

Integrated assessment of sources, chemical stressors and stream quality along a groundwater fed stream system

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Streams are impacted by significant contamination at the catchment scale, as they are often locations of multiple chemical stressor inputs. The European Water Framework Directive requires EU member states to ensure good chemical and ecological status of surface water bodies by 2027. This requires monitoring of stream water quality, comparison with environmental quality standards (EQS) and assessment of ecological status. However, the achievement of good status of stream water also requires a strong focus on contaminant sources, pathways and links to stream water impacts, so source management and remedial measures can be implemented. Fate and impacts of different contaminant groups are governed by different processes and are dependent on the origin (geogenic, anthropogenic), source type (point or diffuse) and pathway of the contaminant.

To address this issue, we identified contaminant sources and chemical stressors on a groundwater-fed stream to quantify the contaminant discharges, link the chemical impact and stream water quality and assess the main chemical risk drivers in the stream system potentially driving ecological impact.

The study was conducted in the 8 m wide Grindsted stream (Denmark) along a 16 km stream stretch that is potentially impacted by two contaminated sites (Grindsted Factory site, Grindsted Landfill), fish farms, waste water discharges, and diffuse sources from agriculture and urban areas. Water samples from the stream and the hyporheic zone as well as bed sediment samples were collected during three campaigns in 2012 and 2014. Data for xenobiotic organic groundwater contaminants, pesticides, heavy metals, general water chemistry, physical conditions and stream flow were collected. The measured chemical concentrations were converted to toxic units (TU) based on the 48h acute toxicity tests with *D. magna*.

The results show a substantial impact of the Grindsted Factory site at a specific stretch of the stream. The groundwater plume caused elevated concentrations of chlorinated ethenes, benzene and site specific pharmaceuticals in both the hyporheic zone and the stream water. Observed stream water vinyl chloride concentrations (up to 6 $\mu\text{g/L}$) are far above the Danish EQS (0.05 $\mu\text{g/L}$) for several km downstream of the discharge area. For heavy metals, comparison with EQS in stream water, the hyporheic zone and streambed showed concentrations around or above the threshold values for barium, copper, lead, nickel and zinc. The calculated TU was generally similar along the stream, but for arsenic and nickel higher values were observed where the groundwater plume discharges into the stream. Also, log TU sum values for organic contaminants were elevated in both the hyporheic zone and stream. Thus, the overall chemical stress in the main discharge area is much higher than upstream, while it gradually decreases downstream.

In conclusion, this work clearly shows that groundwater contaminant plumes can impact stream water quality significantly in discharge areas, and extend far downstream. A surprisingly high impact of heavy metals with diffuse and/or biogenic origin on stream quality was identified. This work highlights the importance of a holistic assessment of stream water quality to identify and quantify the main contaminant sources and resulting chemical stream stressors leading to potential ecological impacts.