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A DPSIR Approach to Selected Cr(VI) Impacted Groundwater Bodies of Central Greece

Konstantina Pyrgaki[1] · Ariadne Argyraki[1] · Efstratios Kelepertzis[1] · Fotini Botsou[2] · Ifigeneia Megremi[1] · Sotirios Karavoltsos[2] · Emmanuel Dassenakis[2] · Thanasis Mpouras[3] · Dimitrios Dermatas[3]

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Abstract

The holistic approach of Driver-Pressure-State-Impact-Response (DPSIR) methodology was applied to selected Cr(VI) impacted groundwater bodies of Central Greece. The main driving forces in the study areas are agricultural activities, urban and industrial development as well as tourism. The main pressures induced by the anthropogenic activities are fertilizer use, uncontrolled urban sewage disposal and industrial effluents discharges. Groundwater stress is caused by the qualitative degradation due to Cr(VI), NO_3^-, Cl^- and SO_4^{2-} contamination. Hexavalent chromium occurrence is attributed to both geogenic and anthropogenic sources. The maximum Cr(VI) concentration (11.7 mg/L) was measured in Oinofyta area. Important impacts are the deterioration of groundwater body chemical status as well as the decline of groundwater use efficiency. Based on the applied DPSIR, a management framework is proposed in order to address the complex environmental issue of Cr(VI) in the study areas.

Keywords Hexavalent chromium · Geogenic chromium · Anthropogenic chromium · Groundwater management · Ultramafic rocks

The Water Framework Directive (WFD) 2000/60/EC establishes the principles for the environmental protection of inland, transitional and coastal waters. Several approaches have been developed and proposed for analyzing environmental issues caused by human activities. Among these, the Driver-Pressure-State-Impact-Response (DPSIR) approach, adopted by the European Environment Agency (EEA 1999), has been extensively used in the literature for the analysis of complicate water resource management issues (Gari et al. 2018). According to the DPSIR framework, there is a chain of causal links starting with "driving forces" (causes) through "pressures" (e.g. pollution sources) to "states" (e.g. chemical status) and "impacts" on water use and ecosystems (structure and function), eventually leading to "responses" (policy).

Hexavalent Cr occurrence in groundwater of Greece is an issue of public concern with its origin to be attributed both to natural and anthropogenic sources. Geogenic Cr(VI) has been found in several aquifers of the globe where the geological background consists of ultramafic rocks. Such areas have been reported both in Greece and in many other countries including Italy, USA and others (Kaprara et al. 2015; Hausladen et al. 2018; Apollaro et al. 2019). It is noteworthy that the highest concentrations of Cr(VI) have been found in alluvial aquifers consisting of clastic material of weathered serpentine rock. Within such a framework, the scope of the present study is to implement the DPSIR approach in order to: (a) identify the main anthropogenic factors and their pressures causing the deterioration of groundwater quality in selected ultramafic rock related groundwater bodies of Central Greece (Loutraki, Schinos, Thiva-Assopos-Oinofyta and Central Evia), and (b) propose a framework for the sustainable groundwater management in these areas.

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✉ Konstantina Pyrgaki
kpyrgak@geol.uoa.gr

[1] Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, 15784 Athens, Greece

[2] Department of Chemistry, National and Kapodistrian University of Athens, 15784 Athens, Greece

[3] Department of Civil Engineering, National and Technical University of Athens, 15780 Athens, Greece

