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Persistent water pollutants: case of ethylenediaminetetraacetic acid in the Czech Republic

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Abstract: Reuse and recycling of products composed of natural matter is relatively without significant environmental problems. However, recycling of products produced using modern synthetic technologies often brings new challenges. Our analysis has shown that substitution of citric acid with artificial substance of ethylenediaminetetraacetic acid causes important environmental problems. The case study carried out in the Elbe river basin shows that the ethylenediaminetetraacetic acid concentration standard has been exceeded, particularly from confluence of the Vltava and Elbe rivers. Open questions and tasks for future technological development and environmental policies are formulated, particularly the idea to replace artificial substances with nature-based ones. This would enable better introduction of circular economy ideas in the use of resources.

Keywords: ethylenediaminetetraacetic acid; EDTA; circular economy; environmental policy; wastewater management; organic pollutants; substitutes; Czech Republic.

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Petr Šauer is working as the Director of the Institute of Sustainable Business at UEP. He founded the Department of Environmental Economics at UEP. His long-term research orientation deals with environmental economics, policy and management; multiple projects focusing on surface water quality management, voluntary environmental agreements, methodology of ex-post analyses in environmental policy, municipal solid waste management, optimisation of expenses on environmental protection, environmental tax reform, multi-criteria analysis in quality of living and recreation, and curricula development in the respective field. He is the author of the first textbook on environmental economics and policy in the Czech Republic and many scientific publications.

Karolína Keprtová works as an expert in integrated pollution prevention and control at CENIA, Czech Environmental Information Agency. She is a young researcher as well. Her major research projects have focused on optimising of processes in chemical industry, management of selected chemicals; and treatment of municipal and industrial wastewater including sludge management. Within the Agency's scientific work, she participates in assessment of processes leading to groundwater and surface water pollution. She has also worked on projects dealing with spreading of pollution from old industrial contaminated sites in chemical industry. In the past, she worked as a specialist in a multinational waste management company. In the area of waste management, she has specialised mainly in waste evaluation and problems of large-scale waste. She holds a professional qualification in category 4 according to the IPPC Act. She is also a PhD student at The University of Chemistry and Technology, Prague.

1 Introduction

Circular economy has an important position in the EU environmental policy strategies. Current legislation provides for parameters and environmental limits which are monitored in surface waters.

However, there are many more organic contaminants in nature which are not regulated by the current legislation. One of the reasons is that toxicological characteristics are not known for some of the contaminants. It is important to have information not only on current production and consumption of sources but also on the contribution of sediments and aquatic organisms in water bodies.

In recent years, high concentrations of organic pollutants such as polychlorinated biphenyls (PCB), ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), chlorinated benzene, naphthalene and other organic compounds were found out. Many of these compounds degrade neither through natural processes nor in wastewater treatment.

They enter the nature environment where, inter alia, they get into the food chain with all the negative impacts on human and ecosystems health; but they are not monitored.

The article aims at presenting the results of research focused on the EDTA occurrence in the Elbe river basin, which is the largest one in the Czech Republic. We went beyond the details of standard studies provided by the Elbe River Administration.

2 EDTA – the properties and use

2.1 *The properties of EDTA*

Patented in Germany in 1935, it was developed to replace citric acid in the process to prepare water for dyeing of textiles. The EDTA synthesis was then patented six years later. For the first time, EDTA was made from ethylenediamine, chloroacetic acid and sodium hydroxide. In 1941, EDTA was synthesised in a way that is still in use today, i.e., using alkaline cyanomethylation of ethylenediamine. The third most commonly used method of EDTA production was discovered in the 1960s. It separates the cyanomethylation process from hydrolysis (Paolieri and Münz, 2017).

Disodium and tetrasodium EDTA are also commonly referred to as EDTA (Paolieri and Münz, 2017; IHCPECB, 2004). EDTA is a crystalline substance that is most frequently applied in aqueous solution (Oviedo and Rodríguez, 2003). It forms complexes with divalent and trivalent metal cations. The stability of metal complexes in the removal of metals from soils according to stability constants is as follows: $\text{Na}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Fe}^{2+} < \text{Al}^{3+} < \text{Zn}^{2+} < \text{Cd}^{2+} < \text{Pb}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} < \text{Hg}^{2+} < \text{Fe}^{3+}$; the formation of individual complexes is conditioned by optimum pH of the medium (Engelhardt et al., 2007; WHO, 1998). The stability of complexes with individual metals is reflected in their degradability. Despite its high stability constant, the Fe^{3+} EDTA complex (as the only one) undergoes photodegradation in aqueous solutions under normal conditions. The biodegradation of the complexes strongly depends on the bonded ligand. Methods have been described that support biodegradation of EDTA, such as a long sludge retention time or pH increase but EDTA is generally poorly biodegradable (Oviedo and Rodríguez, 2003; Nörtemann, 1999).

