

Article

Aspects of Hexavalent Chromium Pollution of Thebes Plain Aquifer, Boeotia, Greece

Dimitrios I. Koilakos

Department of Water Resources and Agricultural Mechanics, Agricultural University of Athens, Iera Odos 75 Street P.C., 11855 Athens, Greece; dikoilakos@aua.gr; Tel.: +30-210-6014082

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Abstract: The present work focuses on the environmental problem of Thebes Plain—since considerable amounts of Cr (VI) have been reported—and tries to find out the reasons of such a phenomenon and the sources of the pollution. For this issue, a complete chemical analysis of 20 samples from the study area was conducted as well as an isotopic analysis of Cr and Sr isotopes. Hexavalent chromium pollution can be triggered by human pollutant activity or specific geological environments. Stable Cr isotopic analysis gave $\delta^{53}\text{Cr}$ positive values in several samples which supports the second hypothesis, but the limitations of that theory do not allow safe conclusions in all cases. Nitrates and Sr ratios suggest fertilizer contamination and the presence of SiO_2 -leaching of silicate rocks.

Keywords: hexavalent chromium; strontium; isotopes; geogenic pollution; nitrates; leaching

1. Introduction

Hexavalent chromium pollution is a common phenomenon, since several case studies can be mentioned from all around the world such as Urania State of Sao Paolo, Brazil [1]; La Spezia Province, Italy [2]; Leon Valley, Mexico [3]; and Mojave Desert, California, USA [4]. Also in the USA., in four major lakes of the Mississippi, pollutant toxic metals including chromium have been detected [5]; additionally, pollutant substances have been found in bottom sediments of Lake Symsar, Poland [6]. In several areas of Greece, Cr (VI) has been detected, such as Central Euboea and Avlonas [7,8].

Cr (VI) pollution may cause several diseases such as cancer; leuchemy, if it comes into contact with blood; and if inhaled (in the form of gas), it can destroy the lag [9,10], which means that the measurement and the monitoring of that parameter is essential not only for environmental protection but also for public health. The international, European and Greek legislations impose certain guidelines for Cr (VI) [11–13].

There are several reasons for Cr (VI) pollution. According to the literature, industrial activity creates wastes of Cr (VI) mainly due to treatment of inorganic and organic matters [14]. Another pollutant factor is agricultural activity since several fertilizers and agrochemicals contain Cr (VI) [15]. This has been reported in fertilizers of the study area [16]. Also, over pumping and the mixture of aquifers are also pollutant factors [17]. Mining activity is another factor [18]. Stock farm activity throughout manures, stables and slaughterhouses can also generate Cr (VI). Sewers and cesspools, especially from urban networks, directly lead the humid elements into the groundwater. Another factor is the improper manufacture of drillings which can result in the mixture of aquifers and pipe leaching.

Cr (VI) may be generated by the rocks, especially those containing Cr such as peridotites or serpentines on ophiolitic belts [19,20]. Nature may generate Cr (VI) in the ground water and four geological environments have been reported [21,22] which may produce natural Cr (VI): arid alluvial basins such as those in southwest USA; saline brines in evaporate basins; chromite ore bodies; serpentinite ultramafic terrains. In the first two environments, the redox conditions tend to favor the

generation and preservation of Cr (VI) while in the last two, the hydrolysis of chromites and peridotites is the basic mechanism of Cr (VI) enrichment. Natural Cr (VI) has been detected on Presidio of San Francisco. Cr (VI) was attributed to natural factors because no human sources were present. On the other hand, the serpentine bedrock could provide Cr (VI), as proved by leaching tests on borehole cores [20].

The study area is Thebes Plain located on Boeotia Prefecture-Greece. Cr (VI) pollution has been reported in boreholes of Avlonas and the town surroundings of Thebes [23,24]. In the study area groundwater, the Cr (VI) levels come up to 204 µg/L as a maximum value [25]. Other researches and independent works [26,27] also give evidence of the issue. Last but not least, Institute of Geological and Mineralogical Exploration of Greece (IGME) has worked on this area and came to some serious conclusions in 2010 [28].

The study area is a complex environment where the geogenic factor plays an important role in the presence of hexavalent chromium in soil and groundwater. The development of ophiolites and peridotites, which are characterized by the presence of chromium, is the main geogenic factor. Additionally, the weathering of the ophiolites has contributed to the enrichment of the soils with chromium. Apart from the natural factor, human contribution plays an important role, including industries, stock-farms and ranches and quarries. Last but not least, the study area is under intense agricultural exploitation. All these factors contribute to Cr (VI) pollution in the study area.

The modern theory of chromium stable isotopes may answer if Cr (VI) has natural or human origin. Several case studies in Mojave Desert and Snake River in USA [4,29] have been carried out in this direction. In Greece, the issue has also been under discussion [7,30]. Another question which had to be answered was if the calcium/magnesium ratios matched those of peridotites. For that purpose, it was suggested to conduct further isotope analysis and measure isotopes of strontium and dissolved SiO₂ to check if the values match and leaching of silicate rocks indeed takes place.

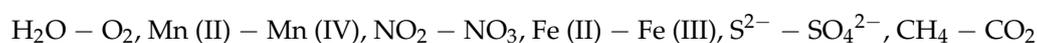
2. Generally Information about Chromium

Chromium is found in lithosphere in low concentrations. The highest concentrations are found in magmatic rocks (198 mg/kg) and clay (120 mg/kg), while the lowest ones are found in carbonate rocks (7.08 mg/kg) and evaporites (10.6 mg/kg). The major chromium minerals are chromite (FeOCr₂O₃) which is dominant in peridotites and crocoite (PbCrO₄) which can be found in the oxidation zone of lead deposits [22]. In sea water, the concentration is about 0.2 µg/L, whereas in surface and ground waters the chromium concentrations have an average concentration of 0.4 µg/L. In California's boreholes, there have been detected values up to 21 µg/L [31]. The usual concentrations on potable water do not exceed 5 µg/L. The European Union classes chromium as a toxic substance and imposes 50 µg/L as an upper limit for total chromium on potable water.

2.1. Oxidation States of Chromium

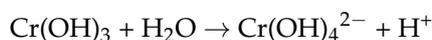
Chromium in nature occurs in two oxidation states [19,22,31]: the trivalent and the hexavalent form. The trivalent form is more common in soils. In the study area, the concentrations in soil are between 32 and 906 mg/kg d.w. [32]. The average of chromium in soils worldwide is 54 mg/kg while in study area is 280 mg/kg d.w. [32].

In aquatic environments, chromium occurs also in two oxidation states, i.e., Cr (III) in chromic compounds and Cr (VI) in anionic form in chromates CrO₄²⁻ and di-chromates Cr₂O₇²⁻ [22]. Cr (VI) may be transformed to Cr (III) and vice versa. In the first case, Cr (VI) is reduced to Cr (III), while in the second case, Cr (III) is oxidized to Cr (VI). The oxidation of Cr (III) to Cr (VI) or the reduction of Cr (VI) to Cr (III) requires another redox couple which accepts or gives the necessary electrons. The significant redox couples are the following [33–35].



Under normal conditions in the Cr–H₂O–O system, the zone of Cr (VI) stability ranges in a wide area in comparison with the trivalent form. The species of Cr (VI) appear in oxidant conditions (Eh > 0) and alkaline pH > 6. The fate of chromium in the environment may also be controlled by the Eh and pH conditions. In natural waters and average redox conditions, a common transformation [22] takes place according to reaction 1:

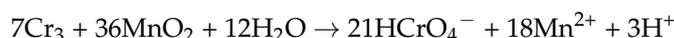
Reaction 1:



This reaction takes place in relatively high Eh conditions at pHs between 6.5 and 8.5 [34]. According to laboratory experiments, ⁵¹Cr (III) has been oxidized in five days at pH 8 to 10.