Materials and Methods

The specific characteristics of the study areas are presented in Table S1. The unconfined aquifer of Loutraki develops in the Quaternary alluvial deposits, rich in weathered ophiolite material. The thickness of the unsaturated zone increases gradually from southwest to northeast of the aquifer and ranges from zero to 125 m (Kounis and Vitoriou-Georgouli 2003). According to existing hydrogeological studies, the maximum water elevation is of about 50 m. Schinos shallow alluvial aquifer has a thickness ranging from 2 to 15 m. The water level elevation ranges from – 0.9 to 10.2 m. The alluvial aquifer of Thiva is located in Quaternary and Neogene deposits. It is unconfined in shallow depths, while in greater depths becomes confined. The water level of the unconfined aquifer ranges from 60 to 70 m. In Oinofyta, the studied aquifer is developed in Neogene formations. According to Giannoulopoulos (2008) the water level ranges from 80 to 95 m and the aquifer has hydraulic connection with the Assopos river (Fig. 1). Finally, the main aquifers comprising the groundwater body of Central Evia are (a) a shallow unconfined Quaternary alluvial aquifer (close to the coastal zone) and (b) a deeper porous aquifer located in the Neogene formations.

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. These, were acquired from the public body of Special Secretariat for Water which is responsible for the implementation of the European Water Framework Directive in Greece. For the characterization of "state" of groundwater quality, 154 samples were collected from 59 sampling stations (Fig. 1) during the wet and dry seasons of 2017 and 2018. Particularly, 31 groundwater samples were collected from Loutraki, 32 from Schinos, 28 from Thiva, 11 from Oinofyta and 52 from C. Evia. The sampling in Oinofyta industrial area was focused on existing bores for Cr(VI) monitoring (Dermatas et al. 2017). At each water sampling station, three sub-samples were collected in separate clean polyethylene bottles for cation, Cr(VI) and anion analysis. During sampling, the following parameters were measured in situ: pH, redox potential, dissolved oxygen, electrical conductivity, total dissolved solids and temperature. A total of 25 chemical parameters were determined including alkalinity, Ca^{2+}, Mg^{2+}, Na^+, K^+, dissolved organic carbon, Cl^-, NO_3^-, NO_2^-, NH_4^+, SO_4^{2-}, As, Cd, Cr, Cr(VI), Cu, Fe, B, Co, Al, Si, Mn, Ni, Pb, V according to the analytical methods

