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Chlorophenolic compounds in bottom sediments of the boreal lake as a specific mark of anthropogenic impact

Kolpakova E.S.*, Velyamidova A.V.

N. Laverov Federal Center for Integrated Arctic Research, Ural Branch of the Russian Academy of Sciences, Severnaya Dvina Emb., 23, Arkhangelsk, 163069 Russia

ABSTRACT. The paper presents the results of multi-year studies of bottom sediments of a boreal lake (the south-west of the Arkhangelsk region,Russian Federation), which exist under a specific anthropogenic impact, namely, the long-term usage of a chlorophenol-containing biocide (NaPCP) in the past. It is shown that levels of pentachlorophenol (PCP) significantly decreased after more than two decades since the discontinuation of biocide usage. However, an increase in levels of PCP derivatives (namely, toxic chlorinated guaiacols and catechols) in lake sediments was found. These chlorophenolic compounds were detected in a state inaccessible for biodegradation, which indicates their persistence in sediments for a long time.

Keywords: chlorophenolic compounds, chlorophenolic-containing biocide, bottom sediments, boreal lake

1. Introduction

In the northern regions of Russia for a long time, until the 1990s, the chlorophenol-containing biocide (NaPCP) was intensively used for timber treatment, which led to soil contamination at the industrial sites of timber mills with residual amounts of biocide components (Kolpakova and Velyamidova, 2019). Its main component was pentachlorophenol (PCP). Due to its high toxicity, ability to transboundary transfer, accumulation in the environmental compartments and bioaccumulation in higher trophic levels, PCP was included in the list of persistent organic pollutants (POPs), which are the subject to the complete elimination of production and use in accordance with the Stockholm Convention on Persistent Organic Pollutants (May 17, 2004). The study of the distribution, "fate" and transformation of POPs in natural ecosystems refers to a set of practical measures aimed at reducing its negative impact on the environment and public health. Over time, PCP can be converted in environmental media to other organochlorine compounds, in particular chlorophenolic compounds (Field and Sierra-Alvarez, 2007). At the same time, the toxicity of some chlorine derivatives exceeds the toxicity of PCP itself (Field and Sierra-Alvarez, 2007).

This paper presents the results of multi-year monitoring studies of the bottom sediments of a small shallow boreal lake (in the south-west of the Arkhangelsk region, RF), located near the industrial site of the shutdown timber mill and the timber treatment site itself.

2. Materials and methods

Sampling and analysis of bottom sediments were carried out by employees of the Laboratory of Eco-Analytical Research of the N. Laverov Federal Center for Integrated Arctic Research (Arkhangelsk). The detailed description of the object of studies and the analytical procedure were presented in Kolpakova and Velyamidova (2019).

3. Results and discussion

Reconnaissance studies of the bottom sediments of a small shallow boreal lake in the south-west of the Arkhangelsk region were carried out in 2002, 7 years after the timber treatment was discontinued. Pentachlorophenol has been detected in lake sediments at concentrations from 22 to 30 ng g^{-1} (Kolpakova and Velyamidova, 2019). To obtain information on trends in the behavior of residual toxic organochlorine components of the biocide, studies were continued in 2012 and 2017. A decade after this reconnaissance studies, content of PCP in lake sediments increased up to 189 ng g^{-1}, exceeding the predicted no effect concentration of this pollutant in sediments (124 ng g^{-1}) (Toxicological profile..., 2001). According to the results

*Corresponding author.
E-mail address: kolpelen@yandex.ru (E.S. Kolpakova)

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of studies in 2017, contents of PCP in lake sediments have noticeably decreased (to 1-8 ng g^{-1}).

As is known, bottom sediments of small shallow low-flow lakes are considered effective "traps" for bioaccumulative toxic organochlorine components of biocide (including PCP), the accumulation of which in silty sediments with a high content of organic matter was especially significant during the period of intensive NaPCP usage (Kolpakova, 2018). One of the reasons for the decrease in the levels of these pollutants in sediments during the observation period is most likely the decrease of their soil "residues" in the drainage area of the studied lake as the result of more intensive organochlorines transfer into the aquatic environment in previous years. In addition, the residual amounts of the organochlorine components of biocide associated with the organo-mineral matter of soils are less mobile to date (Kolpakova and Velyamidova, 2019).

On the other hand, the behavior of ionogenic PCP (including migratory mobility) strongly depends on the physicochemical properties of the environmental media itself, and, first of all, on the pH value (Toxicological profile…, 2001). It has been established that over the past decade there has been no significant change in the pH values of lake sediments: pH 6.60-7.03. At these pH values, PCP was present in sediments mainly in the ionized form (more mobile and water-soluble form, with a low ability to be sorbed in silty sediments), which favored intensive transfer of this pollutant in the aquatic environment and participation in degradation/ transformation reactions (Lyytikainen, 2001).

