*)	n. e.*)	n. e.*)	0.09	0.13
WWPT 12	n. e.*)	n. e.*)	n. e.*)	n. e.*)	n. e.*)	0.05	0.05

*) n. e. – not examined

Table 6 presents the results of the analysis of the NPEO content in the examined sewage sludge samples. Although it is expressed as a sum of all ethoxylates we presume that the compounds dominating here were nonylphenol mono- and diethoxylates. This statement is supported by the results of the studies performed by Chang et al. (CHANG et al. 2005a; CHANG et al. 2005b) and LANGFORD et al. 2005).

Additionally the average yearly concentrations of nonylphenol ethoxylates in sewage sludge samples from the six wastewater treatment plants examined continuously throughout the research period (WWTP 3 – WWTP 8) are presented in figure 1.

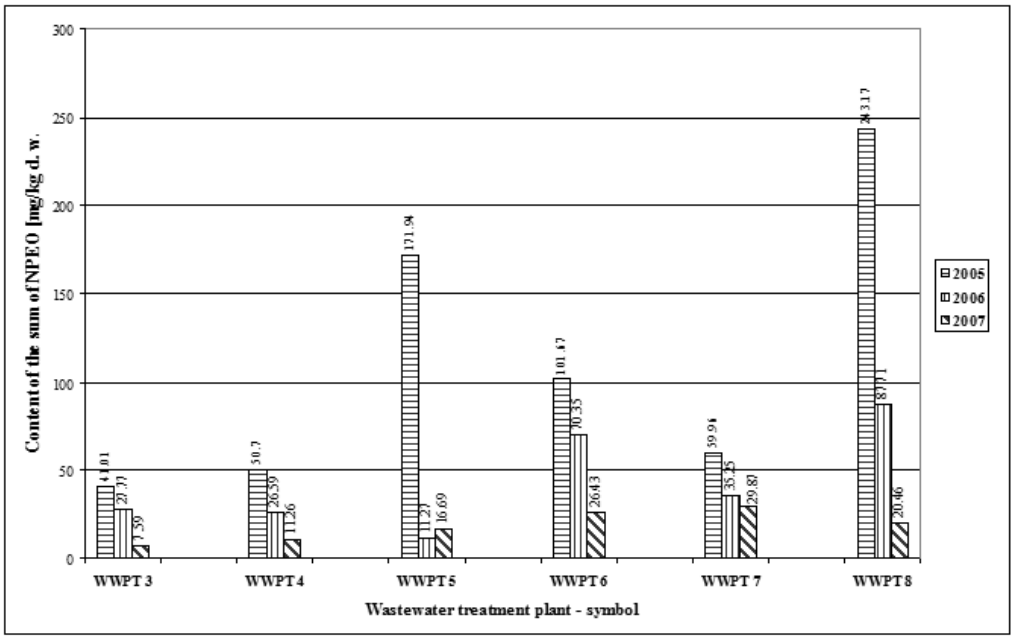

Fig. 1. Average yearly concentrations of NPEOs in sewage sludge from wastewater treatment plants WWTP 3 – WWTP 8

The content of 4-nonylphenol was determined in seven samples taken in March 2005 and in those collected in 2007. In all other samples the 4-NP could not be quantified because its content was either below the quantification limit – 0.01 mg/kg d. w., or even below the method's detection limit (0.005 mg/kg d. w.). Even in the samples where it was determined, the concentration of 4-NP was very low, nowhere exceeding the level of 1 mg/kg d. w. It was also observed that the values measured in the samples collected in 2007 were lower than those from March 2005. The only exception was WWPT 8, where only in samples taken in 2007 it was possible to determine the concentrations of the 4-NP.

These results stand in clear contrast to the findings made by GIGER et al. (1984), ELJERTSSON et al (1999), MAGUIRE et al (1999) and recently by LANGFORD et al. (2005). According to these authors in anaerobically processed sewage sludge 4-nonylphenol is the terminal and predominant degradation product of the higher nonylphenol ethoxylates. The results of these studies showed that in sewage sludge the concentrations of 4-NP reached the levels well above 10 mg/kg d. w. This com-

pound was moreover considered by these researchers as being stable under anaerobic conditions.