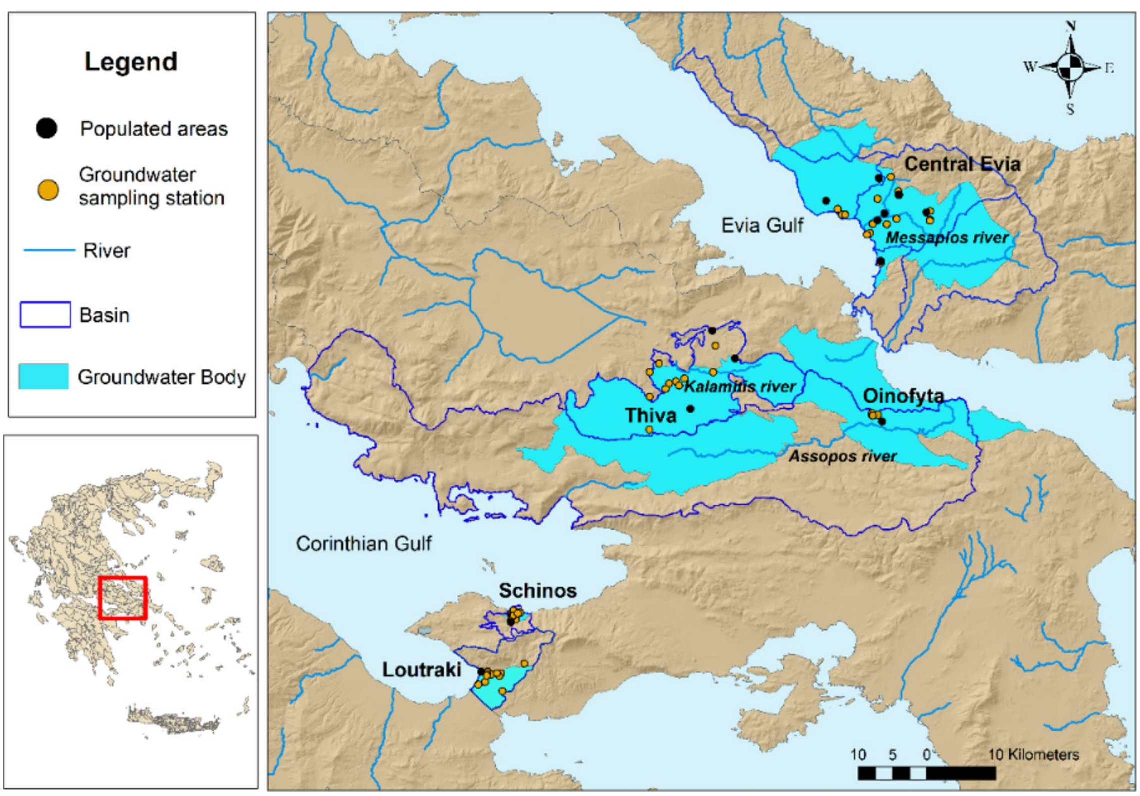


Fig. 1 Map with sampling stations, groundwater bodies and river basins

provided in the Table S3. The samples for trace metal analysis were acidified to pH < 2 by adding a few drops of 1 M HNO_3. The water samples for cation and Cr(VI) analysis were filtered through 0.45 μm cellulose acetate membrane filters in situ. The quality control of analytical results for each method respectively was achieved by using quality control standards, blank and replicate samples (Table S4).

Results and Discussion

The main identified driving forces in the study areas are agricultural activities, livestock, industrial and urban development and tourism (Table 1).

In C. Evia basin, agricultural land covers 15.8% of the total area (Fig. 2a). As a result, the dominant water demand in C. Evia municipality is for irrigation (Fig. 2b). In Loutraki basin, agriculture is also present with agricultural

Table 1 Implementation of the DPSIR framework in the study areas

Driving forces	Pressures	State	Impact	Responses
Agricultural activities – Agricultural land – Water demand for irrigation *(Thiva-Assopos-Oinofyta, C.Evia, Loutraki)*	– Fertilizer, pesticide use – Groundwater abstractions for irrigation	N, P, SO_4, Cl	– Deterioration of GWB chemical status, – Decrease of groundwater use efficiency – Increased risk to public health – Loss of trust to public bodies involved in groundwater management – Increase of GWR environmental cost	– Monitoring of groundwater bodies – Establishment of Cr(VI) natural background range of concentrations – Establishment of Cr(VI) thresholds for each water use – Identification and mitigation of pollution sources – Groundwater remediation – Increase of stakeholder participation – Identification of alternative water resources for specific uses
Livestock – Water demand for livestock *(Thiva-Assopos-Oinofyta, C.Evia)*	– GWR abstractions for livestock – Organic waste	N, P		
Industrial sector – Land for industry – Demand for industrial water *(Thiva-Assopos-Oinofyta)*	– Industrial waste disposal – Wastewater discharges – Groundwater abstractions for industrial purposes	Cr(VI), Cl		
Urban development and tourism – Urban land – Demand for domestic-drinking water *(Schinos, Loutraki)*	– Uncontrolled urban sewage discharges – Groundwater abstractions for domestic-drinking water	N, P, Cl		

