



Contents of 4-Nonylphenol in Surface Sea Water of Amur Bay (Japan/East Sea)

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ARTICLE INFO

Article history:

Received 9 March 2016

Received in revised form 13 May 2016

Accepted 31 May 2016

Available online 23 June 2016

Keywords:

4-Nonylphenol

HPLC

Sea waters

Amur Bay

ABSTRACT

The determination of 4-nonylphenols has been developed using HPLC with fluorescence detection method. 4-Nonylphenols in sea water samples were extracted using a liquid–liquid extraction. Acidification and adding salting-out agents (NaI) of water samples increased the extraction degree. The extraction of 4-nonylphenols was done twice with 20 mL of methylene chloride. The applied concentrated range was over 5–1000 ng/mL for the 4-nonylphenol. The recovery test ranged from 78.5 to 89.9% with relative standard deviations between 1.0 and 7.5% of 100 ng/mL of the standard phenols spiked with the water sample and the detection limit was 1 ng/mL. The proposed method was applied satisfactorily for the determination of 4-nonylphenole in sea water samples. Levels of 4-nonylphenol were determined in the sea waters of the Amur Bay. Water samples were collected every year from 2008 to 2015. Concentrations of 4-nonylphenol in the waters ranged from levels below the detection limits up to 1.24 µg/L.

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Introduction

Alkylphenol compounds appear in waste waters of major industrial centers, and their content in coastal sea water areas may be rather high and influence living organisms negatively (Taylor and Harrison, 1999). One of the representatives of alkylphenol class is 4-nonylphenol not allowed to be dumped in the exclusive economic zone of the Russian Federation (<http://base.garant.ru/12147594/>). However there are some data about the presence of 4-nonylphenol and other compounds of alkylphenol class in sea waters (Kondakova et al., 2012).

4-Nonylphenol, as well as some other alkylphenols, has strongly marked xenoestrogen properties (Bernacka et al., 2009; Peng et al., 2006). For the first time estrogenic activity of phenols was noted in 1978 (Muller and Kim, 1978). Xenoestrogens (destroyers of endocrine system) are substances of anthropogenic origin, simulating, copying or blocking the effect of natural hormones synthesized by the endocrine glands; they interact with estrogen receptors and change a normal course of biochemical processes of the cell (Renner, 1997). Xenoestrogens influence the reproductive and endocrine systems of animals as well as estrogen, cause feminization of the population and have mutagenic and carcinogenic effects (Vazquez-Duhalt et al., 2005).

4-Nonylphenol formed in the environment by the degradation alkylphenolpolyethoxylates (AP) (Ike et al., 2002; Jonkers et al., 2001). AP are actively used in various industrial processes (Kneeper and Berna, 2003). Oil, mining, chemical, textile, plastic and pulp-and-paper industries are the major consumers of these products (Kneeper and Berna, 2003; Maguire, 1999; Soto et al.,

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Peer review under responsibility of Far Eastern Federal University.

1992). Alkylphenol polyethoxylates are the most widespread non-ionogenic surface-active substances all over the world due to their high stability and excellent cleaning and emulsifying properties (Maguire, 1999; Berryman et al., 2004).

Despite the fact that alkylphenolpolyethoxylates are not classified as highly toxic substances and can be effectively removed from waste waters by means of standard cleaning, they represent a class of highly environment-hazardous compounds (Canadian Council of the Ministers of the Environment, 2001). The reason for that is the fact that anaerobic condensation and biotransformation result in nonylphenol polyethoxylates transforming into stable short-chain metabolites, such as 4-nonylphenol which is considered as a potential destroyer of the endocrine system (Berryman et al., 2004).

In connection with marked lipophilic properties, 4-nonylphenol can be accumulated in the organic matter and lipids of solid matrices and animals, respectively. Bioaccumulation effects, which may be present in the next generations though may be of sharp-toxic nature as well (Peng et al., 2006).

