Hexavalent chromium and other toxic elements in natural waters in the Thiva – Tanagra – Malakasa Basin, Greece*

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ABSTRACT: Trivalent chromium (Cr(III)) is considered to be essential for the human metabolism, whilst hexavalent (Cr(VI)) is very toxic and soluble in water and can be migrated into the direction of the groundwater. Using the GFAAS and ICP-MS for total chromium, diphenylcarbohydrazide-Cr(VI)-complex colorimetric method for hexavalent chromium, and flame-AAS and ICP-MS for other elements, their concentrations were determined in 63 surface and groundwater samples from the Thiva – Tanagra – Malakasa basin, Eastern Sterea Hellas, Greece.

In that area, which is notorious for the industrial activities during the last 40 years, significant chromium concentrations were determined in the urban water supply of Oropos (up to 80 μg/L Cr(VI)) and Inofyta (up to 53 μg/L Cr(VI)). High concentrations of Cr(VI), ranging from 5 to 33 μg/L, were also found in the groundwater that is used for the urban water supply of the town of Thiva (NW). High As content (up to 34 μg/L As) among with Cr(VI) (up to 40 μg/L) were detected in the urban water supply of Schimatari. In the Asopos River, although total chromium values are up to 13 μg/L, hexavalent chromium less than 5 mg/L and other toxic elements were relatively low, during our research, their values suggest a connection with the industrial activity in the area.

The pollution of groundwater by Cr(VI) in the majority of water wells in the Thiva – Tanagra – Malakasa basin, is related to the widespread industrial activity, the usage of hexavalent chromium in various processes and the discharges of Cr-bearing wastes.
Key-words: *water pollution, hexavalent chromium, toxic elements, Asopos river.*

ΠΕΡΙΛΗΨΗ: Το τρισθενές χρώμιο (Cr(III)) θεωρείται απαραίτητο στον ανθρώπινο μεταβολισμό, ενώ το εξασθενές (Cr(VI)) είναι ιδιαίτερα τοξικό και ευδιάλυτο στο νερό και μπορεί να μεταφέρεται στο υπόγειο και επιφανειακό νερό. Οι συγκεντρώσεις εξασθενούς χρωμίου, ολικού χρωμίου, καθώς και άλλων τοξικών στοιχείων προσδιορίστηκαν σε 63 δείγματα επιφανειακών και υπογείων νερών από τη λεκάνη Θήβας –Τανάγρας–Μαλακάσας της Ανατολικής Στερεάς Ελλάδος. Οι αναλύσεις έγιναν με χρήση GFAAS και ICP-MS για το ολικό χρώμιο, flame-AAS και ICP-MS για τον προσδιορισμό των υπόλοιπων τοξικών στοιχείων και χρωματομετρίας με τη χρήση του συμπλόκου diphenylcarbohydrazide (διφαινυλο-καρβαζίδιο-Cr(VI)) για το εξασθενές χρώμιο. Στην λεκάνη της Θήβας –Τανάγρας–Μαλακάσας, γνωστή για τη βιομηχανική δραστηριότητα τα τελευταία 40 χρόνια, προσδιορίστηκαν σημαντικές συγκεντρώσεις χρωμίου στο νερό του δικτύου υδροδότησης του Ωρωπού (μέχρι 80 μg/L Cr(VI)) και των Οινοφύτων (μέχρι 53 μg/L Cr(VI)). Υψηλές συγκεντρώσεις εξασθενούς χρωμίου, κυμαινόμενες από 5 έως 33 μg/L, προσδιορίστηκαν και στο υπόγειο νερό, το οποίο τροφοδοτεί το δίκτυο υδροδότησης της πόλης των Θηβών (ΒΔ). Υψηλές περιεκτικότητες σε As (μέχρι 34 μg/L As) μαζί με Cr(VI) (μέχρι 40 μg/L) προσδιορίστηκαν στο δίκτυο υδροδότησης του Σχηματαρίου. Στον ποταμό Ασωπό, αν και το ολικό χρώμιο φθάνει τα 13 μg/L, το εξασθενές χρώμιο είναι λιγότερο από 5 mg/L. Γενικά, οι συγκεντρώσεις των τοξικών στοιχείων στον Ασωπό ήταν σχετικά χαμηλές κατά τη διάρκεια της μελέτης μας, αλλά οι τιμές τους υποδηλώνουν την σχέση τους με τη βιομηχανική δραστηριότητα της περιοχής.

Η ρύπανση του υδροφόρου ορίζοντα από Cr(VI), που προσδιορίσθηκε στην πλειονότητα των γεωτρήσεων στην λεκάνη Θήβας–Τανάγρας–Μαλακάσας, σχετίζεται με τη χρήση του εξασθενούς χρωμίου και άλλων τοξικών μετάλλων σε ποικίλες διεργασίες και την απόρριψη χρωμιούχων βιομηχανικών αποβλήτων.
Λέξεις-κλειδιά: *περιβαλλοντική Γεωχημεία, μόλυνση υδροφόρου ορίζοντα, εξασθενές χρώμιο, τοξικά στοιχεία, Ασωπός ποταμός.*

INTRODUCTION

The environmental impact of Cr(VI) is a controversial issue critical to the protection of groundwater resources. The Erin Brokovich movie highlighted the need to understand and protect drinking water sources from contamination by hexavalent chromium [Cr(VI)].