GWB groundwater body, *GWR* groundwater resources

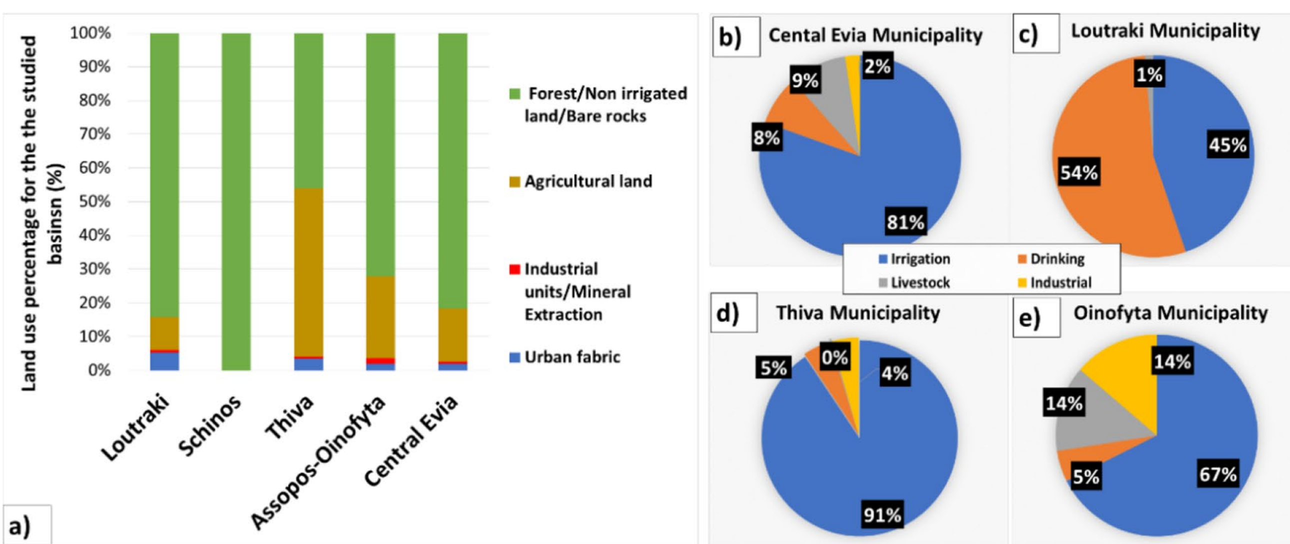


Fig. 2 **a** Land use percentage for each basin according to Corine land use 2012, **b–e** Water demand for different uses in the respective municipalities

land covering 9.8% of the total basin area whereas urban fabric follows with a 6.5% coverage. Loutraki municipality is characterized by the highest water demand for drinking water, whereas the demand for irrigation water is also high (Fig. 2c). Touristic activity is also intense in Loutraki town and in Schinos village (Fig. 1), resulting in increased water demand during the summer months with groundwater abstractions increasing by a factor of two during August (Figs.S1, S2). In the small basin of Schinos, the water demand is mainly for domestic-drinking purposes. Nevertheless, dozens of wells are located in the alluvial aquifer, showing that the need for domestic irrigation is also intense. In Thiva basin, the agricultural sector represents one of the most important economic activities of the region, covering almost 50% of the total available land surface (Fig. 2a). Arable crops and vegetables are mainly cultivated in the plain area. In Thiva municipality, the water demand for irrigation is the highest covering 91% of the total (Fig. 2d). In the wider basin of Assopos-Oinofyta, agricultural land occupies the highest percentage after forest land, as well. In the wider area of Assopos basin a total of 350 industries exist (Despotidou 2016) whereas within the groundwater body of Thiva-Assopos-Oinofyta (Fig. 1), there are approximately 186 active industries of which 71 industries can be associated with Cr containing waste (textile, tannery, agrochemical and pigment production, metallurgy and metal plating) (Figs. S3, S4). This, results in increased water demand for industrial purposes in the respective municipalities (Fig. 2e,). Finally, in Oinofyta municipality the water demand for livestock constitutes 14% of the total water demand.

The main pressures induced by the anthropogenic activities in the studied basins are presented in Table 1. At all study areas, the water needs for irrigation of agricultural land are totally covered by groundwater resources.

