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SCREENING ANALYSIS OF SELECTED PLASTICIZERS AS EMERGING SUBSTANCES IN THE SURFACE WATERS

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ABSTRACT: The two most common phthalate type plasticizers used today are di-2-ethylhexyl phthalate (DEHP) and di-isononyl phthalate (DINP), which are generally used in PVC related products. In modern market many medical appliance systems, children's toys, and baby devices are made of PVC. In the preliminary qualitative screening and analysis of surface water from the Danube River near Novi Sad, the presence of phthalates species, industrial chemicals that belong to the list of emerging substances have been registered. Compounds detected in Danube surface water, 100 m downstream of the discharge were di(2-ethylhexyl) phthalate (DEHP) and di-isononyl phthalate (DINP). This type of research within the International Project has been conducted for the first time.
KEYWORDS: Phthalates, Plasticizers, Surface water, Danube

INTRODUCTION

Phthalates belong to the group of dominant industrial pollutants and are ubiquitous overspread class of compounds with low water solubility/high fat solubility and low volatility. Due to their low water solubility, the phthalates hydrolyse relatively slowly, but the actual dynamic rate varies according to temperature, concentration and solubility. The physical and chemical properties of the phthalates have made them suitable as plasticisers in polymers such as plastic and rubber.

The use of plasticizers began in the mid 1860's when castor oil was added to Cellulose Nitrate (CN). The most commonly measured physical effects include melt viscosity, elastic modulus, and glass transition. Other types of plasticizers have been used through the years, but in the late 1930's phthalates were introduced because they were believed to be less toxic. The two most common types used today are di-2-ethylhexyl phthalate (DEHP) and di-isononyl phthalate, which are generally used in PVC related products. In today's market many medical delivery systems, children's toys, and baby devices are made of PVC. Recently there has been increasing debate about the danger of phthalates leaching out of the PVC and into individuals. It is still unclear what dangers these chemicals pose to humans, but research on a variety of other species has been conducted for quite a while and has shown mixed results.

Plasticizers are used to produce flexible PVC products for many different end uses or market segments. Figure 1 depicts a worldwide analysis of plasticizer consumption by PVC market segments.

The largest market segment is film, sheeting, and coated substrates. In this segment, the majority of plasticizer consumed is for products produced in calendaring operations. The primary factors in plasticizer selection are low cost and ease of processing, DINP is the preferred plasticizer choice based on the above criteria.

For products that need a slight reduction in gelation or fusion temperature, DEHP (diisooheptyl phthalate) can be used to replace a small portion of the primary plasticizer.

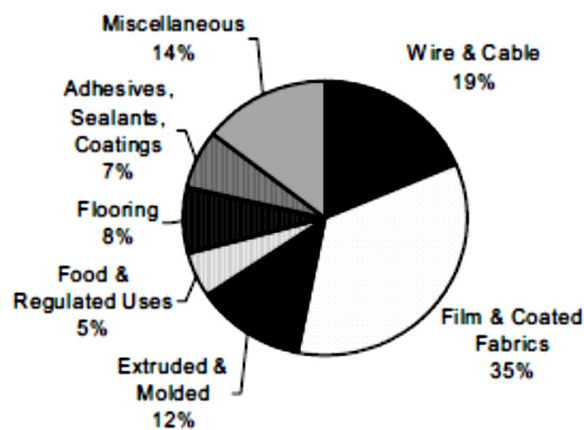


Figure 1. End use markets for plasticized PVC

Research activities within the NATO project started with a review of available data on organic and inorganic pollutants analyzed in the earlier projects in order to collect reliable information on water quality and pollution for the part of the Danube River and its tributaries in the vicinity of Novi Sad.

For establishing the monitoring network of the surface Danube water in the vicinity of Novi Sad, selection of sampling points and defining of monitoring dynamic have been defined using knowledge and recommendations of the experts in close co-operation with Public Utility Company Waterworks and Sewage Novi Sad, as well as on experience of the research teams involved in the DriWaQ-NS project.

The selected sampling points include surface water from the Danube River.

BASIC PROPERTIES OF SELECTED PHTHALATES

Two typical examples of phthalate plasticizers are DEHP (Di-Ethylhexyl Phthalate), and DINP (Di-Isononyl Phthalate).

DEHP has been the most commonly used, and is still the plasticizer of choice for all PVC medical and surgical products. However due to evidence of the toxicity of DEHP in laboratory animal studies it was replaced in children's products with DINP. The structures of both are shown below in figures 2 and 3 respectively.

DINP is oily colorless liquid with a slight ester odor. Denser than water. Insoluble in water. It is insoluble in water. DINP reacts exothermically with acids to generate isononyl alcohol and phthalic acid. Strong oxidizing acids may cause a vigorous reaction that is sufficiently exothermic to ignite the reaction products. Heat is also generated by interaction with caustic solutions. Flammable hydrogen is generated by mixing with alkali metals and hydrides.

Next table show basic physico chemical properties of DEHP and DINP.