The most effective mechanism of PCP degradation is considered to be the microbial degradation/transformation with the formation of its derivatives (Field and Sierra-Alvarez, 2007) under various conditions of the aquatic environment. At the same time, it is known that, depending on the pH, both bioavailable and non-bioavailable PCP forms (easy and hard to extract fractions, respectively) with different degrees of sorption on soil particles are formed (Lyytikainen, 2001). Earlier, in 2002 and 2012, PCP was found mainly in the easy to extract fraction, which contributed to its active involvement in the microbial degradation/transformation with the formation of other chlorophenolic compounds with varying toxicity and lipophilicity. In 2017, PCP was found in sediments in both easy and hard to extract fractions.

Another significant factor is the content of organic carbon (C_{org}). In 2012 and 2017, C_{org} in lake sediments was determined in large amounts – from 11.19 to 30.89%. According to some researches (Field and Sierra-Alvarez, 2007; Gaofeng, 2004), the rate of PCP transformation increases in bottom sediments and soils with a high C_{org} content. However, when interacting with soil organic matter, PCP is able to form various more persistent compounds, diffusing into soil aggregates, elementary soil particles, thus becoming less bioavailable (Lyytikainen, 2001).

In 2012, the composition of chlorophenolic compounds in the bottom sediments of the anthropogenically loaded lake reflected the profile of the compounds found in the soils of the adjacent industrial site of the timber mill. PCP (46-189 ng g^{-1}), 3,4,5-trichlorguaiacol (15-150 ng g^{-1}), and 4,5,6-trichlorguaiacol (up to 13 ng g^{-1}) accounted for 60-70% of the total content of chlorophenolic compounds in lake sediments. Also, 2,4,5-trichlorophenol was found in lower concentrations (1-8 ng g^{-1}). Other high-chlorinated compounds (2,4,6- and 2,3,4-trichlorophenols, 2,3,5,6-tetrachlorophenol) were found less frequently and in very small concentrations, less than 3 ng g^{-1}. Low-chlorinated compounds were mainly represented by 4-chlorophenol (34-69 ng g^{-1}) and 2,6-dichlorophenol (16-17 ng g^{-1}).

After 15 years from the date of reconnaissance studies, the content of chlorophenolic compounds in recent lake sediments has increased significantly. Thus, once in 2012 concentrations of chlorophenolic compounds were 80-337 ng g^{-1}, then in 2017 they were already 700-3146 ng g^{-1}. At the same time, low-chlorinated compounds already dominated in the chlorophenolic composition (from 59 to 77%), while in 2012 high-chlorinated compounds still prevailed (from 64 to 100%).

Moreover, the concentrations of the dominant toxic PCP and trichlorguaiacols decreased over time by an order of magnitude (to 2-8 ng g^{-1}). Such a strong decrease in their concentrations was apparently associated with the active reductive dechlorination under the influence of anaerobic microorganisms, the products of which are low-chlorinated compounds. Indeed, the concentrations of mono- and dichlorinated compounds were by orders of magnitude higher than the concentrations of PCP, tetra- and trichlorophenols and their derivatives.

In 2017, low-chlorinated phenols were determined in the lake sediments in the greatest amounts: 2-chlorophenol (71-535 ng g^{-1}g), 4-chlorophenol (96-188 ng g^{-1}), 2,4-dichlorophenol (76-329 ng g^{-1}), 2,6-dichlorophenol (14-124 ng g^{-1}), and 2,4,5-trichlorophenol (31-788 ng g^{-1}).

Such toxic derivatives of chlorophenolic compounds as hydroxychlorophenols (chlorcatechols) were found in recent lake sediments in concentrations of the same order. 3,4-, 3,5-and 4,5-dichlorocatechols, as well as 3,4,5-trichlorocatechol and tetrachlorocatechol were identified. The chlorcatechols contribution ranged from 24 to 50% in the total content of chlorophenolic compounds. The presence of chlorcatechols in lake sediments was possibly associated with both the supply of these compounds from the soils of adjacent territories and their formation as the result of aerobic microbial transformation of chlorophenols (mainly in the soils of adjacent territories).

4. Conclusions

Thus, 22 years after the timber treatment was discontinued on the timber mill, the concentrations of PCP as the main component of chlorophenol-containing biocide (NaPCP) in lake sediments have significantly decreased. The composition of chlorophenolic compounds in recent lake sediments

was mainly represented by toxic chlorguaiacols and chlorcatechols. The presence of chlorinated derivatives of PCP in a state difficult for biodegradation and their amounts suggest that the compounds remain in bottom sediments for an indefinitely long time. The obtained data on the content of PCP and other chlorophenolic compounds can be used to assess the current state of the studied lake and other similar aquatic ecosystems in the Arkhangelsk region in terms of contamination with persistent toxic organochlorine components of biocide because of its long-term usage in the past.

Conflict of interest

The authors declare no conflict of interest.

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