EDTA is not toxic to mammals at concentrations that are commonly found in the aquatic environment but from the ecotoxicological point of view, if present in the aquatic environment, EDTA may cause mobilisation of metals adsorbed in sediments (Oviedo and Rodríguez, 2003, Nörtemann, 1999). Mild renal changes have been observed in laboratory rats at a short-term direct exposure to pure EDTA disodium salt. Due to the chelating properties of EDTA, the results of long-term exposure are not provable (WHO, 1998).

2.2 *The use of EDTA in production and consumption*

In industrial production, EDTA is used due to its complexing ability, especially where presence of metal ions is undesirable, such as in paper and cellulose industry (kraft and sulphite pulp treatment), textile industry (textile fibre dyeing), cosmetics, pharmaceuticals (e.g., eye preparations, antidote to heavy metal poisoning), fertilisers (liquid fertilisers), paints, in the photographic industry, metal surface finishing, soil

remediation and others. It is used as a stabiliser – it inhibits oxidation processes (Whittaker et al., 1993).

EDTA is a part of commonly used cosmetic products, shampoos, soaps, detergents, softeners and others that serve people's daily needs. EDTA is also used in agrochemistry and food industry as a preservative and stabiliser (indicated as E 386).

It is clear from the above that, in addition to the direct application of EDTA containing preparations on plants and soil, its main source is wastewater (including treated water) discharged into surface water.

Another EDTA source is industrial contaminated sites. These sites have been assessed roughly in the territory of the Czech Republic. At present, detailed mapping of these sites is being done. Records of the contaminated sites are kept by the Ministry of Environment of the Czech Republic.

3 EDTA analysis in the Czech Republic

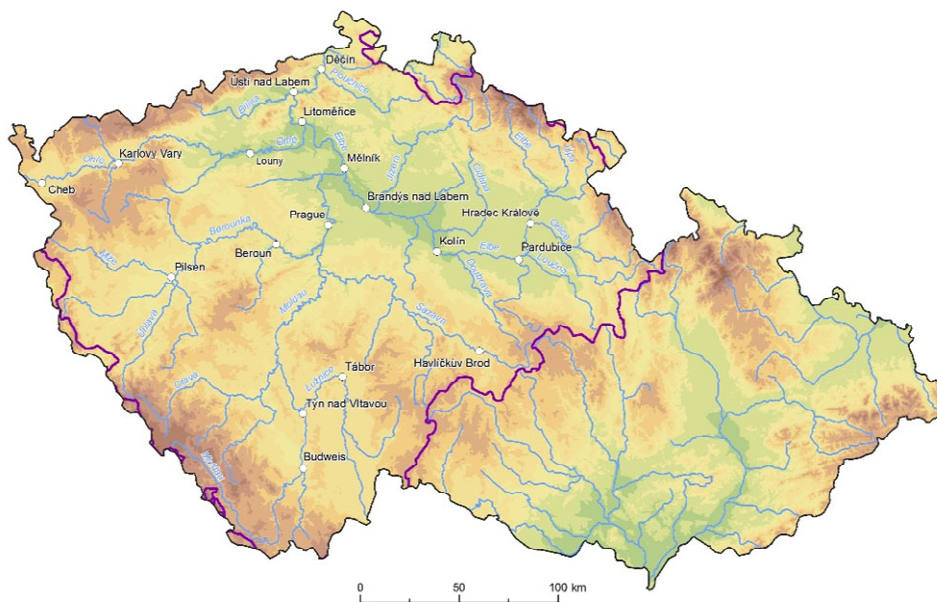
3.1 Data and methodology of the analysis

In the Czech Republic, EDTA is monitored in surface water according to the Government Regulation No. 401/2015 Coll. on indicators and values of permissible pollution of surface water and wastewater, requirements of permits for wastewater discharge into surface water and sewerage and on sensitive areas. The Regulation sets the environmental quality standard of 5 µg/l for EDTA content in surface water and requires that “its content is not increased in sediments, depositions and living organisms”. Under the Act No. 254/2001 Coll. on water, as amended, EDTA is a dangerous and harmful substance.

Measurements made by the Elbe River Authority (*Povodí Labe*), which is the river basin administration body, were the source of the data (PL, 2018). Systematic monitoring has been carried out since 2016; however, a series of partial measurements was performed before this period. Similar measurements also take place in sub-basins of the Vltava River and other watercourses in the Czech Republic. Spot samples are taken and then analysed in a specialised laboratory. Synthetic complexes (EDTA, NTA) are determined by esterification, hexane extraction and gas chromatography using an NPD detector.

