A DPSIR Approach to Selected Cr(VI) Impacted Groundwater Bodies within Attica and Eastern Sterea Ellada River Basin Districts

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Abstract
The holistic approach of the Driver-Pressure-State-Impact-Response (DPSIR) analytical framework in combination with Geographical Information Systems was applied to selected Cr(VI) impacted groundwater bodies. For the characterization of water-quality "state" 157 samples including field blanks were collected during the wet and dry seasons of 2017 and 2018 and several physicochemical parameters were determined. In Loutraki area, Cr(VI) in groundwater ranged from 12 to 62 μg/L while NO_3 and Cl maximum values were 157mg/L and 218mg/L respectively. Very high concentrations of Cr(VI) (up to 430μg/L), NO_3 (up to 245mg/L) and Cl (up to 1039mg/L) were measured in the Schinos alluvial aquifer. Additionally, Cr(VI) up to 131μg/L and NO_3 up to 156mg/L were identified in the groundwater ofThiva agricultural area. In C. Evia, Cr(VI) was up to 96μg/L while NO_3 and Cl concentrations were also high reaching 362mg/L and 793mg/L respectively. Finally, the highest Cr(VI) concentrations (up to 11.7 mg/L) were measured in Oinofyta area. The main identified pressures are: i) NO_3 pollution due to intensive agriculture and urban waste disposal, ii) sea water intrusion due to overpumping and iii) Cr(VI) contamination due to both natural processes and industrial activities (clearly in the case of Oinofyta). In many cases, Cr(VI), NO_3 and Cl are above the upper drinking water threshold values of the European Directive 98/83/EC. Therefore, the implementation of a constant monitoring program as well as the development of a common database for water managers are among the first steps to address these issues.
Keywords: hexavalent chromium, geogenic, anthropogenic, pressures, land use, groundwater

1. Introduction

Hexavalent Cr occurrence in groundwater of many areas in Greece is an issue of public concern, with its origin to be attributed both to natural and anthropogenic factors. Industrial effluents have been considered in the past to be the only source of Cr(VI) contamination in natural waters. However, geogenic Cr(VI) has been found in areas where the geological background consists of ultramafic rocks. Such areas have been reported both in Greece and in many other countries including Italy, Sacramento valley, USA and others (Dermatas et al., 2015). Nevertheless, according to Hausladen et al., (2018), Cr(VI) origin in groundwater may be also linked to agricultural activities. Therefore, in the case of mixed natural and anthropogenic sources, it is difficult to set a threshold for the natural Cr(VI) background as the Water Framework Directive 118/2006/EC defines. The complexity of the different factors (natural versus anthropogenic) contributing to the origin of Cr(VI) in groundwater in combination with the lack of legislated upper thresholds for Cr(VI) for the different water uses prevent water managers to implement a common strategy in order to deal with this issue. Within such a framework, the scope of the present study is to identify the main anthropogenic factors and their pressures causing the deterioration of groundwater quality in the Cr(VI) impacted groundwater bodies of Loutraki and Schinos basins of the Attica River Basin District and in Thiva, Oinofyta and Messapia basins of the Eastern Sterea Ellada River Basin District.

2. Materials and Methods

A variety of data (hydrogeological, hydrogeochemical, land use, water demand etc.) were collected for the implementation of a reliable DPSIR framework**.** Some of the data were collected from the national water management reports for the river basin districts of Attica and Eastern Sterea Ellada. For the characterization of "state" of the groundwater quality, 157 samples including field blanks were collected from the study areas during the wet and dry seasons of 2017 and 2018 and several physicochemical parameters were determined including trace elements**.** Water chemical analysis data were coupled with mineralogical analysis by SEM-EDS of suspended material collected on water filters to identify Cr main sources.

3. Driving Forces and Pressures

It is estimated that in Loutraki-Perachora Municipality the annual groundwater abstractions for water supply reach approximately 2.5 million m^3. Touristic activity is also intense in Loutraki town and in Schinos village having as a result the increase of water demand and sewage effluents during the summer months. It is estimated that in the municipality of Loutraki-Perachora exist approximately 12000 secondary dwellings. In Schinos, the sewage effluents from the outnumbered domestic sinks are the main sources of nutrient pollution in the aquifer, while the high density of wells has led to overpumping and subsequent sea water intrusion. In addition, irrigation of agricultural land exists in all areas except Schinos where groundwater is used mainly for domestic irrigation. In Thiva municipality, the groundwater abstractions for irrigation are the highest (33.67 million m^3), followed by Dirfys-Messapia municipality (11.5 million m^3), Oinofyta municipality (7.17 million m^3) and Loutraki-Perachora municipality (1.68 million m^3). The main pressure is the use of agrochemicals (pesticides and fertilizers). Furthermore, industrial activity is very intense in Oinofyta area where industrial effluents polluted the water bodies of the area for at least three decades (Dermatas et al,2015). It is estimated that 186 industries (mainly textile, metallurgy related and food industries) are operating in the area of Thiva-Assopos Schimatari.

4. State, Impacts and Responses

According to the chemical analyses results, Cr(VI) ranged from 12 to 62 μg/L in Loutraki alluvial aquifer while NO_3 and Cl maximum values were 157mg/L and 218mg/L respectively. High concentrations of Cr(VI) (up to 430μg/L), NO_3 (up to 245mg/L) and Cl (up to 1039mg/L) were measured in Schinos. Additionally, Cr(VI) up to 131μg/L and NO_3 up to 156mg/L were identified in the groundwater of Thiva. In C. Evia, Cr(VI) was up to 96μg/L while NO_3 and Cl were also elevated with its respective maximum values to be 362mg/L and 793mg/L. Finally, the highest Cr(VI) concentrations (up to 11.7 mg/L) were measured in Oinofyta area. The main Cr sources in the areas can be the: a) Cr rich minerals (geogenic origin) and/or b) industrial wastewater and/or the c) agrochemicals which may contain Cr as a trace element. Data from the chemical and mineralogical study performed during this research, combined with land use data and field observations suggest that each one of the above sources contributes in different degrees to the Cr(VI) concentrations in groundwater. Regarding the associated impacts, the suitability of groundwater for human consumption was assessed according to the European directive 98/83/EC while the suitability for irrigation was assessed according to Food and Agricultural Organization (FAO) guidelines. It is noteworthy that according to FAO the recommended concentration for total Cr is 100 μg/L. The highest median concentration of Cr(VI) (64.4μg/L) was identified in Schinos exceeding the upper limit of 50 μg/L. The percentage of total Cr exceedance of the threshold (50μg/L) in groundwater samples was 63% for Schinos, 57% for Thiva, 32% for Loutraki and 27% for C. Evia respectively. Regarding the suitability of groundwater for irrigation, the percentage of exceedance of FAO recommended value (100μg/L) for total Cr was 46% for Schinos, 25% for Thiva and 6% for C.Evia. Among the first steps to deal with the occurrence of Cr(VI) in groundwater is the quantification of either geogenic or anthropogenic contamination. To address this issue, a constant monitoring network and a common database targeting to resolving Cr(VI) sources in these areas must be implemented. This will enable decision makers to set Cr natural background thresholds and aid water managers to develop a common water management strategy.

Acknowledgements

The present work was co-funded by the European Union (ERDF) and Greek national funds through the Operational Program "Competitiveness, Entrepreneurship and Innovation", under the ERANETMED 1st Joint Call on Water Resources (project acronym: CrITERIA/ project code: T3EPA-00004).

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