Dissolved oxygen has been found to oxidize Cr (III) according to experiments in aquatic solutions. In natural waters, the rate of oxidation is too slow and other factors have to coexist in order for such transformation to take place [35]. In soils and aquatic environments, the absorption of trivalent chromium from oxides of Manganese is the first step for it to transform (oxidation) to hexavalent. This process takes place in the presence of iron oxides, and clay minerals [36]. The following equation has been proposed [37,38] after long experiments.

Reaction 2:

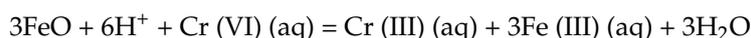


This process takes place relatively quickly. According to experiments [19,33], the rate of oxidation in the presence of MnO₂ depends on its quantity. At the ratio MnO₂:Cr = 200: 1, the added Cr (VI) oxidized totally after 42 min, while in 10 times higher concentration of MnO₂ only 3 min was required [35].

The reduced sulfur (S, S²⁻, H₂S, S₂O₃²⁻) may be a basic factor in the reduction of Cr (VI) to Cr (III). Laboratory studies have reported that the reduction of Cr (VI) involving sulfides is initially rapid, slows down in a few minutes, but reaches completion after one day [35].

Iron (II) is a major factor in the reduction of Cr (VI) to Cr (III) [35,39]. Dissolved Fe (II) ions in environmental waters may be generated by the discharges of some industrial wastes, but also may result from the weathering of Fe(II)-containing minerals. Numerous minerals in geologic materials contain Fe (II) for Cr (VI) reduction, including silicates, oxides, or sulfides [40]. Cr (VI) reduction via Fe (II) in silicate minerals (e.g., biotite in solution rather than at the mineral surface) takes place according to the following chemical reaction [40].

Reaction 3



This reduction is complete after 2 min; the end-products of this reaction are Fe (III) and Cr (III) which precipitate in acidic solution [41].

Finally, nitrates could pose a potential problem in Cr (VI). If direct reduction of Cr (VI) were to dominate, then NO₃⁻ could potentially inhibit Cr (VI) reduction since Cr (VI) and NO₃⁻ have similar redox potentials [42].

2.2. Isotopic Chemistry

Stable Isotopes Chromium Systematics

Chromium has four stable isotopes with the following abundances [21]: ⁵⁰Cr 4.35%, ⁵²Cr 83.79%, ⁵³Cr 9.50%, ⁵⁴Cr 2.36%

The value δ⁵³Cr is crucial for distinguishing the pollution source.

The δ⁵³Cr value is calculated as follows (according to National Institute of Standards and Technology Standard Reference Material)

$$\frac{R_{\text{sample}}}{R_0} = \left(\frac{C}{C_0} \right)^{a-1} \quad (1)$$

where:

R_{sample} : the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio in the sample water

R_0 : the initial $^{53}\text{Cr}/^{52}\text{Cr}$ ratio

C : the concentration of Cr in the sample water

C_0 : the initial Cr concentration of the sample

α : Cr fractionation factor

$\delta^{53}\text{Cr}$ is related with R_{sample} with the following equation

$$R_{sample} = \frac{\delta^{53}\text{Cr} \times R_{std}}{1000} + R_{std} \quad (2)$$

where R_{std} is the $\text{Cr}^{53}/\text{Cr}^{52}$ ratio of the National Institute of Standards and Technology Standard Reference Material 979, equal with 0.113418 which represents the average natural abundance of Cr on the Earth's crust.

When pollution is anthropogenic, the $\delta^{53}\text{Cr}$ value is near to zero [4,43,44]. This happens because the industrial materials have the properties of chromite whose $\delta^{53}\text{Cr}$ value is near to zero; additionally, no significant fractionation takes place during the industrial activities [43,44]. The theory of isotopes has to be used with great attention since hexavalent chromium tends to oxidize to trivalent chromium under suitable conditions, this results in fractionation of the considering sample and it may give positive $\delta^{53}\text{Cr}$ values [21] even if the Cr (VI) concentrations are from anthropogenic sources.

2.3. Strontium Isotopes Systematics

Sr isotopes are considered to be an excellent tracer in hydrogeology [45,46]. In contrast to stable chromium isotopes, they do not fractionate considerably in nature. Groundwater acquires dissolved Sr in two hydrogeological environments. The first is the recharge area through infiltration and the percolation process, while the second is found along the flow path, through dissolution or ion exchange with minerals. The Sr isotopes are used as tracers in hydrogeological applications because they give insight into the water–rock interaction process. In Grand Sasso, Central Italy, Sr isotopes are used as tracers to find the recharge area. This took place by following the highest $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios. In another case study in Monte Volture volcano, Italy, Triassic dolomite limestones such as those of the study area, are found to have a 0.70882 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio [47].

Several ranges are given in the literature for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Carbonate rocks have $^{87}\text{Sr}/^{86}\text{Sr}$ values between 0.7068 and 0.7094 [48–50]. In silicate rocks, such as granite and gneiss, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range between 0.7135 and 0.717 [48,51]. For basalts, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range between 0.703 and 0.705 [52]. The anthropogenic influence on $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is also evident: fertilizers contain very large contents of Sr (3–1500 ppm) [50] and the isotopic ratio ranges between 0.70794 and 0.70950. The carbonate amendments used in agriculture are of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios around 0.70987 [52]. In rainwater, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are around 0.709 and 0.7106. In seawater, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are around 0.709 [50].

3. Geology and Hydrogeology

The study area belongs geotectonically to the Pelagonian zone and is structured by Mesozoic, Tertiary and Quaternary formations. Mesozoic formations consist of carbonate rocks, limestones, dolomites, peridotites, ophiolite mélanges and flints as Figure 1 depicts [53]. The Tertiary formations consist of marls and sandstone clays. The Quaternary formations are represented by clastic sediments, debris and Holocene deposits. The description of the geological formations from the newer to the older formations goes as follows.

Alluvium: These formations are the alluvial deposits, the debris, and the slide rocks. There are loose deposits that consist of clastic polymict coarse material, i.e., gravels, breccia and grits, but it also contains thinner material such as sand and clay. This material originates from the surrounding hills and the mountains. The depth of the deposits ranges from a few meters to more than 100 m at the

central part of the basin. At the surface, there is fertile cultivated land rich in clay. The coarse material originates from the erosion of limestones, dolomites, and ophiolites of the surrounding hills.

Pliocene-Pleistocene deposits: The lower Pliocene formations are formed in lake and lagoon environments and appear as layers, while Pleistocene formations deposited on terrestrial environments appear as thick layers. They are alternated with thinner material in circles (thin, coarse). At the eastern part, the lower Pliocene deposits dominate, while at the western part Pleistocene deposits occur.

Flysch: It is undivided and its age has been determined by the geological mapping and the fossils of Paleocene-Eocene. The flysch transits to the following limestones.

Limestones-dolomites: They underlie the flint series and include:

Low-middle Jurassic limestones of middle thickness contained in the upper and the lower part flints

Low Jurassic-Upper Triassic carbonate rocks are dark colored limestones with medium thickness in the upper part. Crystalline limestones underlie them and overlie colored limestones, dolomite limestones and dolomites.

It has been observed by borehole sections that the limestones are expanding below the alluvial deposits to the west and southwest part of the basin [53].

Ophiolites-flints: The ophiolite mélange consists of peridotites which have been under serpentinization, diabases and cherts. This system is more than 300 m deep. The ophiolites occur at the northeastern part of the area in Mouriki Village.