In the groundwater body of C. Evia, (Fig. 1), the abstractions are mainly for irrigation of agricultural land (Table S2). In Loutraki municipality, the water needs are covered exclusively by the alluvial unconfined aquifer (Fig. 1). It is estimated that the annual groundwater abstractions for the different uses reach approximately 2.86 million m^3 with the main use to be for domestic-drinking water purposes (Table S2). The alluvial aquifer of Schinos is mainly exploited for small scale irrigation of allotments but due to lack of data is difficult to estimate the respective groundwater abstractions. Regarding water supply, only 29,000 m^3 annually are abstracted from the alluvial aquifer for this purpose (Fig. S2; Table S2). The water supply of Schinos village is covered mainly from local springs which are located outside the basin with the annual abstractions to be approximately 230×10^3 m^3. In Thiva-Assopos-Oinofyta groundwater body, the majority of groundwater abstractions are for irrigation of agricultural land (Table S2). The studied groundwater bodies are characterized by a moderate to good quantitative status based on the respective indicator (total groundwater abstractions versus groundwater body recharge) ranging from 22 to 64% (Table S2). Furthermore, at the coastal part of the alluvial aquifers of Schinos, Loutraki and C. Evia sea water mixes with groundwater as indicated by the high Cl concentrations showing that salinization risk is high along the coastal zone. Both in Loutraki and Schinos basins, the main pressures posed to the alluvial aquifers are contamination by sewage effluents due to presence of domestic septic tanks. In C. Evia and Thiva basins, the main pressures are associated with the use of agrochemicals (pesticides and fertilizers). Among the study areas, the municipality of Thiva presents the highest P, N flows while the area of C. Evia follows (Fig. S5). The discharges of ammonium rich effluents in such alluvial aquifers may enhance Cr mobility in the vadose zone due to acidic nitrification (Mills and Goldhaber 2012). In addition, PO_4^{3-} enhances the desorption of the anionic Cr(VI) sorbed on the iron oxide surfaces (Becquer et al. 2003) since phosphates and chromates are competitive ions. Papazotos et al. (2019) have highlighted the synergistic role of P, N bearing fertilizers on Cr mobility in C. Evia. As a result, it is important to take into account the anthropogenic pressures which lead to increased P, N flows in such aquifers as they can increase the natural background concentration levels of Cr(VI).

In Assopos- Oinofyta area, industrial effluents have polluted the water bodies for at least three decades (Dermatas et al. 2017). It is estimated that 7605 m^3 of industrial effluents are produced at a daily basis. The majority of industrial effluents are treated with physicochemical or biological methods from which 78.7% is discharged into Assopos river (Despotidou 2016). Therefore, in the study areas, water stress is caused mainly by the degradation of groundwater quality.

The main Cr sources in the studied basins can be: (a) Cr bearing minerals (geogenic origin) and/or (b) industrial waste/wastewater (anthropogenic origin) (Table 1). Each one of these sources may contribute in different degrees to the Cr(VI) concentrations in groundwater. Hexavalent Cr concentrations ranged from below the limit of detection (0.9 μg/L) to 430 μg/L in Schinos shallow alluvial aquifer (excluding the area of Oinofyta) (Figs. 3, 4a). However, the highest Cr(VI) concentration (up to 11.7 mg/L) was measured in the monitoring bore in Oinofyta area (Fig. 3b). It is noted that there is a decreasing trend in Cr(VI) concentrations in the specific borehole of Oinofyta from 2017 to 2018 (Fig. 4b).

High NO_3^-, SO_4^{-2-}, PO_4^{3-} and Cl^- concentrations due to fertilizer use, sewage effluents and salinization were also identified. Nitrate concentrations ranged from 0.5 to 362 mg/L (Fig. 4c). The maximum concentration was measured in C. Evia groundwater body. Regarding PO_4^{-3}, groundwater samples from Schinos presented the