Analytical work was carried out on two levels. On the first level, data and reports obtained from the Elbe River Authority (*Povodí Labe*) and reports of other sub-basins (publicly available sources) were analysed. The obtained data were processed using methods of mathematical statistics and displayed in graphs and profiles. A clearly arranged map of the river basin was prepared to illustrate the territorial extent of the Elbe river basin and distribution of some of the cited localities (see Figure 1).

The profile name, river kilometre and hydrological order number are available for each profile monitored. Furthermore, the average value of EDTA content in the surface water of the Elbe River in µg/l for the hydrological year 2018 is determined; it is calculated as the arithmetic mean of 12 measured values. The minimum and maximum values and the number of measurements at which the limit value of 5 µg/l was exceeded (as provided for by Czech legislation) are determined. Sampling dates and exact time as well as the EDTA values in µg/l are available for each sample.

Figure 1 Elbe River basin in the Czech Republic (see online version for colours)

Note: _____ Elbe river basin border.

The annual average values for individual measuring profiles were then recorded in a longitudinal profile of the Elbe river, supplemented with river kilometre and profile names. Measurement values in individual profiles were then analysed over time.

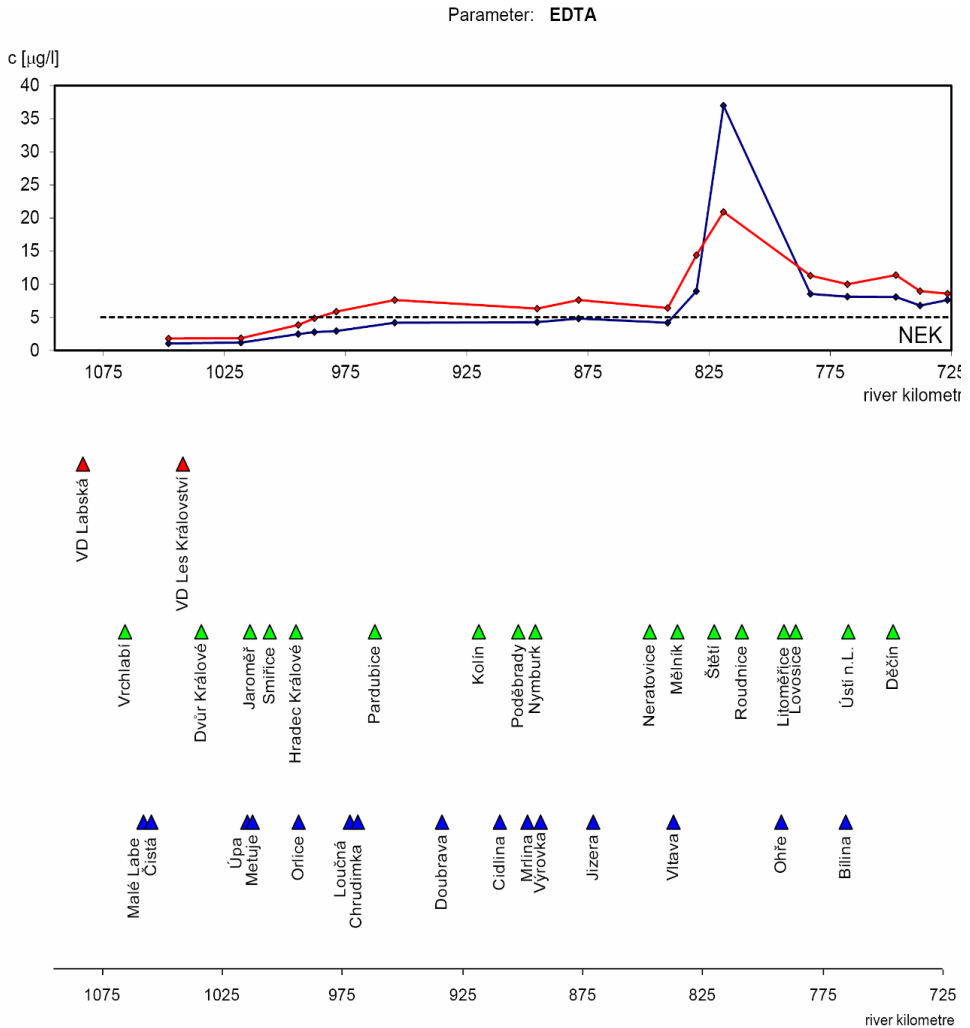
Detection of general EDTA occurrence was the second level of the analytical work. For these purposes, categories of EDTA sources (own EDTA production, EDTA import, use within industrial production, use within consumption, use in agriculture and food industry, old contaminated sites) were defined. Data were obtained from publicly available sources, from the IPPC database and from published works.