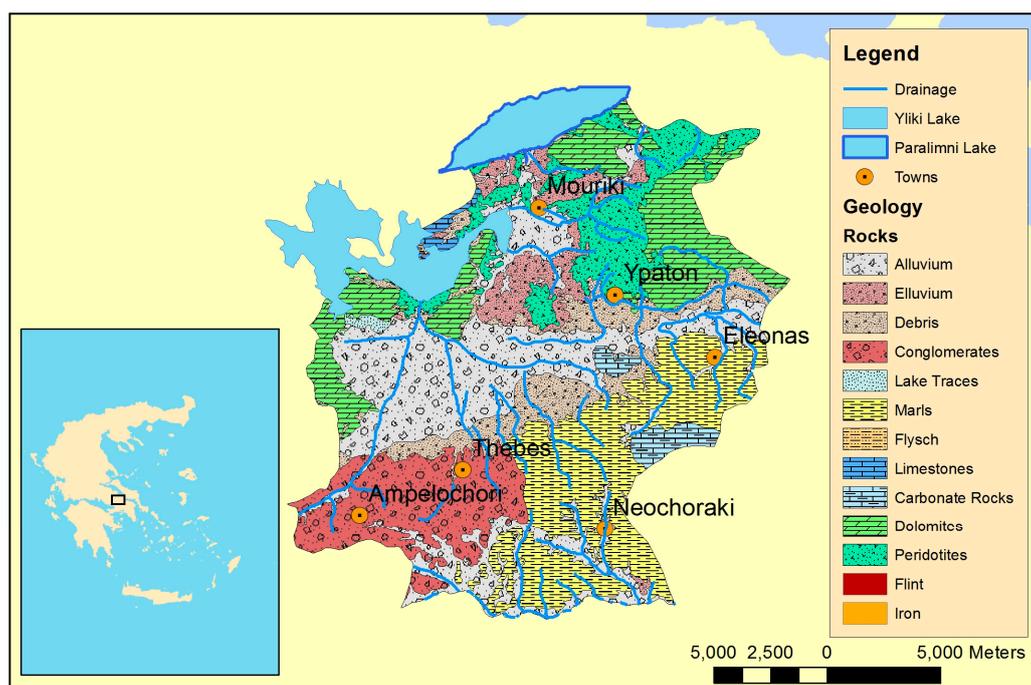


Figure 1. Geological map of the study area.

3.1. Hydrogeological Aspects

According to IGME, a geological map in the area develops four kinds of aquifers. Firstly, porosity aquifers occur which are divided into high productive aquifers and extensive productive aquifers (alluvium on Figure 1). Secondly, karstic formations appear which are divided into high productive aquifers and extensive productive aquifers. These formations appear on the limestone and dolomite formations. Hard rock practical permeable formations occur in the Mouriki Revenia area and these formations are considered to be responsible for natural Cr (VI). Practically impermeable rocks such as marls of Neocene exist between the areas of Thebes and Neochoraki.

The porous aquifers are of particular hydrogeological interest due to their wide occurrence and thickness. Inside these formations, alternated aquifers exist which are under exploitation through several wells and boreholes. Their critical supply is more than $100 \text{ m}^3/\text{h}$ [54]. The carbonate aquifers are highly productive aquifers due to their intense karstification. Boreholes deeper than 170 m present critical recharge more than $120 \text{ m}^3/\text{h}$ [54]. Finally, the ophiolite mélange hosts aquifers of limited productivity and the critical recharge ranges between 10 and $35 \text{ m}^3/\text{h}$ [54].

3.2. Sampling Campaign

In the dry period of 2012, 20 samples were collected. We have focused on the polluted areas of Thebes plain and the peridotite zone on Mouriki. This sampling campaign aimed at focusing on particular areas of intense pollutant phenomena. All the points are illustrated in Figure 2. The particular areas were indicated after year-long research on the study area, taking into consideration all the available publications and data [7,16,23–27]. In the field, the coordinates of the water points were estimated with a GPS device. The electric conductivity, the temperature, pH, redox, and dissolved oxygen were measured with special equipment. The water samples were collected in polyethylene bottles of 1 L and preserved in the refrigerator until further analysis. In separate bottles of 100 mL, similar samples which had undergone a 45 nm filtering, have been collected [55].

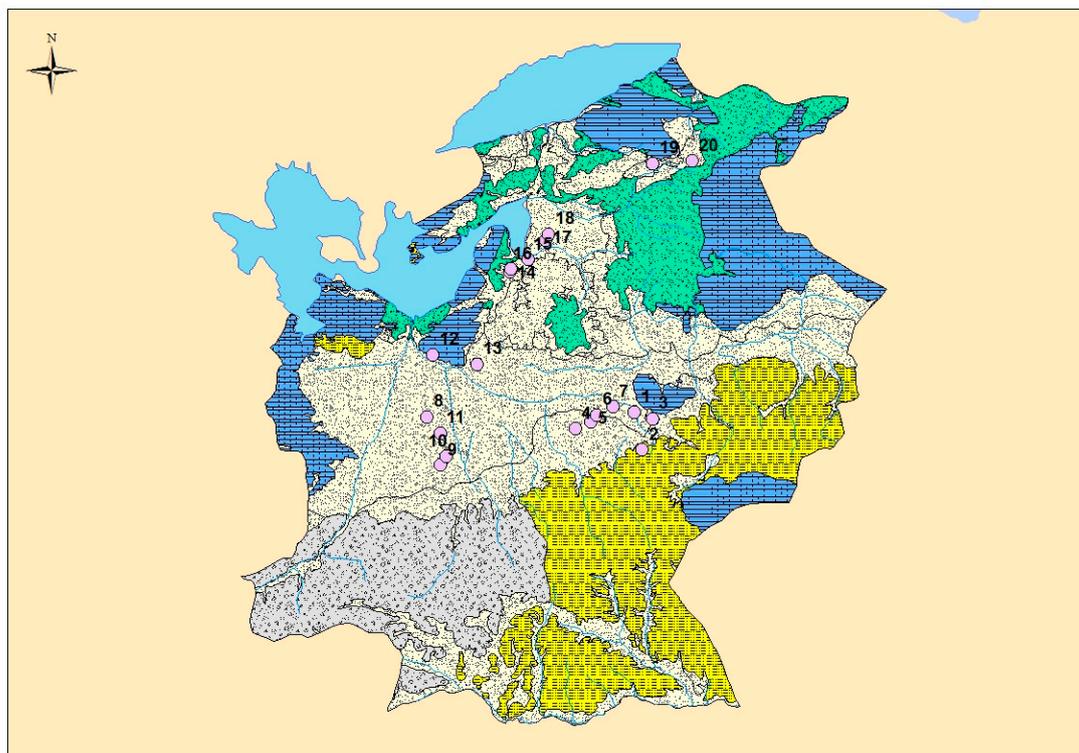


Figure 2. Sampling points.

3.3. Anthropogenic Sources of Pollution

There are several sources of anthropogenic chromium in the study area. According to the Institute of Geological and Mineralogical Research (IGME 2010), their spatial distribution is as shown in Figure 3. Almost all the recorded sources release hexavalent chromium to the environment. We will focus on industrial units which release: As, Cd, Cr, Cu, F, Hg, Ni, Pb, Zn, NH_3 , NO_x , SO_x and on the farms which produce: As, B, Cd, Cr, Cu, Hg, Ni, P, Pb, Sb, Se, Zn, NH_3 .

Agricultural activity is intense in the Alluvial Basin and Mouriki region. The pollutant sources that IGME recorded are gathered in Mouriki and the west part of the Basin. The Mesovouni area

(east part) has a quarry and some ranches. The west part (Thebes) has ranches, quarries, a cemetery, Thebes dump and an industry.