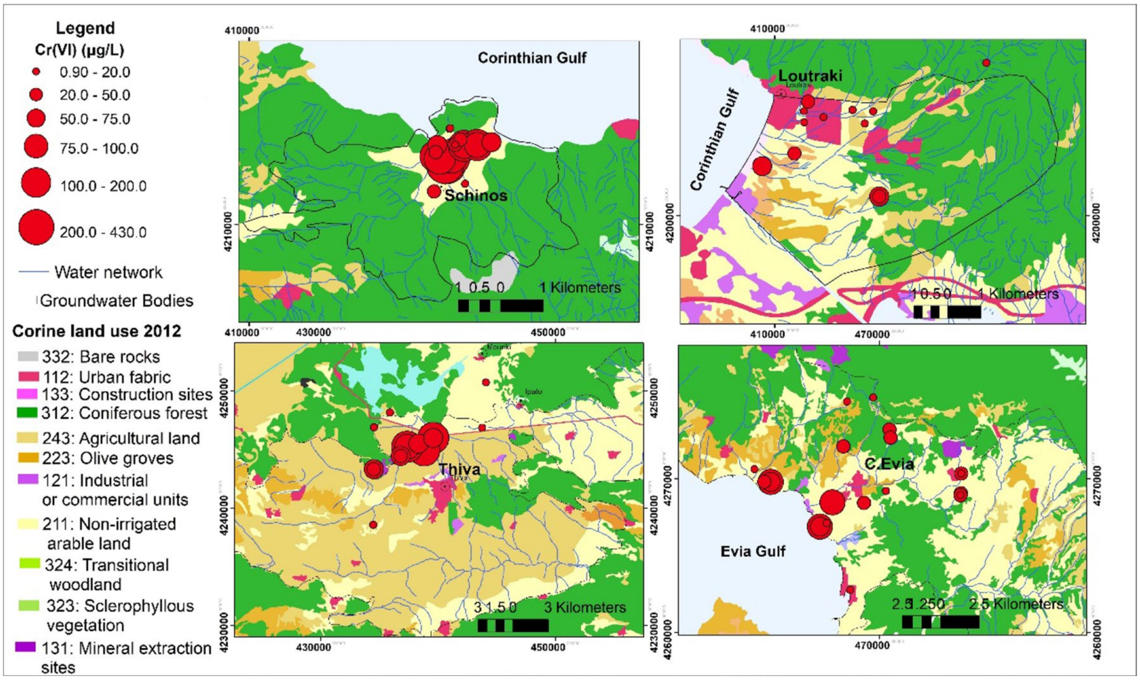
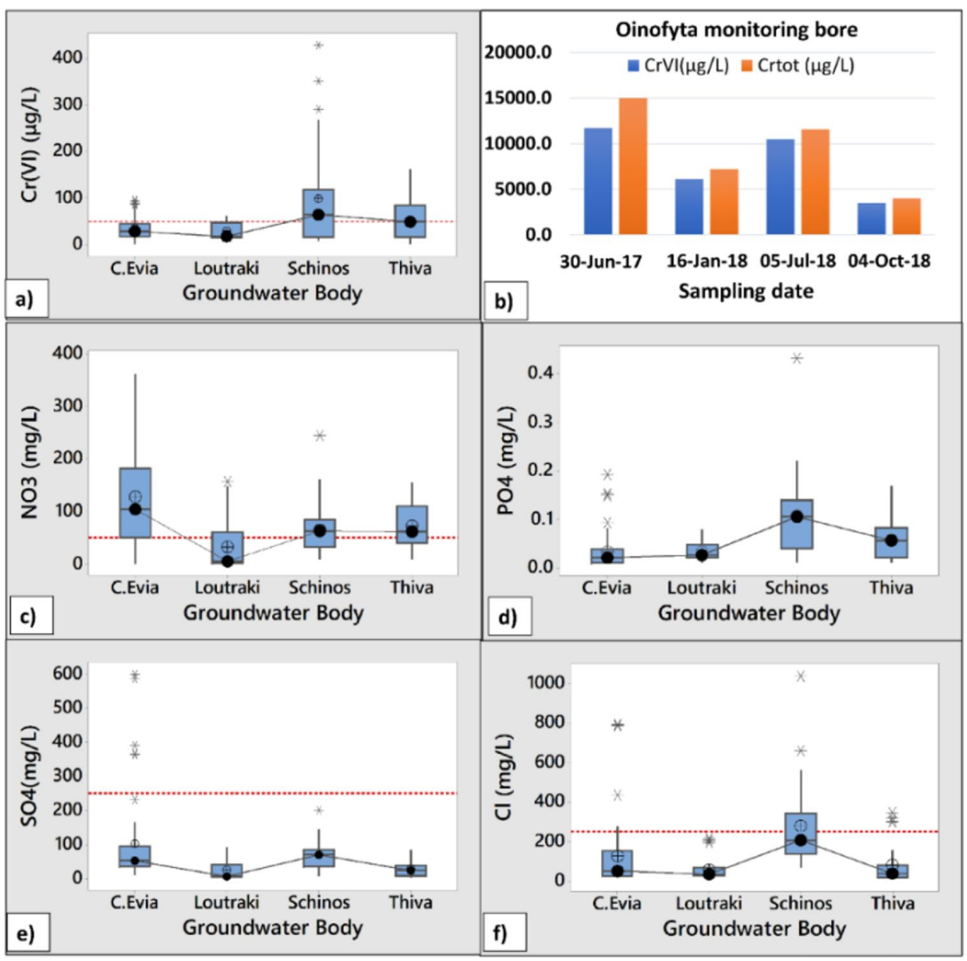


