XXXVIII IAH Congress

Groundwater Quality Sustainability Krakow, 12–17 September 2010

Extended Abstracts

Editors: Andrzej Zuber Jarosław Kania Ewa Kmiecik





University of Silesia Press 2010



abstract id: 508

topic: 6

General hydrogeological problems

6.3

Groundwater contamination — monitoring, risk assessment and restoration

title: Development of a methodology to characterize the reactive transport of organic contaminants in groundwater impacted by a Chemical Complex

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keywords: contamination, organic compounds, methodology

Estarreja Chemical Complex (CQE) is an industrial complex located on NW Portugal, near Ria de Aveiro, an environmentally and economically important coastal lagoon. The CQE was constructed in the early 30's on top of high permeable dune and beach sand formations, which are part of the Aveiro Quaternary groundwater body (AQGWB) classified as "at risk" under the implementation of Water Framework Directive. The upper unconfined AQGWB aquifer is regarded as particularly vulnerable to contamination due to: (1) the high permeabilities of the sediments; (2) the small thickness of the unsaturated zone; (3) the plain topography; and, (4) the high groundwater recharge rates. Moreover, the Portuguese Environmental Agency (APA) classified the CQE surrounding area as at high risk due to social, environmental and economical impacts, which makes it a priority remediation area under the Environmental Liabilities Recover Program.

CQE surrounding area has been subjected to several research and technical studies, focusing on different aspects of the natural surrounding ecosystem: geology; hydrogeology; groundwater recharge; soil, surface and groundwater contamination. These studies also refer the CQE past practices regarding the rejection of solid and liquid effluents. For decades, the different CQE industries disposed solid wastes directly on the permeable sands without any kind of containment or impermeabilization, and discharged liquid effluents directly on streams connected to the coastal lagoon, without any previous treatment. Nowadays, and although waste management practices improved significantly, there are still signs of long term soil and groundwater contamination.

Recent work developed in the study area (Ordens, 2007) characterized the groundwater contamination (both inorganic and organic) and identified the processes responsible for the hydrochemical evolution of groundwater, including interactions with surface water. This study used geophysical methods to identify electromagnetic anomalies that can be related to different origins of contaminants and to surface and groundwater interactions. It also delimitates the extension and the magnitude of the contaminant plume.

The hydrochemical studies characterized the spatial evolution of groundwater quality due to both natural and antropogenic influences. The identified background properties give evidence to groundwaters with sodium-chloride facies, low mineralization (SEC \leq 300 µS/cm), Eh ~ 300 mV, dissolved O₂ ranging from 2.4 to 5.5 mg/L, and pH ~ 5.4. Hydrochemical data also indicate that groundwater is mainly originated by rainfall infiltration; rainwater in the study region is basically diluted seawater.

In the contaminated sites, groundwater SEC is often over 20,000 μ S cm⁻¹; pH presents either very low values (<5.0) or very high (>8.5), depending on the origin of contamination; Cl reaches values of 10 300 mg l⁻¹; NO₃ and SO₄ are well above 100 and 2000 mg l⁻¹, respectively; the concentrations of most heavy metals in groundwater are often well above background concentrations and in close relation to pH and Eh values.

Different types of groundwater contamination have been identified, depending on the type of rejected effluent, interaction between contaminants and on the natural hydrochemical characteristics of the aquifer. The main types of groundwater inorganic contamination identified in the study area are: (1) acid mine drainage or metallic sulphide tailings drainage — low pH with high levels of sulphates and pyrites associated metals; (2) halite dissolution — high concentration of chloride and sodium, and low [Br]/[Cl] rates; (3) agricultural activities — typically with

high levels of nitrates, sulphates and potassium; (4) mercury sludges: high concentrations of mercury.

Generally the hydrochemical data shows groundwater contamination levels that compare well with the electromagnetic survey data (Figure 1).



Figure 1. Correspondence between electromagnetic survey data and hydrochemical data (source: Ordens, 2007).

Previous investigations also identified the main organic contaminants present in the groundwater of the study area. These include chloroform, benzene, trichlorethylene, tetrachlorethylene, chlorobenzene, phenanthrene, naphthalene, aniline, vinyl chloride, 2-chlorofenol and mononitrobenzene (Figure 2). Five of these compounds are classified as priority substances according with the Directive 2008/105/EC (directive on priority substances), being two of them classified as priority hazardous substances according with the same directive.





Organic contamination is a major contamination issue worldwide and there is an increasing interest and necessity of study organic compounds transport and degradation mechanisms. The main objective of this research, which is part of CRUDE research project (PTDC/CTE-GEX/72959/2006), is to delineate and test a new methodology for deriving coherent and broad understanding of the reactive transport mechanisms of organic compounds in soil-vadose zone-aquifer media, using the surroundings of CQE as a case study.

The development of a coherent multidisciplinary investigation protocol (integrating geology, hydrogeology, geochemistry, geophysics, geostatistics, modeling, GIS) for soil/groundwater contaminated sites will contribute for the selection of the most appropriate technologies for the mitigation and remediation of contaminated sites.

ACKNOWLEDGMENTS

The authors would like to thank Fundação Ciência e Tecnologia (FCT) for funding Project CRUDE (PTDC/CTE-GEX/72959/2006); a Post Doctoral Research Position (Ciência 2007) and two PhD grants (SFRH/BD/47778/2008 and SFRH/BD/43625/2008).

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International Association of Hydrogeologists



AGH University of Science and Technology

2-vol. set + CD ISSN 0208-6336 ISBN 978-83-226-1979-0