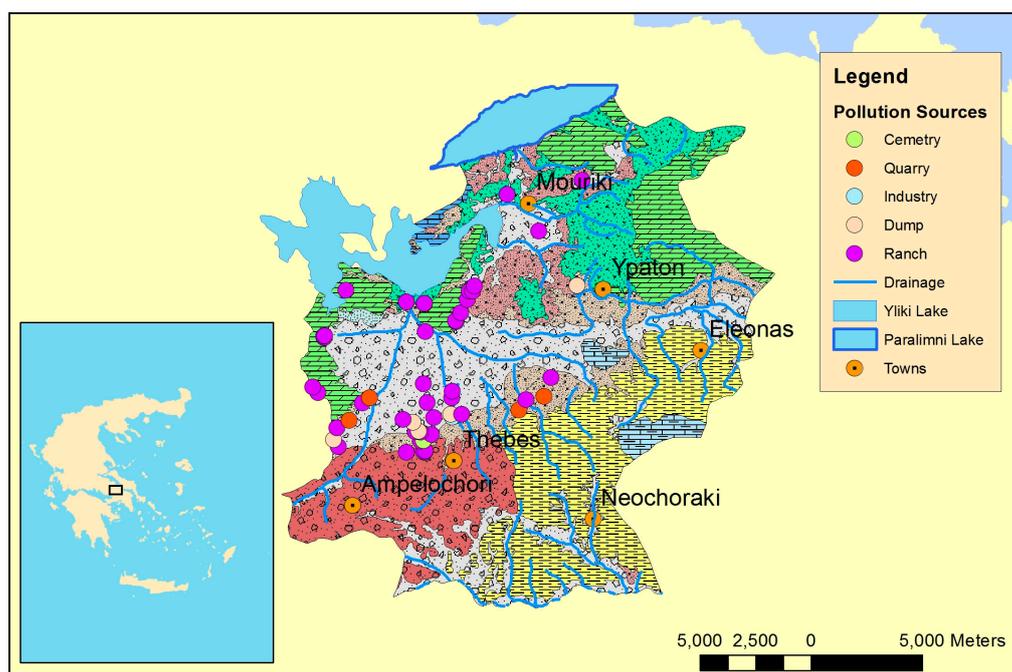


Figure 3. Sources of anthropogenic pollution according to the Institute of Geological and Mineralogical Research (IGME) 2010.

4. Material and Methods

4.1. Major Chemistry and Heavy Metals

The anion, cation and heavy metal analyses were carried out in the Laboratory of Agricultural Hydraulics in the Agricultural University of Athens. For anion and cation determination, we used ion chromatography. The anions Cl^- , NO_3^- , NO_2^- and SO_4^{2-} were measured by ion chromatography with a simple injection of the sample. The methodology required an eluent which consisted of 0.137 g sodium carbonate and 0.168 g sodium hydrogen carbonate diluted in 1000 mL ultrapure water. Additionally, a stock of 2.5 mL H_2SO_4 diluted in 1000 mL ultrapure water was necessary in order for the process to be carried out with suppression.

The cations (Li^+ , Na^+ , NH_4^+ , Mn^{2+} , K^+ , Ca^{2+} and Mg^{2+}) have been measured using another method. The eluent consisted of 0.6 g tartaric acid and 0.167 g dipicolinic acid diluted in 1000 mL ultrapure water. The cation process has undergone no suppression. The ion chromatograph was constructed by Metrohm in Stockholm of Swiss. It was consisted of an IC Interface, Detector, Separation center, liquid handling unit and pump. The system was connected to a computer and printer.

Polarography was used for Cr (VI) and heavy metal determination. For Cr (VI) determination, the following methodology was used: a buffer was produced which contained 1.64 g oxic sodium, 1.96 g DTPA (Pentetic acid) 21.3 g nitric acid in a 100 mL volumetric flask which was filled up to the mark with ultrapure water and mixed with a stirrer. We prepared a mixture containing 10 mL of the measured sample and 2.5 mL buffer. The pH should be regulated to 6.2 ± 0.1 . A standard for the estimation of hexavalent Chromium was used and inserted when standard addition was required. The calculations and the presentation of the results were applied by computer software [56].

Polarography was also used for Lead, Copper and, Zinc. These metals were estimated under a specific method. For their measurement, we introduced 10 mL of the sample and we added 0.5 mL acetate buffer. We measured the pH of the mixture; the final pH was controlled by importing a small

quantity of acetic oxide in order to be about 4.6 ± 0.2 [57]. The polarograph (Metrohm, Stockholm, Swiss) was a VA 797 Computrace model, connected with a computer such as an Ion Chromatograph.

Titration has been used in order to measure the bicarbonate anion. The indicator was blue phenolphthalein and the titrator 0.1 N HCl. The titration took place until the sample became blue. Cr (VI), Cr_{tot}, Fe_{tot} and SiO₂ were measured by a spectrophotometer. For Cr (VI), a Chroma-ver powder was used, while for Fe_{tot}, the appropriate indicator was used. For SiO₂ and Cr_{tot}, the methods were more complex and appropriate methodologies have been followed [58]. All the methods that we used were suggested by the relative protocols in compliance with the instructions of the instruments and the requirements of the methodologies. The samples were analyzed for Cr (VI) no later than 24 h after the samples' collection as suggested by the relative protocol [55]. For Cr (VI) and Fe_{tot}, special spectrophotometers were used. For Cr_{tot} and SiO₂ estimations, a DR 2700 instrument was used.

4.2. Isotopic Ratios

The instrument which was used for isotopic determination was an IsotopX "Phoenix" multi-collector (Thermal Ionization Mass Spectrometer—TIMS (Middlewich, UK)). The analyses took place in the Department of Geoscience and Natural Resource Management, at the University of Copenhagen.

4.2.1. Stable Isotopes of Chromium

For the chromium isotopes composition, the following method, described in detail, was used: 10 mL of water aliquots were spiked with an appropriate amount of ⁵⁰Cr-⁵⁴Cr double spike and dried on a hotplate. After addition of 1 mL of aqua regia, followed by renewed drying and uptake in 1 mL 6 N HCl, the sample solutions were diluted to 0.5 M HCl with MQ water and passed over 8 mL stem volume columns charged with 100–200 mesh AG-50W cation resin. Cr was eluted in 0.5 N HCl in an elution scheme based on a particular recipe [59]. The procedure yields for Cr in this separation method varied from 70–80%, and Cr procedure blanks were in the order of 5–10 ng, which is negligible compared to the amount of chromium separated from the samples studied herein.

The addition of a ⁵⁰Cr-⁵⁴Cr double spike of known isotope composition to a sample before chemical purification allowed accurate correction of both the chemical and the instrumental shifts in Cr isotope abundances [21,43]. Thanks to this method, we achieve a 2 s external reproducibility of the $\delta^{53}\text{Cr}$ value with 1.5 mg Cr loads of the NIST SRM 3112a standard on an IsotopX/GV IsoProbeT thermal ionization mass spectrometer (TIMS) of $\pm 0.05\%$ with ⁵²Cr signal intensities of 1 V and of $\pm 0.08\%$ for ⁵²Cr beam intensities of 500 mV. The double spike correction returns Cr isotope compositions of samples as the per mil difference to the isotope composition of the NIST SRM 3112a Cr standard (used for the spike calibration; [21]).

To maintain inter-laboratory comparability of Cr isotope data, we recalculated our data of natural samples relative to the certified Cr isotope standard NIST SRM 979 as follows:

$$\delta^{53}\text{Cr sample (SRM 979)} = \left[\left(\frac{^{53}\text{Cr}}{^{52}\text{Cr}} \text{ sample} / \frac{^{53}\text{Cr}}{^{52}\text{Cr}} \text{ SRM 979} \right) - 1 \right] \times 1000 \quad (3)$$

Cr isotope measurements were performed on an IsotopX/GV IsoProbe T TIMS equipped with eight Faraday collectors that allow simultaneous collection of all four chromium beams (⁵⁰Cr⁺, ⁵²Cr⁺, ⁵³Cr⁺, ⁵⁴Cr⁺) together with ⁴⁹Ti⁺, ⁵¹V⁺, and ⁵⁶Fe⁺ to monitor for small interferences of these masses on ⁵⁰Cr and ⁵⁴Cr.