There are, however, several factors that may explain such low concentrations of 4-NP in sewage sludge observed in this study.

First of them is the fact that 4-NP actually undergoes the biological degradation not only in aerobic conditions, what is a well known and widely described fact (FUJI et al. 2000; SCHMIDT et al. 2004; SOARES et al. 2005; SOARES et al. 2006, CORVINI et al. 2006), but also in anaerobic conditions (CHANG et al. 2004, CHANG et al. 2005a, CORVINI et al. 2006). Especially, the experiments carried out by CHANG et al. (2004, 2005a, 2005b) demonstrated that the 4-NP might have been considered as a minor degradation product of the biological degradation process of nonylphenol ethoxylates both under anaerobic and aerobic conditions.

It is also possible that low quantities of 4-nonylphenol in examined sewage sludge samples can be attributed to the change in the conditions from anaerobic to aerobic during post-treatment storage of sludge.

Also the time of the anaerobic treatment of the analysed sludge could play an important role in relative and absolute concentrations of 4-NP and NPEOs. As show the results of the research by LUPPI et al. (2007) during first two weeks of the anaerobic treatment of the sewage sludge the predominant forms are NP2EO and, later, NP1EO, while 4-NP is practically not observed. It becomes predominant degradation product of the nonylphenol ethoxylates only in the third week, although NP1EO and NP2EO can still be quantified then. In this context it should be also pointed out that the content of the NPEOs in examined sewage sludge samples cannot be a definitive indicator of predictable content of 4-NP, even though it is significantly high. One of the limitations of the applied analytical method, although not influencing the overall conclusions drawn from this study, is that it does not enable identification and quantification of individual nonylphenyl ethoxylates in the examined samples. Therefore, this parameter is reported here as a content of the sum of nonylphenyl ethoxylates. Based on the literature data, it was assumed that in processed sewage sludge predominant, if not sole, nonylphenol ethoxylates present are NP2EO and NP1EO, with the latter being a direct precursor of 4-NP. Therefore it cannot be excluded that NP2EO predominates in the examined samples, what may explain the low quantities of 4-NP observed.

These are possible reasons for the low content of 4-NP in the examined samples of sewage sludge. However, as the determination of the possible degradation pathways of nonylphenols in examined sewage sludge was not one of the aims of this study, it is not possible to clearly identify which of the factors listed above can be considered responsible for such low contents of 4-NP in examined sludge samples.

In all sewage sludge samples from examined wastewater treatment plants the content of nonylphenol ethoxylates was comparable to that established for sewage sludge in Nordic countries (Norway, Sweden, Denmark) (for Norway it was 22–650 mg/kg d. w.

in 2000, for Sweden 23–171 mg/kg d. w. in 1993, while for Denmark 0.3–67 mg/kg d. w. in 1995) (EU, 2000). It was also much lower than in the United States, where, according to PRYOR et al. (2002) it ranged from 1130 to 1840 mg/kg d. w.

One of the main tasks of the present study was to determine how the introduction of a new regulation restricting the use of nonylphenol ethoxylates – the Decree of the Minister of Economy (Minister of Economy of the Republic of Poland, 2004), may possibly influence the content of these compounds in processed sewage sludge during a long period (up to three years). Although the direct conclusions cannot be drawn here, mainly because of the lack of the data predating the introduction of the Decree, a good indication are data obtained for the six of the examined wastewater treatment plants, codenamed WWTP 3 – WWTP 8. These cover the period between spring 2005 (shortly after the Decree had entered into force) and autumn 2007. In general, for all those plants a radical decrease in content of the sum of NPEOs to the levels below 50 mg/kg d. w, which is the threshold value set by the project of the new EU Directive on Sewage Sludge (EU, 2000), was observed. This decrease was in some cases significant, like in case of WWTP5, where the concentrations of NPEOs dropped from 455 mg/kg d. w. at the beginning of the study to about 13 at its end, or of WWTP8, where the initial value was 309 mg/kg d. w. while the final one only 23 mg/kg d. w. It should be noted that not in all of the examined plants the rate of this decrease was the same. In some of them, like in WWPT3, WWTP4, WWTP5 or WWTP7 the decrease was rapid, observed within the period between the first and the second uptake of the sludge samples, and followed by stabilisation or a slow decrease of the content of NPEOs in sewage sludge samples, while in the others, like in WWTP6 or WWTP8 this process was slower.

