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Source identification of high glyme concentrations in the Oder River

D.K. Stepien*, W. Püttmann

Goethe-University Frankfurt am Main, Institute of Atmospheric and Environmental Sciences, Department of Environmental Analytical Chemistry, Altenhöferallee 1, 60438 Frankfurt am Main, Germany

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ABSTRACT

The objective of the following study was to identify the source of high concentrations of glycol diethers (diglyme, triglyme, and tetraglyme) in the Oder River. Altogether four sampling campaigns were conducted and over 50 surface samples collected. During the first two samplings of the Oder River in the Oderbruch region (km 626–690), glymes were detected at concentrations reaching 0.065 μg L^{-1} (diglyme), 0.54 μg L^{-1} (triglyme) and 1.7 μg L^{-1} (tetraglyme). The subsequent sampling of the Oder River, from the area close to the source to the Poland–Germany border (about 500 km) helped to identify the possible area of the dominating glyme entry into the river between km 310 and km 331. During that sampling, the maximum concentration of triglyme was 0.46 μg L^{-1} and tetraglyme 2.2 μg L^{-1}; diglyme was not detected. The final sampling focused on the previously identified area of glyme entry, as well as on tributaries of the Oder River. Samples from Czarna Woda stream and Kaczawa River contained even higher concentrations of diglyme, triglyme, and tetraglyme, reaching 5.2 μg L^{-1}, 13 μg L^{-1} and 81 μg L^{-1}, respectively. Finally, three water samples were analyzed from a wastewater treatment plant receiving influents from a Copper Smelter and Refinery; diglyme, triglyme, and tetraglyme were present at a maximum concentration of 1700 μg L^{-1}, 13,000 μg L^{-1}, and 190,000 μg L^{-1}, respectively. Further research helped to identify the source of glymes in the wastewater. The gas desulfurization process Solinox uses a mixture of glymes (Genosorb®1900) as a physical absorption medium to remove sulfur dioxide from off-gases from the power plant. The wastewater generated from the process and from the maintenance of the equipment is initially directed to the wastewater treatment plant where it undergoes mechanical and chemical treatment processes before being discharged to the tributaries of the Oder River. Although monoglyme was also analyzed, it was not detected in any of the water samples.

1. Introduction

Glymes (glycol diethers) are polyethylene glycols or polypropylene glycols, end capped with a methyl-, ethyl-, butyl-, or vinyl group. For this study four polyethylene glycols end capped with a methyl group were selected. Monoethylene glycol dimethyl ether (monoglyme), diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme), and tetraethylene glycol dimethyl ether (tetraglyme) are widely used industrial solvents. The lack of reactive functional groups makes glymes inert chemically;

* Corresponding author. Tel.: +49 69 798 40232; fax: +49 69 798 40240.
E-mail addresses: dstepien@iau.uni-frankfurt.de, dstepien@ymail.com (D.K. Stepien).

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hence they are often used in chemical synthesis applications. Additionally, their high solvating power and their thermal and chemical stability make them ideal for use as solvents and processing aids in the manufacture and formulation of industrial chemicals. Moreover, their application extends to formulation of paints, inks, cleaning fluids, brake fluids, anti-icing agents etc. (Table 1). Glymes are also applied as a gas absorption media. Several processes have been developed, such as the Solinox and Selexol, that use a mixture of polyethylene glycol dimethyl ethers [$CH_3O(CH_2CH_2O)_nCH_3$; $n = 3–9$] as a physical solvent to remove sulfur dioxide and/or hydrogen sulfide from flue gases (Clariant, 2013a). The major sources of glyme pollution in surface waters will most likely emerge from their use, manufacturing and processing. According to the European Chemicals Agency (ECHA), numerous glyme suppliers exist in Europe although the actual production volumes are confidential. The European Chemical Substances Information System (ECSIS) lists monoglyme as a low production volume chemical with production and/or import volume of 10–1000 tons per year (ECSIS, 2013). Diglyme is listed by ECSIS as a high production volume chemical, with a production and/or import volume in excess of 1000 tons per year (ECSIS, 2013). According to ECHA, the annual triglyme and tetraglyme import and/or production volume in Europe is between 10 and 100 tons and at above 100 tons per year, respectively (ECHA, 2013).