The pollution by Cr(VI) of natural and municipal water in the Thiva – Tanagra – Malakasa basin was identified two years ago. That basin has been notorious till nowadays as "Asopos (River) Valley". During last months Asopos River had been known, from the mass media and the newspapers, for its red water, that was assumed it was due to its hexavalent chromium content. The international attention has been focused on the pollution of the Asopos River by hexavalent chromium, through Friends of the Earth, a U.S. network of environmental groups. Asopos is a river that rises in Viotia and discharges into the South Euboean Gulf, about 60 km away north of Athens. Forty years ago, in 1969, Asopos was proclaimed a "processed industrial waste receiver" (Fig. 1). The river runs through areas that turn out almost 20% of Greece's total industrial production. Today, Asopos' waters receive waste from hundreds of industries,

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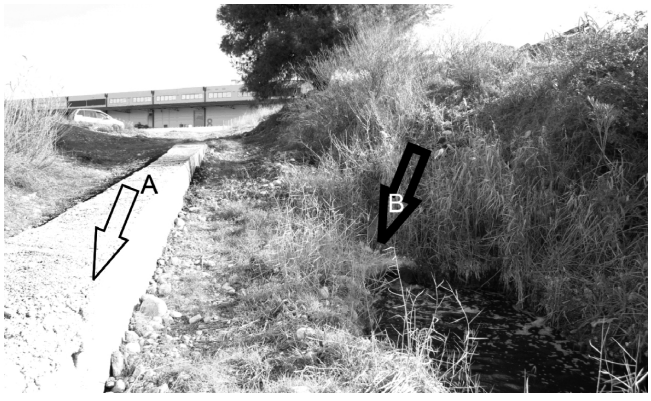

Fig. 1. Both legal (A) and illegal (B) pipes, sometimes some kilometers long, sluiced aqueous wastes from the industrial area into Asopos River.

Fig. 2. A view of Inofyta industrial area neighboring the cultivated area.

situated at a nearby industrial area (Fig. 2).

The higher mobility and toxicity of Cr (VI) compared to Cr(III) for biological systems, due to its strong oxidizing potential has been extensively documented (KOTAS & STASICKA, 2000). Due to toxicity of hexavalent chromium, the California Office of Environmental Health Hazard Assessment recommended a PHG (Public Health Goal) of 2.5 mg/L in drinking water. However, this PHG was withdrawn in 2001 and is currently under review (TSENG & BIELEFELDT, 2002; U.S.E.P.A., 2002). Italy has regulated the Cr(VI) in drinking water at 5 μg/L, (FANTONI *et. al*., 2002; STEPEK, 2002). Most countries including the European Union and Greece have currently regulated the limit of 50 mg/L for total chromium in drinking water (EC, 1998). No maximum acceptable limit has been established yet for Cr(VI) in drinking water, neither in EU nor in Greece.

The objective of the present study is the determination of Cr(VI) and other toxic metal contents in ground and surface water of Thiva – Tanagra – Malakasa basin. These preliminary results and discrimination diagrams are given.

1.1. The environmental chemistry of chromium

Chromium is a polyvalent element, found naturally in the air, soil, water and lithosphere. Oxidation states ranging from 2+ to 6+ are characteristic of chromium.

The water chemistry, environmental mobility and the toxicity of chromium have been widely studied (MERTZ, 1974; BAES & MESMER, 1976; BURRELL, 1977; BARRETT *et al*., 1985; CALDER, 1988; RAI *et. al*., 1989; ALEXANDER *et al*., 1990; FRANQOISE & BOURG, 1991; GAUGLHOFER & BIANCHI, 1991).

In Table 1 the chemical species of Cr in the environment according to its oxidation state, are presented. However, only the oxidation states 3+ and 6+ represent the chromium form existing practically in the environment.

The oxidation states of Cr develop different biological activity. It is assumed that hexavalent chromium is about 100-1000 times more toxic than trivalent chromium (ROBLES-CAMACHO & ARMIENTA, 2000).

In environmental systems, Cr (VI) exists as oxyanions such as chromate (CrO_4^{2-}), bichromate ($HCrO^{4-}$) and dichromate ($Cr_2O_7^{2-}$) and therefore has a high solubility in water and is far more mobile than the trivalent chromium. In contrast, Cr(III) has a low solubility in water and readily precipitates as $Cr(OH)_3(s)$ or mixed Cr-Fe hydroxides at pH values greater than 4 (SCHLAUTMAN & IHNSUP, 2001). The trivalent chromium is immersed into poorly soluble substances that are inaccessible to organisms.

