

Determination of background levels of free cyanides in surface waters

B. Knopf¹, D. Hansknecht¹, H. Rüdel¹, A. Mieth², J. Ohlemacher² and K. Kreuzer³

¹Fraunhofer Institute for Molecular Biology and Applied Ecology IME, Auf dem Aberg 1,
57392 Schmallenberg, Germany

²CyPlus GmbH

³Evonik Performance Materials GmbH

E-mail contact: heinz.ruedel@ime.fraunhofer.de

Natural background concentrations of cyanide can originate from the degradation of plants and microbes such as algae. Besides, cyanides may also be emitted from anthropogenic sources. Recently, environmental quality standards (EQSs) for free cyanide were proposed under the European Water Framework Directive (WFD). The EU Joint Research Centre, for example, has proposed an annual average EQS of 0.5 µg/L free cyanide. Since there is a lack of reliable data on background concentrations of free cyanide in surface waters it is not clear whether the proposed EQS values can be practically implemented. To this end a project was initiated to implement and test a method that allows reliable measurements of free cyanide background concentrations in surface waters.

Current methods for the measurement of free cyanide in waters only achieve limits of quantifications (LOQs) of about 1 µg/L. Here an existing continuous flow analysis (CFA) method was selected using a system with a special cuvette installation allowing a higher sensitivity. The protocol was validated and accredited according to standard ISO/IEC 17025. With this system an LOQ of 0.15 µg/L can be reached under optimal conditions while an LOQ of about 0.3 µg/L is achieved during routine operation. Previous to field testing it was verified that samples can be stabilized for at least 24 h by adjusting the pH of the sample to 12 and storage in the dark at 4°C. Samples spiked with low concentrations of a cyanide standard were used as positive controls.

The field validation results were satisfactory, confirming that the protocol is fit for purpose. Finally, samples from several sites of a small stream with low anthropogenic influences (River Lenne) were taken and analyzed. Free cyanide concentrations of up to 0.4 µg/L were detected. There were significant differences in free cyanide concentrations between the spring, with levels mostly below the limit of detection (LOD, 1/3 of the LOQ), and downstream sampling points where free cyanide concentrations were at least 50% higher, possibly due to degraded plant biomass in the water.

This first measurements revealed that background concentrations of free cyanide in the tested surface waters can be below the proposed EQS of 0.5 µg/L. However, the analysis of further parameters (e.g. geographical regions, seasonality) is necessary to create a reliable database on the range of free cyanide background levels as basis for EQS implementation.