Fig. 3 Spatial distribution of Cr(VI) concentrations in the study areas

Fig. 4 Boxplot diagrams of **a**, **b** Cr(VI), **c** NO_3^-, **d** PO_4^{3-}, **e** SO_4^{2-} and **f** Cl^- concentrations. Red lines correspond to the upper limits of the drinking water directive 98/83/EC



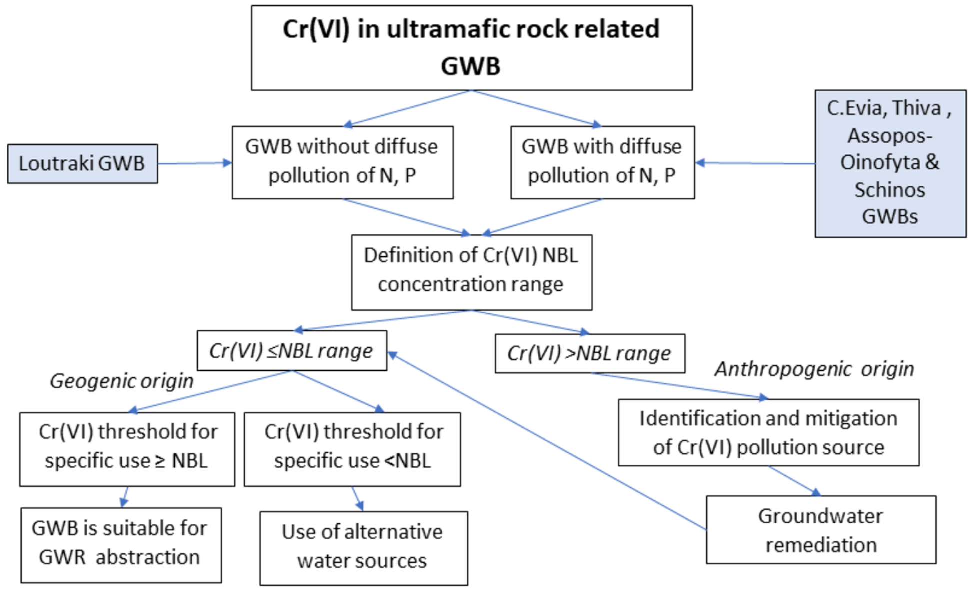


Fig. 5 Management framework for ultramafic rock related groundwater bodies

highest median, whereas some outliers also existed in C. Evia (Fig. 4d). Sulfate concentrations ranged from 2.6 to 600 mg/L (Fig. 4e) with maximum concentration occurring in C. Evia. Finally, Cl^- concentrations varied from 11.9 to 1039 mg/L. The maximum concentration has been recorded in Schinos aquifer (Fig. 4f).