4.2.2. Strontium Isotopic Measurements

The method used to determine the ⁸⁷Sr/⁸⁶Sr ratios, is described in detail. Water aliquots were filtered with disposable syringe filters (0.45 μm) and between 2 and 4 mL aliquots were transferred to 7 mL Teflon (Savillex™) vials. The aliquots were evaporated down on a hotplate at 80 °C overnight. Samples were taken up in a few drops of 3 M HNO₃ and then loaded on

commercially available (Eppendorf™) 1 mL pipette tips with a pressed-in filter designed to be used as an extraction column. These “columns” were charged with 200 µL of an intensively pre-cleaned mesh 50–100 Sr Spec™ (Eichrome Inc./Tristchem, Chicago, IL, USA), resin and an appropriate elution recipe essentially was followed [60]. Strontium was eluted/stripped by pure deionized water and then the eluate was dried on a hotplate. Samples were dissolved in 2.5 L of a Ta₂O₅–H₃PO₄–HF activator solution and loaded directly onto previously outgassed 99.98% single Re filaments. Samples were measured at 1250–1300 °C in dynamic multi-collection mode on a VG Sector 54 IT mass spectrometer (Middlewich, UK) equipped with eight Faraday detectors. Five ng loads of the NBS 987. Sr standard gave ⁸⁷Sr/⁸⁶Sr = 0.710236 ± 0.000010 (*n* = 14, 2 s).

The ⁸⁷Sr/⁸⁶Sr values of the samples were corrected for the offset relative to the certified NIST SRM 987 value of 0.710250. The errors reported are within-run (2 sm) precisions of the individual runs.

5. Results and Discussion

In Table 1, the descriptive statistics of all the measured values, i.e., their units, their average, their standard deviation, the minimum and maximum values and the number (N) of the measured samples are presented. In the following paragraphs, the results are presented in detail.

Table 1. Descriptive statistics of chemical analyses of the dry period of 2012.

Parameter	Unit	Average	St. Dev.	Min.	Max.	N
Cond	µs/cm	736.6	119.7	466	957	20
D.O.	mg/L	8.89	4.2	2.4	14.4	20
pH		8.18	1.2	7.4	9.41	20
Eh	mV	157.65	60.3	80	268	20
T	°C	21	0.4	20	21.9	20
F ⁻	mg/L	0.2	0.1	0.1	0.5	19
Cl ⁻	mg/L	42	18.7	16	80.9	20
Br ⁻	mg/L	1.2	0.2	0.9	1.7	20
NO ₃ ⁻	mg/L	44.9	36.9	4.6	145	20
SO ₄ ⁻	mg/L	12.5	9.8	3.3	45.7	20
HCO ₃ ⁻	mg/L	375.5	66.5	280	540	20
Na ⁺	mg/L	26	9.2	10	50.3	20
K ⁺	mg/L	1.7	2.5	0.2	9.9	20
Ca ²⁺	mg/L	25	26.4	2.9	92.6	20
Mg ²⁺	mg/L	81.1	20.1	42	122	20
SiO ₂	mg/L	36.1	21.6	13	87	20
Cr (VI)	µg/L	80.8	79.2	3	255	20
Zn	µg/L	137.4	341.2	19	1500	18
Pb	µg/L	13	4.6	3	19.4	18
Cu	µg/L	8.8	17	2.2	75.6	18

5.1. Physicochemical Properties

The groundwater of the area is characterized by relatively increased electric conductivity with a mean value of 736 µS/cm. and temperature (20.1–21.9 °C). All pHs are relatively alkaline and the average pH is 8.19 in the east part of the study area. Redox values are positive and between 80 and 267 mV (average 157.65 mV). D.O. (2.4–14.4 mg/L) is also present with an average value of 8.9 mg/L. The average values of Eh and pH are depicted in the Cr(OH)₃ field which means that redox conditions favor natural attenuation, as shown in Figure 4. Increased pH values were evident (2012 dry period) due to the occurrence of peridotites which favor alkali conditions while in the west part they are slightly lower.

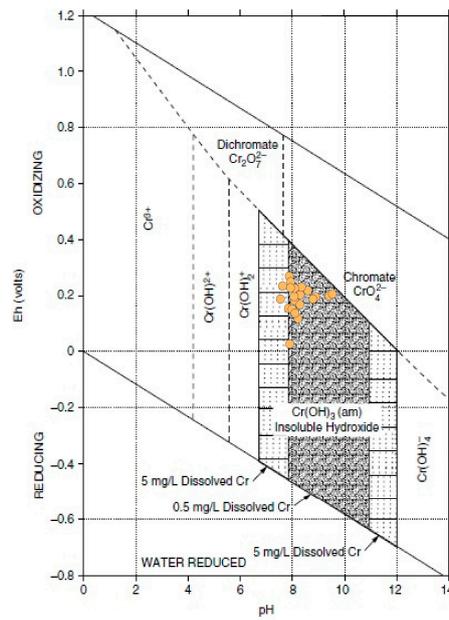


Figure 4. In situ redox conditions in the study area.

5.2. Anions and Cations

Chlorine concentrations range from 16 to 80 mg/L. HCO_3^- is stable between pH 6.5 and 11 and it is the dominant anion with an average concentration of 375 mg/L (Table 1). One of the characteristics of Thebes Basin is the deterioration of water quality from nitrates NO_3^- (4.6–144.5 mg/L). The average value is about 36.9 mg/L but the maximum value exceeds by far the E.U. and state guideline of 50 mg/L [11–13]. Sulfates are also present and their average concentration is 12.5 mg/L.

Sodium concentrations in the study area range from 10.4 to 50.3 mg/L. Potassium (0.2–9.9 mg/L) may originate from specific rocks, but also from fertilizers used in agricultural activities. Calcium (3–92 mg/L) concentrations may be generated from carbonate rocks and igneous rocks rich in calcite minerals. High magnesium concentrations (41–121 mg/L) are attributed to the dissolution of the minerals contained in the ophiolite mélanges and the occurrence of dolomites in the study area.

The dominant water type among the 20 samples is Mg- HCO_3 . It is obvious that magnesium plays an important role in the groundwater chemistry of the area. The Mg/Ca ratio was >1 in all samples, which is an indicator that the ophiolites and their eroded materials are the source of magnesium [61]. The water types and the dominance of magnesium over calcium are depicted in the Piper and Durov (expanded) diagram of Figure 5.

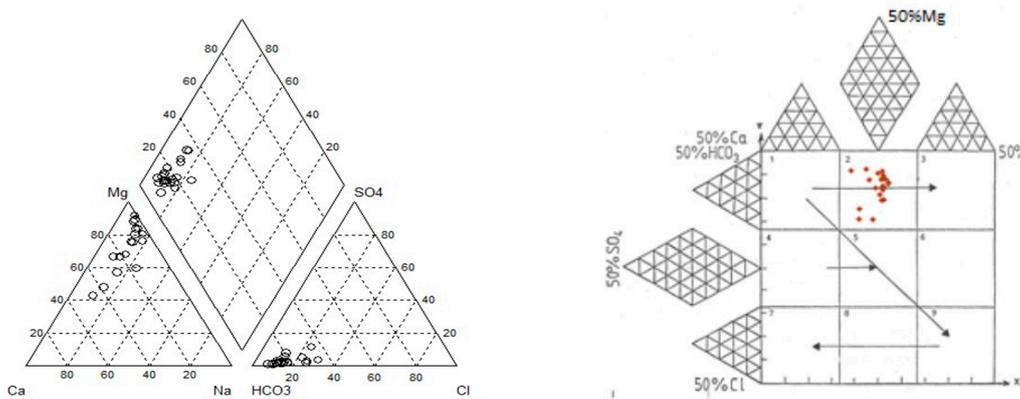


Figure 5. Piper and Durov diagrams.

5.3. Trace Elements and SiO₂

Fluorine and bromide are present as trace elements and their averages are 0.2 mg/L and 1.2 mg/L, respectively. SiO₂ concentration varies between 13 and 87 mg/L. The SiO₂ detection indicates silicate rock leaching.

Another point which must be highlighted was that neither Mn²⁺ nor Fe_{tot} were detectable by our methods. The detection limit of Mn²⁺ was 0.1 ppb in the ion chromatograph and Fe_{tot} 1 ppb in the spectrophotometer.