It was found out that in the Czech Republic there is a single EDTA producer with an annual production volume that cannot meet the needs of the manufacturing industry. Imports from abroad (although demonstrably carried out) could not be documented. On the other hand, it has been proved that a great number of EDTA-containing products are imported from EU and non-EU countries. EDTA consumption in the paper industry is falling rapidly as a result of requirements for application of best available techniques (use was found out in one case; the factory is owned by an EU company). On the contrary, consumption of liquid EDTA-containing fertilisers is increasing due to climate change.

In the area of waste and water management (and in connection with transition to circular economy), e.g., the use of packaging waste and packaging itself is more frequent. EDTA gets into wastewater during their processing. Due to the fact that EDTA removal technologies are not in use (do not exist), it is possible to transfer this pollutant into surface water. Although wastewater is not used commonly for watering purposes in the Czech Republic, this possibility is being discussed and it cannot be excluded that the situation could change in the future. Municipal sewage treatment sludge is applied onto the soil or it is composted and the compost is subsequently used to improve soil. These procedures ensure a continuous supply of EDTA to soil and surface water and

groundwater. By taking such water for drinking purposes, humans ultimately become consumers of EDTA again.

Figure 2 EDTA values in longitudinal profile of the Elbe River in 2016–2017 (see online version for colours)



Notes: - - - EDTA concentration standard (according to the Government Regulation No. 401/2015 Coll. on indicators and values of permissible pollution of surface water and wastewater, requirements of permits for wastewater discharge into surface water and sewerage and on sensitive areas).
 — values in 2017, — values in 2018, ▲ dam lakes, ▲ towns, ▲ confluences.

3.2 Key findings

Our analysis shows that the increased content of EDTA in surface water is a consequence of its use not only in industrial production but especially in food, cosmetics, medicines, fertilisers and other everyday consumer products. Given the scale of using EDTA and its

salts, it is clear that, although in small quantities, the process of replenishing it into the environment is ongoing. The slow increase in values is irreversible under the conditions of the EDTA use and there is a real risk that all surface water, except for upper rivers and uninhabited areas, will be affected by this increase and the required pollution limit will be reached or exceeded gradually.

In circular economy, which emphasises efficient use of resources including the reuse of products, waste and also wastewater, this all means a way to constant environmental pollution, especially of surface water bodies, while methods to eliminate such burdens are neither known nor used in industrial scale, according to the information available to us. In fact, EDTA is only one of many substances used in this way, which are of interest to the professional public in relation to water pollution for a relatively short time.

The 2017 report concerning surface water quality within the territorial competence of the Elbe River Administration (*Povodí Labe*) says that the situation related to the EDTA indicator is unsatisfactory because the environmental quality standard is exceeded in basically the entire length of the Elbe section, especially between the confluence with the river Vltava and the border with Germany. The values of the EDTA indicator measured in the upper and middle Elbe sub-basin are shown in Figure 2 (PL, 2018).

The report concerning surface water quality in the sub-basin of the Lower Vltava for the period 2016–2017 states that the EDTA indicator is unsatisfactory in most of the profiles monitored (PV, 2017). Although EDTA is monitored in watercourses and it is a substance of interest, a system to remove EDTA from wastewater has not yet been developed and applied in practice.

4 Discussion and conclusions

The main result of our analysis is that the EDTA concentration standard was exceeded, particularly beyond the confluence of the Vltava and Elbe rivers. Similar findings concerning EDTA can be found in the Report by the Elbe River Administration (*Povodí Labe*) (PL, 2018) and the Report by the Vltava River Administration (*Povodí Vltavy*) (PV, 2017). Our analysis was more detailed comparing to the studies above. It shows the relation between EDTA concentration in surface water and territorial water pollution distributions within the river basins. During our research, point and non-point sources of EDTA pollution were identified. It pointed out the role of consumption as the mayor source of the EDTA pollution.

The results of our work has given rise to many new questions both for research and practical actions and policies. It will be particularly important for technological development to find new and economically feasible water treatment technologies related to special organic pollutants. It is also important to improve monitoring and analytical methods. In our case it is desirable to substitute EDTA with more environmentally friendly compounds.

It will be important to develop objective assessment of special organic pollutant sources and to formulate and enforce respective new policies, which will reduce intake of the special organic pollutants into the nature environment. These policies have important international dimensions. The EDTA issues are a subject of a collaboration between Czech and German experts within International Commission for the Protection of the Elbe River.

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