# Identification of direct and indirect industrial dischargers as dominating sources of 1,4-dioxane in German rivers

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1,4-Dioxane is a cyclic ether used extensively as a processing solvent in industrial scale chemical reactions as well as in finished products, such as fabric cleaners, adhesives, lacquers, and paints. Personal care products and detergents containing ethoxylates as surfactants (e.g. shower gels, shampoos, and liquid soaps) can contain 1,4-dioxane as impurities in the order of parts per million. 1,4-Dioxane has been classified by the EPA as a probable human carcinogen (group B2)[1]. Based on its physico-chemical properties (complete miscibility with water and its low Henry’s Law constant of 4.88×10-3 atm × m3 × mol-1), combined with its very low soil retardation and microbial degradation[1], 1,4-dioxane is expected to remain in the aquatic environmental compartment, once introduced.

Previous studies have proven the ubiquitous presence of 1,4-dioxane in surface waters in Germany and Poland (Rhine river load of 173 kg/d), as well as the occurrence in drinking water produced from bank filtration at concentrations frequently exceeding the guidance level of 0.1 µg/L set by the German Umweltbundesamt[2]. Therefore, identification of the input sources of 1,4-dioxane to surface waters constitutes the main objective of the present study, particularly focussing on rivers in the federal states of Hesse and North Rhine-Westphalia. Results have shown that effluents of wastewater treatment plants (WWTPs) cleaning only domestic wastewater contain relatively low concentrations of 1,4-dioxane (<0.3 µg/L), probably originating from 1,4-dioxane impurities in ethoxylate-based detergents. Effluents of municipal WWTPs linked with indirect industrial dischargers provided 1,4-dioxane concentrations of up to 46 µg/L. Even higher concentrations (up to 3000 µg/L) were detected in effluents of industrial WWTPs. Downstream of effluents from WWTPs connected to both direct and indirect industrial dischargers, there is a notable increase of 1,4-dioxane concentrations in many small German rivers, resulting locally in levels of, for instance, 0.54 µg/L (Rur), 9.17 µg/L (Kinzig), 24.04 µg/L (Rodau), and 105.11 µg/L (Emscher). In big rivers such as Rhine, Main, and Oder concentrations of 1,4-dioxane increase along the river course and often exceed values of 1 µg/L[2]. Rhine water samples taken at the Rheingütestation Worms on both river banks have shown that industrial wastewater is causing notably increased 1,4-dioxane concentrations on the corresponding left side compared to the less affected right side of the river (mean: 1.27 µg/L vs. 0.56 µg/L). Apart from WWTPs discharging treated wastewater directly into bigger rivers such as the Rhine, Main, and Oder, additionally many small tributaries contribute to the 1,4-dioxane load of the bigger rivers, causing an increase and not an expected dilution of 1,4-dioxane concentrations along the river course.

Further research is aimed at the identification of particular industrial processes (e.g. ethoxylate production) which can be expected to generate 1,4-dioxane as an unintended byproduct during the production of ethoxylates used as detergents.

[1] Mohr, T. et al. (2010). Environmental investigation and remediation. Boca Raton [FL]: CRC Press.

[2] Stępień, D. et al. (2014). Fate of 1,4-dioxane in the aquatic environment: From sewage to drinking water. Water Research, 48, pp. 406-419.