5.4. Heavy Metals and Chromium

Pb, Zn and Cu (usually divalent) do not change oxidation states in the environment [31], are not considered redox-sensitive and they do not tend to attenuate as Cr (VI) by the redox conditions. Their average values are below the E.U. guidelines [12].

Cr (VI) concentrations range between 3 and 255 µg/L and 12 out of 20 samples exceed the E.U. guideline of 50 µg/L for Cr_{tot} and these waters are classed as unsuitable for human consumption [11–13]. The Plain is polluted in the east and the west part with Cr (VI). Generally, the Mouriki zone with the peridotites has small Cr (VI) concentrations (nitrates distribution is also presented). The point distribution of Cr (VI) concentrations is presented in Figure 6. This figure also includes spatial contribution of the nitrates which is another pollutant factor.

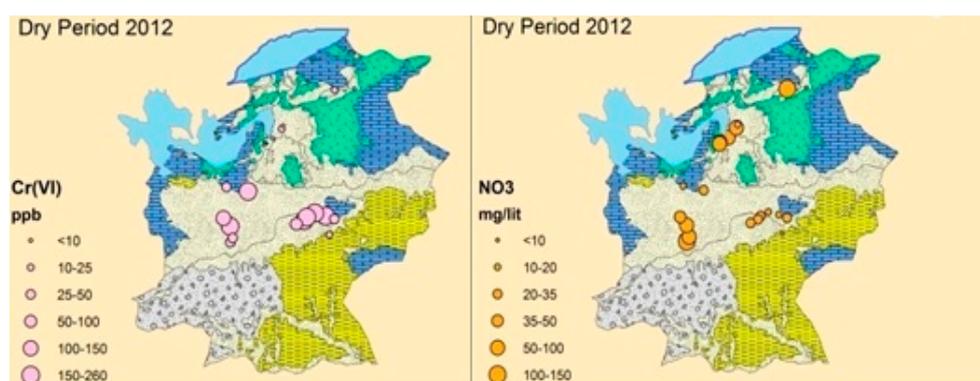


Figure 6. Cr (VI) and NO₃[−] concentrations in the polluted areas of Thebes.

5.5. Isotopic Compositions

The samples were measured for stable chromium isotopes and total chromium values were measured, as shown in Table 2. It should be mentioned that isotopic determination took place in 12 out of 20 samples. In those cases, the samples with the highest Cr (VI) concentration were chosen. The issue of magnesium and the hypothesis of peridotites led to the idea of strontium isotopes, the results of which are presented in Table 2.

All the δ⁵³Cr values are positive; the samples 1 to 7 are from the east part while the samples from 7 to 13 are from the west part. In the east part of the area, the δ⁵³Cr is slightly higher than in the west part. The positive δ⁵³Cr values indicate the geogenic origin of Cr (VI). However, we must be very careful because several samples contain considerable amounts of Cr (III). The presence of Cr (III) indicates natural attenuation of Cr (VI) and therefore considerable fractionation, especially in the west part of the study.

A figure of Cr (VI) vs. δ⁵³Cr values has been constructed (Figure 7), illustrating that the east part of the area is not only high in Cr (VI) concentrations, but also higher δ⁵³Cr values show the impact of peridotites. The isotopic Cr ratios vary between 0.62 and 1.1 and there is an extraordinary value at 1.99 due to fractionation.

Sr ratios have an average value of 0.7089996 which is suitable for leachates of fertilizers or limestones. Since limestones do not control the groundwater chemistry (due to magnesium dominance), the most probable scenario is that such ratios originate from the first cause. The increased nitrate concentrations indicate fertilizer leaching in the study area. A plot of Sr ratios vs. nitrates has been plotted in Figure 8 in order to testify the relation between them, as shown in Figure 4. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are between 0.708807 and 0.709088. Additionally, an extraordinary value at 0.709394 has been reported. The highest nitrate values are mainly between 0.708911 and 0.708956 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. This shows a preference of high nitrates concentrations for these values. Also, it is notable that high nitrate values are gathered in the west part of the study area.

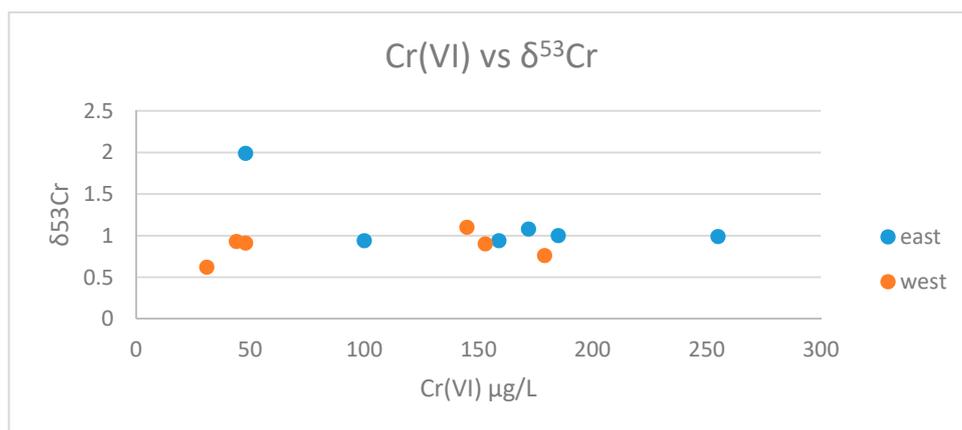


Figure 7. Cr (VI) vs. $\delta^{53}\text{Cr}$ plot.

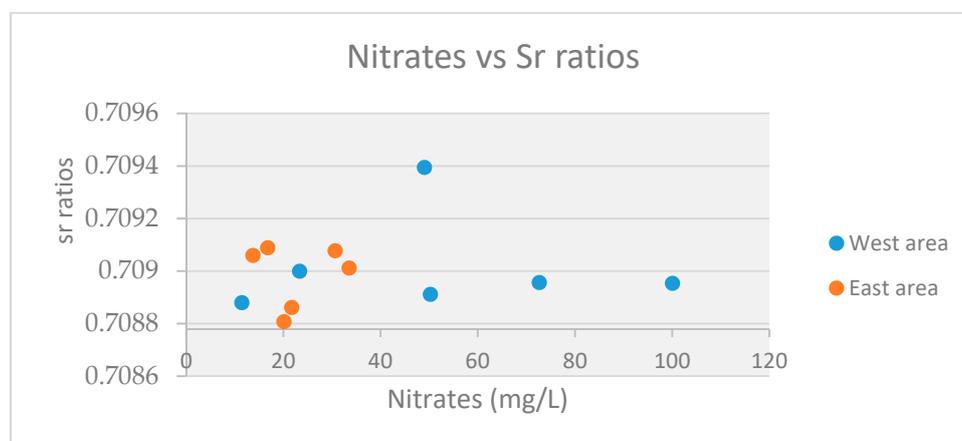


Figure 8. NO_3 vs. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, plot.

Table 2. Cr (tot) and Cr (VI) concentrations and isotopic determination.

Sample	Cr _{tot} ($\mu\text{g/L}$)	Cr(VI) ($\mu\text{g/L}$)	Cr(VI)/Cr _{tot} %	NO_3^- (mg/L)	$\delta^{53}\text{Cr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
1	257	255	0.78%	13.773	0.99	0.709059
3	67	48	28.36%	33.558	1.99	0.709011
4	112	100	10.71%	20.142	0.94	0.708807
5	190	185	2.63%	21.736	1.00	0.708861
6	178	159	10.67%	30.664	0.94	0.709077
7	186	172	7.53%	16.823	1.08	0.709088
8	159	145	8.81%	49.046	1.10	0.709394
9	112	48	57.14%	100.084	0.91	0.708952
10	78	44	43.59%	72.678	0.93	0.708956

Table 2. Cont.