There are several impacts caused by the qualitative degradation of the studied groundwater bodies (Table 1). According to WFD/2006/118/EC, groundwater is a valuable natural resource and as such should be protected from deterioration and chemical pollution. This is particularly important for groundwater dependent ecosystems and for the use of groundwater in water supply for human consumption. Nevertheless, according to the article 10 of the WFD/2006/118/EC, groundwater chemical status provisions do not apply to high naturally-occurring levels of substances or ions or their indicators, contained in a groundwater body, due to specific hydrogeological conditions, which are not covered by the definition of pollution. Therefore, geogenic Cr(VI) is not considered as an ecological damage for the chemical status of such aquifers. On the contrary, geogenic Cr(VI) contamination contributes to the decrease of groundwater use efficiency. The suitability of groundwater for human consumption was assessed according to the European directive 98/83/EC which defines as an upper limit for total Cr the 50 µg/L. According to the thresholds of the Drinking Water Directive 98/83/EC it is clear that NO_3^- and Cr are the main pollutants in the studied groundwater bodies, while Cl^- and SO_4^{2-} exceedances are lesser (Fig. S6). The percentage of examined samples exceeding the total Cr limit for drinking water purposes was 63% for Schinos, 57% for Thiva, 32% for Loutraki and 27% for C. Evia, respectively. Nevertheless, only in Loutraki and Schinos (only in summer months) the aquifers are exploited for domestic-drinking water purposes with the threshold exceedances to be observed only in irrigation wells. It is clear that in the case of drinking water, the associated impacts on public health have to be further examined. Additionally, the suitability for irrigation was assessed according to Food and Agricultural Organization (FAO) guidelines. According to FAO, the recommended upper concentration limit for total Cr in irrigation water is 100 µg/L. Regarding the suitability of groundwater for irrigation, the percentage of exceedance of FAO recommended value (100 µg/L) for total Cr was 46% for Schinos, 25% for Thiva and 6% for C. Evia. Furthermore, the impact of polluted irrigation water on crops has also to be assessed. Socioeconomic issues such as the loss of public trust on water managers, the loss of income for farmers are also significant impacts that have to further be assessed. In both Schinos and Loutraki, many households prefer to use bottled water than water from the supply network. Finally, the polluted water (due to human intervention) has a higher environmental cost as according to both European WFD/2000/60/EC and Greek legislation there is a need for implementing mitigation measures. All the above indicate that water governance in these areas is facing serious problems.

The complex water management issue of geogenic Cr(VI) occurrence will not be solved unless all the different aspects of the DPSIR framework are taken into account. Therefore, a water management flow sheet (Fig. 5) is proposed to indicate the first steps that have to implemented when dealing with ultramafic rock related groundwater bodies where both geogenic and anthropogenic pressures coexist. Firstly, there is an urgent need to define a range of Cr(VI) concentrations representing the natural background which will be used to distinguish among geogenic and anthropogenic origin by taking also into account the synergistic role of P, N flows. To achieve this, a constant monitoring network has to be established in the studied groundwater bodies at a seasonal basis. Secondly, it is very important to legislate Cr(VI) upper thresholds for the different water uses. In addition, mitigation measures for both point and diffuse pollution sources have to be implemented. For example, the restriction of the extensive fertilizer uses along with the establishment of strictly protected zones where land cultivation should be done with ecological techniques should pe promoted in C. Evia and Thiva-Assopos-Oinofyta groundwater bodies. Finally, cost-efficient technologies have to be applied for the remediation of anthropogenic Cr(VI) contamination (Gueye et al. 2016) such as in the case of Thiva-Assopos-Oinofyta groundwater body.

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