Table 1. Summary of physico- chemical properties

Chemical name	Di(2-ethylhexyl) phthalate	1,2-benzenedicarboxylic acid
CAS Number	117-81-7	68515-48-0; 28553-12-0
Molecular Formula	$C_{24}H_{38}O_4$	$C_{26}H_{42}O_4$ [average]
Molecular weight	390.56	420.6 [average]
Water solubility	3×10^{-5} g/L (20°C)	6×10^{-5} g/L (20°C)
Melting point	ca. -50°C	-55°C to -50°C
Boiling point	>400°C	230°C at 5mmHg 385°C at 1013 hPa
Density	ca. 975 kg/m ³ (20°C)	980 kg/m ³ (20°C)
Vapour pressure	6×10^{-8} kPa (20°C)	3.4×10^{-8} kPa (20°C)
Henry's Law Constant:	4.43 Pa m ³ /mol	41.4 Pa·m ³ /mol
Partition coefficient n-octanol/water (log Kow)	7.50	8.8

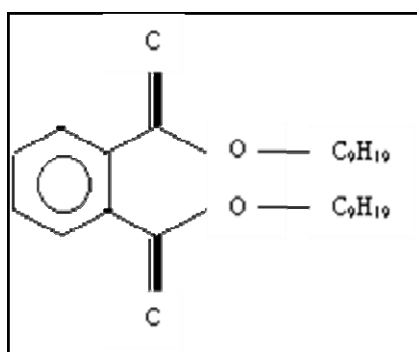


Figure 2. DINP-Chemical Structure

Figures 2 and 3 are representing structural formula of selected phthalates.

DINP is not a single compound, but a complex mixture containing mainly C9-branched isomers. The composition of CAS No. 68515-48-0 is represented as mixed phthalates with side chains made up of 5-10% methyl ethyl hexanols, 45-55% dimethyl heptanols, 5-20% methyl octanols, 0-1% n-nonanol, and 15-25% isodecanol; and the composition of CAS No. 28553-12-0 is represented as mixed phthalates with side chains made up of 5-10% methyl ethyl hexanols, 40-45% dimethyl heptanols, 35-40% methyl octanols, and 0-10% n-nonanol. Thus, diisononyl phthalate [side chains of dimethyl heptanols (i.e. iso-nonanol)] makes up about 50% of the two DINP' mixtures which appear to be available on the market.

Chemical DEHP is an oily colourless liquid with slight odour at room temperature. DEHP is readily soluble in most organic solvents and miscible with alcohol, ether and most oils.

LOCATION DESCRIPTION

Novi Sad is the second largest city in Serbia and administrative centre of the northern Serbian province of Vojvodina, with a population of 335.701. Deriving drinking water from the Danube River or from several groundwater reservoirs, the city of Novi Sad faces a specific problem. Two of three sources of drinking water in Novi Sad are located only a few hundred meters downstream of discharges of the Novi Sad two main sewers, GC1 and GC2.

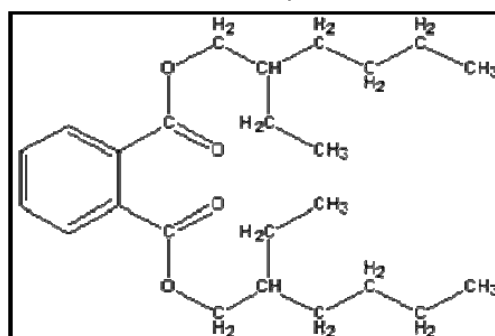


Figure 3. DEHP- Chemical Structure

Additionally, all of groundwater abstraction points are located under densely populated urban areas, and one of them is located in the proximity of the oil refinery and heating and power plant (Vojinović Miloradov et al.).

Samples of surface water from Danube River were taken 100 meters downstream of the each discharge: (100 m downstream of the discharge GC1, GC2, Sever IV discharge Rokov potok).

Monitoring was performed downstream the surface water station at 1254.98 km distance from the Danube mouth (staff gauge from 1919).

MATERIALS AND METHODS

Three sampling campaigns were conducted during the 2011. Sampling period and meteorological parameters are presented in table 2.

One liter water samples were collected in amber glass bottles from all seven localities and were stored under appropriate temperature conditions, at 4°C.

Samples of surface water from the Danube were collected at least 100 meters downstream of the each discharge Figure 4.

Preliminary quality analyses were performed at Institute of Analytical Chemistry STU in Bratislava using optimized procedure developed during first half year of project duration. The GC-MS screening analysis was performed using Agilent 6890 gas chromatograph coupled to Agilent 5973 mass spectrometric detector.

DISCUSSION

In the national scientific literature, there is little information available on the occurrence of emerging pollutants especially phthalates in surface water of the Danube River and its tributaries. Phthalates have high and hazardous pressure on humans, bio system aquatic media, aquatic organisms and environment [6].

Because of their properties, high production volumes, and widespread use, concentrations in various environmental compartments are measurable and expected to reflect a constant and diffuse release into the environment. Phthalates are becoming ubiquitous and pseudo resistant pollutants with high transport potential for most of the environmental media.

The available information and results about pollution of water used for abstraction of drinking water in Novi Sad municipality are insufficient for eco-status of surface water in river Danube, risk management and for protection and improvement of human health and safety.

Screening approaches are either not used at all or very scarcely and most of monitoring is limited just to the selected physical parameters and target compounds

Phthalates belong to the most frequently occurring compounds in studied water samples. Phthalates are commonly used as plasticizers, industrial and lubricating oils, defoaming agents, cosmetics and insect repellents. Di-Isononyl Phthalate, is already on the NORMAN list of emerging substances and di(2-ethylhexyl) phthalate, which is on the list of WFD priority substances, both detected in all samples which confirms statements on its ubiquitous presence.

CONCLUSIONS

Screening analysis of selected plasticizers as emerging substances in the surface waters registered residual concentrations of phthalates in the Danube near Novi Sad. Results are showing serious contamination with these ubiquitous industrial chemicals.

Due to their high toxicity potential teratogenicity and cancerogenicity quantitative analysis has been conducted. More detail research and quantification of emerging substances is in progress. This type of research within the International Project has been conducted for the first time.

Table 2. Samples of municipal and industrial wastewaters

	Survey I	Survey II	Survey III
Sampling period	June 2011	October 2011	December 2011
Mean temperature	20°C	13°C	8°C
Wind speed	8 km/h	30 km/h	10 km/h



Figure 4. Surface water sampling locations - preliminary qualitative analysis

ACKNOWLEDGEMENT

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