Two other important things should be noted, which were also observed for samples from the plants codenamed WWTP1 and WWTP2. The first point is that in the second year the content of the NPEOs slightly increased. This phenomenon can be possibly explained by the fact that after a period of almost total elimination of the NPEOs from the products that ultimately reached the wastewater treatment plants these compounds were re-introduced into some products, although in much lower quantities. Another interesting observation, also made during the second year of the study was the fluctuation in the content of the NPEOs in almost all samples. The increase of the concentration of NPEOs in summer samples, comparing to the spring ones, was observed. This might be explained by the fact that the wastewater reaching the installations in summer is more concentrated.

In general, the examination of the samples taken in 2005 and in 2006 has demonstrated the sharp decrease in content of these compounds in 2005, not followed by a significant increase in 2006, what may, although indirectly, support the assumption that the entrance in force of the Decree resulted in the decrease in content of nonylphenols in sewage sludge from the examined municipal wastewater treatment plants. The results obtained in 2007 for the plants WTP3 – WWTP8 confirmed this conclu-

sion – once again the continuous decrease of the content of NPEOs, and this time significant, was observed. The above statement is further supported by the results obtained for four additional wastewater treatment plants, codenamed WWTP9 – WWTP12. The content of NPEOs in the sludge samples from these plants nowhere exceeded 50 mg/kg d. w. and only in one of them was above 20 mg/kg d.w.

It was stated that the nature of the incoming wastewater and, although to lesser extent, the percentage of the industrial wastewater in the incoming wastewater flux, may influence the content of nonylphenol ethoxylates in sludge. It was clearly visible in case of the plant WWTP 1, where only 5% of the wastewater incoming was the industrial wastewater, originating solely from the food industry. As a consequence the content of NPEOs in sludge during the whole study period was very low. In contrast, for those plants that received greater amounts of the industrial wastewater generated by metallurgy, electroplating and electroengineering industries, the concentration of the NPEOs in sludge was high, at least during the first two years of the study (see WWTP 2, WWTP 6, WWTP 8). However, it should be pointed out that such tendency was not observed in the third year, what may signify, that this factor either did not or stopped to play a significant role in course of the study.

4. CONCLUSIONS

The following conclusions were drawn from the present study:

1) The content of NPEOs in all samples of sludge from examined Plants was in most cases lower than 50 mg/kg d. w. – the threshold value established by the new EU Directive on sludge.

2) There is no clear tendency observed for the content of NPEOs in sewage sludge from the examined Plants – after the decrease in 2005 there is an incerease in 2006 followed once again by the decrease in 2007. Although it seems that the observed and predicted decrease was a well established tendency, the reasons for this brief reversal remain unclear.

3) Apart from the samples collected in March 2005 and those in 2007, in no sludge sample 4-NP was quantified. Moreover in the samples where the quantification was possible the levels of 4-NP were low. This may be attributed to the various factors, but it is not possible to say which of them played the most important role.

4) Although there is no direct evidence supporting the statement that the implementation of the Decree of the Minister of Economy limiting the use of the 4-nonylphenol and its ethoxylates resulted in the permanent decrease of the content of these compounds in the sewage sludge obtained from the examined Plants, there are some indirect evidences that may support it. On the other hand some results still suggest that this can be attributed to periodical, one year and many-years, fluctuations caused by the other factors, what should be examined in future.

5) Some correlation between the content of the NPEO in sludge and the nature of the treated wastewater was stated. The correlation occurs generally between the content of NPEO and the provenience of the industrial wastewaters.

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