Sample	Cr _{tot} (µg/L)	Cr(VI) (µg/L)	Cr(VI)/Cr _{tot} %	NO ₃ ⁻ (mg/L)	δ ⁵³ Cr	⁸⁷ Sr/ ⁸⁶ Sr
11	156	153	1.92%	50.261	0.90	0.708911
12	44	31	29.55%	11.473	0.62	0.708878
13	185	179	3.24%	23.348	0.76	0.708998
Average	144	127	17.08%	36.96	1.01	0.708999

6. Conclusions

This article focused on the environmental problem of Thebes Plain—Cr (VI) pollution—and analyzed the possible sources of human and geogenic pollution. In cases of higher Cr (III) concentrations, fractionation phenomena (due to natural attenuation) take place. In these cases, stable chromium isotopes are not a safe guide. In the case that δ⁵³Cr values are positive and Cr (III) concentrations are not so high, the presence of Cr (VI) has to be attributed to the geogenic factor.

In the east part of the area, the geogenic contribution is more obvious since the δ⁵³Cr values are higher. Also, the fractionation phenomena are not so intense due to the alkaline conditions that peridotites create. The west part of the area seems to be affected by the human factor due to the numerous recorded anthropogenic pollutant sources. The δ⁵³Cr values are closer to zero and we experience fractionation phenomena due to natural attenuation. Table 2 shows that no particular fractionation takes part (see Cr (VI)/Cr_{tot}%) in the east part, while in the west part half of the samples indicate fractionation.

Strontium isotopic ratios gave an average value of 0.708999. This value could originate from limestones leaching and/or fertilizer leachates. It has already been mentioned that Mg dominates over Ca and additionally, dolomite limestones such as those of the study area have slightly lower prices. The most important fact, however, is that nitrates are present in the study area, particularly in the west part. The presence of nitrates is an anthropogenic influence, it creates further pollutant problems and it is very possible that their leachates contain Cr (VI), as several works suggest [16,30].

To conclude, further environmental monitoring should take place and acceptable methods should be applied such as phytoremediation and in situ treatment [4,16,39]. The natural attenuation phenomena, particularly in the west part, provide natural remediation and may be used as a basis for future remediation.

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References

- Bourotte, C.; Bertolo, R.; Almodovar, M.; Hirata, R. Natural occurrence of hexavalent chromium in a sedimentary aquifer in Urandia, State of Sao Paulo, Brazil. *Ann. Braz. Acad. Sci.* **2009**, *81*, 227–242. [[CrossRef](#)]
- Fantoni, D.; Brozzo, G.; Canepa, M.; Cipolli, F.; Marini, L.; Ottonello, G.; Zuccolini, M.V. Natural hexavalent chromium in groundwaters interacting with ophiolitic rocks. *Environ. Geol.* **2002**, *42*, 871–882. [[CrossRef](#)]
- Armenita, M.A.; Quere, A. Hydrogeochemical behavior of chromium in the unsaturated zone and in the aquifer of Leon Valley, Mexico. *Water Air Soil Pollut.* **1995**, *84*, 11–29. [[CrossRef](#)]
- Izbiki, J.A.; Ball, J.W.; Bullen, T.D.; Sutley, S.J. Chromium, chromium isotopes and selected trace elements, western Mojave Desert, U.S.A. *Appl. Geochem.* **2008**, *23*, 1325–1352. [[CrossRef](#)]
- Dash, P.; Silwal, S.; Ikenga, J.O.; Pinckney, J.L.; Arslan, Z.; Lizotte, R.E. Water Quality of Four Major Lakes in Mississippi, USA: Impacts on Human and Aquatic Ecosystem Health. *Water* **2015**, *7*, 4999–5030. [[CrossRef](#)]

6. Potasznik, A.K.; Szymczyk, S.; Skwierawski, A.; Lewczuk, K.G.; Cymes, I. Heavy Metal Contamination in the Surface Layer of Bottom Sediments in a Flow-Through Lake: A Case Study of Lake Symsar in Northern Poland. *Water* **2016**, *8*, 358. [CrossRef]
7. Economou-Eliopoulos, M.; Frei, R.; Atsarou, C. Application of chromium stable isotopes to the evaluation of Cr (VI) contamination in groundwater and rock leachates from central Euboea and the Assopos basin (Greece). *Catena* **2014**, *122*, 216–228. [CrossRef]
8. Megremi, I. Distribution and bioavailability of Cr in central Euboea, Greece. *Cent. Eur. J. Geosci.* **2009**. [CrossRef]
9. Cary, E.E. Chromium in air, soil, and natural waters. Biological and Environmental Aspects of Chromium. In *Topics in Environmental Health*; Elsevier Biomedical Press: New York, NY, USA, 1982; pp. 49–64.
10. National Institute for Occupational Safety and Health (NIOSH). Online Pocket Guide to Chemical Hazards. NIOSH, 1999. Available online: <http://www.cdc.gov/niosh/npg/npg.html> (accessed on 8 August 2017).
11. Ljujic, B.; Sundac, Lj. *Council Directive 98/83/EC Directive of the European Parliament on the Quality of Water Intended for Human Consumption*; The European Parliament and the Council of the European Union, Off J L 330; European Union: Brussels, Belgium, 1998.
12. World Health Organization (WHO). International Standards for Drinking Water. Switzerland, Italy, 1971. Available online: <http://apps.who.int/iris/bitstream/10665/43845/1/a91160.pdf> (accessed on 8 August 2017).
13. Michalopoulou, E. *Legislation for the Environment*; Ziti Publications: Athens, Greece, 2004.
14. Lewis, R.J. *Sax's Dangerous Properties of Industrial Materials*, 8th ed.; Van Nostrand Reinhold: New York, NY, USA, 1992; Volume II.
15. Thornton, I. Geochemistry applied to agriculture. In *Applied Environmental Geochemistry*; Academic Press: London, UK, 1983; pp. 231–266.
16. Mimides, Th. *Investigation of Agricultural Products for Toxic Pollutants in Thebe's Municipality*; Thebe's: Thebes, Greece, 2011.
17. Testa, S. Sources of Chromium Contamination in Soil and Groundwater. In *Cr(VI) Handbook*; CRC Publications: New York, NY, USA, 2005.
18. Morning, J.L.; Matthews, N.A.; Peterson, E.C. Chromium in Mineral Facts and Problems. In *Bulletin 671*; U.S. Bureau of Mines: Washington, DC, USA, 1989; pp. 167–182.
19. Hem, J. *Study and Interpretation of the Chemical Characteristics of Natural Water*, 3rd ed.; U.S.G.S.: Alexandria, VA, USA, 1979.
20. Steinpress, M. Naturally Occurring Chromium(VI) in Groundwater. In *Cr(VI) Handbook*; CRC Publications: New York, NY, USA, 2005.
21. Schoenberg, R.; Zink, S.; Staubwasser, M.; von Blanckenburg, F. The stable Cr isotope inventory of solid Earth reservoirs determined by double spike MC-ICP-MS. *Chem. Geol.* **2008**, *249*, 294–306. [CrossRef]
22. Motzer, W. Chemistry, Geochemistry and Geology of Chromium. In *Cr(VI) Handbook*; CRC PRESS: New York, NY, USA, 2005.
23. Vasilatos, C.; Megremi, I.; Economou-Eliopoulos, M.; Mitsis, I. Hexavalent chromium and other toxic elements in natural waters in the Thiva–Tanagra–Malakasa Basin, Greece. *Hell. J. Geosci.* **2008**, *43*, 57–66.
24. Mimides, T. *Management and Protection of the Aolonas Area*; Research work; Agricultural University of Athens: Athens, Greece, 2007.
25. Economou-Eliopoulos, M.; Antivachi, D.; Vasilatos, C.; Megremi, I. Evaluation of the Cr (VI) and other toxic element contamination and their potential sources: The case of the Thiva basin (Greece). *Geosci. Front.* **2011**. [CrossRef]
26. Dermatas, D.; Vatsieris, C.; Panagiotakis, I.; Chrysochoou, M. Potential Contribution of geogenic chromium in groundwater contamination of a Greek heavily industrialized area. *Chem. Eng. Trans.* **2012**, *28*. [CrossRef]
27. Tziritis, E.; Kelepertzis, E.; Korres, G.; Perivolaris, D.; Repani, S. Hexavalent Chromium Contamination in Groundwaters of Thiva Basin, Central Greece. *Environ. Contam. Toxicol.* **2012**, *89*, 1073–1077. [CrossRef] [PubMed]
28. Institute of Geological and Mineral Exploration of Greece (IGME). *Pollution Factors in Boeotia Prefecture (E.U. Project)*; IGME: Athens, Greece, 2010.