Due to high toxicity, large production volumes and high stability in the environment, the world's ecological and governmental organizations suggested to impose restrictions on the use of APs (Canadian Council of the Ministers of the Environment, 2001). Use of household detergents based on 4-nonylphenol is already forbidden or restricted in most European countries, for example, in Switzerland the ban to use polyethoxylates of 4-nonylphenol was imposed as far back as 1986. In some other countries risk reduction was achieved by voluntary agreement with detergent manufacturing companies (Ahel et al., 2000). According to the Russian legislation (Regulation of the Russian Federation Government no. 251 dated March 24, 2000) and MARPOL Convention 73/78, discharge of nonylphenol to the marine environment is forbidden in the exclusive economic zone of the Russian Federation. Nonylphenol is entered in the "Bulletin of the Russian Register of Potentially Dangerous Chemical and Biological Substances" (<http://rpohev.ru>).

There are some data in the literature about 4-nonylphenol content in river and lake waters as well as in coastal sea water areas. 4-Nonylphenol was found in surface waters, discharged waters and bed silt of most developed countries: Canada, Great Britain, Spain, Japan, USA, Germany, Taiwan, Switzerland and Italy (Li et al., 2004; Bester et al., 2001; Ying et al., 2002). Concentration of nonylphenol in the environmental objects is varied from below detection level values to rather high concentration of 644 µg/L (Bernacka et al., 2009). According to the classification given by Baronti (Soto et al., 1992), surface waters with content of nonylphenol less than 1 µg/L relate to poorly contaminated, 1–10 µg/L to contaminated, and more than 10 µg/L highly contaminated. According to a lot of researches, 4-nonylphenol is toxic for fishes ($LC_{50} = 17\text{--}3000$ µg/L). Invertebrate and marine algae are also sensitive to the effect of 4-nonylphenol (LC_{50} in intervals of 21–3000 and 27–2500 µg/L, accordingly) (Vazquez-Duhalt et al., 2005).

Analytical determination of alkylphenols is complicated due to their low concentration in the investigated matrices, dilution and frequently high saline background of the sample. Therefore, concentration of 4-nonylphenol is necessary prior to its determination.

Earlier, 4-nonylphenol content in coastal waters of the Russian Far East was not analyzed at all, that is why the purpose of this work was to determine 4-nonylphenol levels in the region most affected by anthropogenic influence – the south of Primorsky region.

Materials and Methods

Solvents and Standards

Analytical standard of 4-nonylphenol (>98% pure) was obtained from Alfa Aesar (Ward Hill, MA, USA). Sodium chloride, magnesium sulfate, magnesium chloride, calcium chloride, potassium chloride, sodium bicarbonate, potassium iodide, potassium bromide, sodium hydroxide, and anhydrous sodium sulfate, all >99% pure, were from Neva-reaktiv (St. Petersburg, the Russian Federation). Hydrochloric acid solution (36% v./v. in water) was >98% pure. To perform the extraction, pentanol, benzene, and hexane were used from Vekton (St. Petersburg, the Russian Federation), and methylene chloride, carbon tetrachloride were from Ekos-1 (Moscow, the Russian Federation). All employed organic solvents were of high purity grade.

In the preparation of the basic, working standard solutions and extracts for chromatographic separation, acetonitrile (class 0 for chromatography) was used from Kriohrom (St. Petersburg, the Russian Federation). Basic standard solution with a concentration of 1000 µg/mL was prepared by dissolution of precisely weighed portion of 4-nonylphenol in acetonitrile and stored at a temperature of -18 °C for not longer than 10 days. Standard working solutions of 4-nonylphenol in acetonitrile with concentrations of 0.01, 0.05, 0.1, 0.5, 1.0 and 2.0 µg/mL were used for plotting the calibration curve (Fig. 1). Working standard solutions were prepared immediately before the analysis.

Preparation of Artificial Seawater

Artificial seawater prepared according to Krot (1966) was used as artificial matrix. For this purpose weighed portions of dry salts (sodium chloride, magnesium sulfate, magnesium chloride, calcium chloride, potassium chloride, sodium bicarbonate) were dissolved in 500 mL of distilled water. The derived mixture was put into an ultrasonic bath for 5 min and diluted with distilled water to 10 L. Salinity of the prepared artificial seawater was $35 \pm 0.5\%$. Artificial seawater was stored at a temperature from 0 to $+2$ °C for not longer than 5 days.

Sonication processing was performed used Sonorex Super, RK 52 (Bandelin electronic GmbH & Co KG, Germany, 50 Hz, 220 V).

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