The physicochemical properties of glymes listed in Table 1 indicate that once released into the environment they will persist mainly in the hydrosphere. Glymes are highly soluble in water; they have low octanol–water partition coefficients ($logP_{ow}$) and also low Henry's law constant, which induce their partition to water, rather than evaporation from water into the gas phase. Hydrolysis is not expected to be an important environmental fate process since these compounds lack functional groups that hydrolyze under environmental conditions. The low $logP_{ow}$ values show that glymes are not likely to sorb to soil and have a low bioaccumulation potential.

The rising concern about the use, exposure, and a possible environmental contamination with glycol diethers is reflected in their reproductive toxicity (US EPA, 2011). Monoglyme, diglyme and triglyme have been shown to cause reproductive and developmental effects in experimental animals (Hardin, 1983; George et al., 1987; Schwetz et al., 1992; ECETOC, 2005). Human exposure to these glymes may also cause infertility and harm to an unborn child (US EPA, 2011). Moreover, destruction of red blood cells and the blood forming organs may follow (ECETOC, 2005). Results of metabolic studies suggest that 2-methoxyacetic acid, a product of glyme metabolism, is responsible for their toxicity (WHO, 2002). Supposedly, the presence of longer alkyl groups at the glyme terminal ends and more ethylene glycol groups in the middle of the glyme molecule both act to reduce their toxicity (ECETOC, 2005). According to the data provided by the European Chemicals Agency, the predicted no-effect concentration (PNEC) in the freshwater for three glymes was derived to be 6400 $\mu g\ L^{-1}$ (ECHA, 2013). Moreover, the oral derived no-effect level (DNEL) for general population is 0.23 mg/kg bw/day, 1.04 mg/kg bw/day, and 3.13 mg/kg bw/day for monoglyme, diglyme, and triglyme, respectively (ECHA, 2013).

Recently, the US Environmental Protection Agency presented a "Significant New Use Rule" for 14 glymes that are in use in the United States (US EPA, 2011). The purpose of the document is to control and limit a significant new use of these glymes by manufacturers and users, but it does not create restrictions for previously registered applications of these solvents. Also in Europe, numerous regulations are in place that limit the use of glymes found toxic for reproduction. Annex XV, Group 30 of the REACH regulation (Registration, Evaluation, Authorization and Restriction of Chemicals) confine the presence of monoglyme, diglyme, and triglyme to a generic concentration of 0.3% to be present on the market as a substance, constituent of a substance or in mixtures (ECHA,

Table 1 – Physicochemical properties and applications of glymes.

IUPAC name (common name)	Molecular formula	Boiling point (°C)	Solubility (g/L, at 25 °C)	Henry's law const. (atm × m^3 × mol^{-1})	Log P (At 25 °C)$_{ow}$ [a]	Applications[b]
1,2-dimethoxyethane (Monoglyme)	$CH_3O(CH_2CH_2O)CH_3$	85	85.2	1.07×10^{-6}	−0.21	Lithium batteries, pharmaceuticals, industrial solvent
bis(2-methoxyethyl) ether (Diglyme)	$CH_3O(CH_2CH_2O)_2CH_3$	162	162	5.23×10^{-7}	−0.36	Printing inks, adhesives, pharmaceuticals, sealants, reaction solvent, process chemical
1,2-bis(2-methoxyethoxy) ethane (Triglyme)	$CH_3O(CH_2CH_2O)_3CH_3$	216	208.8	4.88×10^{-12}	−0.76	Adhesives, brake fluids, paints, manufacture and formulation of industrial chemicals
Bis[2-(2-methoxyethoxy) ethyl]ether (Tetraglyme)	$CH_3O(CH_2CH_2O)_4CH_3$	275	263.9	1.04×10^{-14}	−1.03	Inks, paints, gas absorption liquid, textile, plastics, industrial chemical processes

[a] P_{ow} *n*-octanol water partition coefficient.
[b] Source: US EPA (2011), Clariant (2013b).