29. Raddatz, A.L.; Johnson, T.M.; MicLing, T.L. Cr stable isotopes in Snake River Plain Aquifer groundwater: Evidence for natural reduction of dissolved Cr (VI). *Environ. Sci. Technol.* **2011**, *45*, 502–507. [[CrossRef](#)] [[PubMed](#)]
30. Mimides, T. *Hydrogeochemical Autopsy of Stable Chromium Isotopes in Order to Investigate Its Human and Natural Origin*; Euboea–Psachna (Technical Report); Agricultural University of Athens: Athens, Greece, 2015.
31. Mathess, J. *The Properties of Groundwater*; Willey Publications: New York, NY, USA, 1995.
32. Mimides, T.; Koilakos, D. Soil chemistry of Boeotia prefecture and application of Yttrium normalization theory for explaining the origin of chromium in soil. In Proceedings of the CRETE 2014 Conference, Chania, Greece, 7–10 September 2014.
33. Richard, F.C.; Bourg, A.C. Aqueous geochemistry of chromium: A review. *Water Resour.* **1991**, *25*, 807–816. [[CrossRef](#)]
34. Stanin, F. The Transport and Fate of Chromium (VI) in the Environment. In *Hexavalent Chromium Handbook*; CRC Publications: New York, NY, USA, 2005.
35. Schroeder, D.; Lee, F. *Potential Transformations of Chromium in Natural Waters*; Institute for Environmental Sciences; University of Texas-Dallas: Richardson, TX, USA, 1974.
36. Bartlett, R.J. Chromium cycling in soils and water: Links, gaps, and methods. *Environ. Health Perspect.* **1991**, *92*, 17–24. [[CrossRef](#)] [[PubMed](#)]
37. Fendorf, S.E.; Zasoski, R.J. Chromium(III) oxidation by MnO₂, part 1. characterization. *Environ. Sci. Technol.* **1992**, *26*, 79–85. [[CrossRef](#)]
38. Balance Chemical Equation—Online Balancer. Available online: <http://www.webqc.org/balance.php> (accessed on 9 August 2017).
39. Davis, A.; Olsen, R.L. The geochemistry of chromium migration and remediation in the subsurface. *Ground Water* **1995**, *33*, 759–768. [[CrossRef](#)]
40. Rai, D.; Sass, B.M.; Moore, D.A. Chromium(III) hydrolysis constants and solubility of chromium(III) hydroxide. *Inorg. Chem.* **1987**, *26*, 345–349. [[CrossRef](#)]
41. Stollenwerk, K.G.; Grove, D.B. Adsorption and desorption of hexavalent chromium in an alluvial aquifer near Telluride, Colorado. *J. Environ. Qual.* **1985**, *14*, 150–155. [[CrossRef](#)]
42. Viamajala, S.; Peyton, B.M.; Apel, W.A.; Petersen, J.N. Chromate reduction in shewanella oneidensis MR-1 is an inducible process associated with anaerobic growth. *Biotechnol. Prog.* **2002**, *18*, 290–295. [[CrossRef](#)] [[PubMed](#)]
43. Ellis, A.S.; Johnson, T.M.; Bullen, T.D. Chromium isotopes and the fate of hexavalent chromium in the environment. *Environ. Sci.* **2002**, *295*, 2060–2062. [[CrossRef](#)] [[PubMed](#)]
44. Johnson, T.M. *Stable Isotopes of Cr and Se as Tracers of Redox Processes in Earth Surface Environments*; Springer: Berlin, Germany, 2011; p. 239.
45. Barbieri, M.; Boschetti, T.; Petitta, M.; Tallini, M. Stable isotope (²H, ¹⁸O and ⁸⁷Sr/⁸⁶Sr) and hydrochemistry monitoring for groundwater hydrodynamics analysis in a karst aquifer (Gran Sasso, Central Italy). *Appl. Geochem.* **2005**. [[CrossRef](#)]
46. Barbieri, M.; Morotti, M. Hydrogeochemistry and strontium isotopes of spring and mineral waters from Monte Vulture volcano, Italy. *Appl. Geochem.* **2003**, *18*, 117–125. [[CrossRef](#)]
47. Barbieri, M.; Nigro, A.; Petitta, M. Groundwater mixing in the discharge area of San Vittorino Plain (Central Italy): Geochemical characterization and implication for drinking uses. *Environ. Earth Sci.* **2017**. [[CrossRef](#)]
48. Negrel, P.; Roy, S. Rain chemistry in the Massif Central (France). A strontium isotopic and major elements study. *Appl. Geochem.* **1998**, *13*, 941–952. [[CrossRef](#)]
49. Brass, G. The variation of the marine ⁸⁷Sr/⁸⁶Sr ratio during Phanerozoic time: Interpretation using a flux model. *Geoch. Cosmoch. Acta* **1978**, *40*, 721–730. [[CrossRef](#)]
50. Dotsika, E.; Poutoukis, D.; Kloppmann, W.; Guerrot, C.; Voutsas, D.; Kouimtzis, T.H. The use of O, H, B, Sr and S isotopes for tracing the origin of dissolved boron in groundwater in Central Macedonia, Greece. *Appl. Geochem.* **2010**. [[CrossRef](#)]
51. Negrel, P.; Dupre, B.; Seimbille, F.; Allegre, C.J. Quantitative modelisation of differential erosion between crystalline and sedimentary area of a French basin by isotopic analysis of strontium in river waters. *Chem. Geol.* **1988**, *70*, 13. [[CrossRef](#)]

52. Negrel, P.; Deschamps, P. Natural and anthropogenic budgets of a small watershed in the Massif Central (France): Chemical and strontium isotopic and major elements study. *Aquat. Geochem.* **1997**, *2*, 1–27. [[CrossRef](#)]
53. Institute of Geological and Mineral Exploration of Greece (IGME). *Thebes Sheet*; IGME: Athens, Greece, 1967.
54. Koumantakis, I. *Hydrogeological Conditions of Thebes Basin Athens-Greece*; NTUA: Athens, Greece, 1980.
55. Parks, J.L.; Mc Neill, L.; Frey, M.; Eaton, A.D.; Haghani, A.; Ramirez, L.; Edwards, M. Determination of total chromium in environmental water samples. *Water Res.* **2004**, *38*, 2827–2838. [[CrossRef](#)] [[PubMed](#)]
56. METROHM. *Introduction to Polarography and Voltammetry*; Metrohm: Stockholm, Sweden, 2010.
57. METROHM. *Ion Analysis, Chromium in Waste Water*; Metrohm: Stockholm, Sweden, 2010.
58. Hach. *DR 2800 Spectrophotometer*; Hach: Dusseldorf, Germany, 2007.
59. Trinquier, A.; Elliott, T.; Ulfbeck, D.; Coath, C.; Krot, A.N.; Bizzarro, M. Origin of nucleosynthetic isotope heterogeneity in the solar protoplanetary disk. *Science* **2009**, *324*, 374–376. [[CrossRef](#)] [[PubMed](#)]
60. Horwitz, E.P.; Dietz, M.L.; Fisher, D.E. Separation and preconcentration of strontium from biological, environmental, and nuclear waste samples by extraction chromatography using a crown ether. *Anal. Chem.* **1991**. [[CrossRef](#)]
61. Soulios, G. *General Hydrogeology—Volume 4*; University Studio Press: Thessaloniki, Greece, 2006.



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