The speciation of chromium in groundwater is governed by pH and Eh. Cr (VI) in groundwater can be reduced to Cr(III) at low pH and under reducing conditions.

The Eh-pH diagram shown in Figure 2 for chromium provides a generalized depiction of the aqueous species stabilities in different redox conditions. Chromium introduced into or existing naturally in the environment, may undergo changes in oxidation state if the redox of the environment is altered or if chromium that is migrating as aqueous species encounters different redox conditions.

Chromium (VI) is strongly oxidizing only under high redox potentials (Fig. 3), and it reacts rapidly with numerous reducing agents found commonly in the environment. EARY & RAI (1988, 1989), have reported that Cr(VI) is reduced in seconds by reaction with ferrous ions and in a matter of hours to days by ferrous-iron-containing oxide and silicate minerals. Similar reactions were reported to occur in low-pH soils that contained small amounts of ferrous iron in clay minerals (RAI *et al*., 1988). Reduction might occurred rapidly even in the presence of dissolved oxygen. Hexavalent chromium is also reduced by organic matter (SCHROEDER & LEE, 1975; BARTLETT & KIMBLE, 1976; JAMES & BARTLETT, 1983) and by $H_2S(g)$ (SMILLIE *et al*., 1981). Ferrous iron and organic matter are ubiquitous in soils and groundwaters. Consequently, Cr(VI) is reduced to Cr(III) in many natural environments.

The oxidation potential for transforming the trivalent chromium into the hexavalent one is high, and the

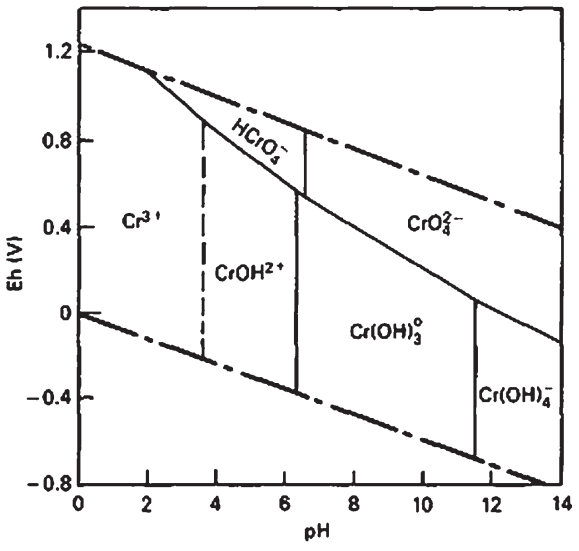

Fig. 3. The pH-Eh diagram of stability of chromium forms, It is valid in chemical equilibrium conditions (RAI *et al*., 1989).

probability of transformation into a higher oxidation form in environmental conditions is reduced. Because the high redox potential of the Cr(VI)/Cr(III), there are few oxidants present in natural systems capable of oxidizing Cr(III) to Cr(VI). The most likely of these oxidants include dissolved oxygen and manganese oxides. However, the oxidation of Cr(III) by dissolved oxygen has been reported to be very slow (SCHROEDER & LEE, 1975; EARY & RAI, 1987). The oxidation of Cr(III) by manganese oxides is reported to be more rapid than by dissolved oxygen. Therefore, manganese oxides are likely to be the more important oxidants for Cr(III) in groundwater systems (RAI *et al*., 1989).

Despite the wide range of chromium in the soil and plants, the hexavalent chromium is rarely found in natural water above the concentration of the natural background, amounting to 1 μg/1. Higher concentrations are indicators of anthropogenic pollution (BRILLY *et al*., 2003).

1.2. The source of the hexavalent chromium

The hexavalent chromium is a chemical that has been used in different industries: in chemical industry for making pigments, in electroplating for coatings, other manufacturing processes such as leather tanning, used by the aircraft and other industries for anodising aluminium, the refractory industry uses chromite for forming bricks and shapes, as it has a high melting point, moderate thermal expansion, and stable crystalline structure.

Steelworks, chromium electroplating, leather tanning and chemical manufacturing produce high chromium wastes.

TABLE 1
Chemical species of Cr in the environment according to its oxidation state

Elemental Cr		It does not occur naturally
Divalent Cr	$CrBr_2$, $CrCl_2$, CrF_2, CrSe, Cr_2Si	It is relatively unstable and is readily oxidized to the trivalent state
Trivalent Cr	CrB, CrB_2, $CrBr_3$, $CrCl_3.6H_2O$, $CrCl_3$, CrF_3, CrN, $KCr(SO_4)_2.12H_2O$	It forms stable compounds and occurs in nature in ores, such as Cr-spinel ($FeCr_2O_4$).
Tetravalent Cr	Cr dioxide CrO_2, Cr tetrafluoride CrF_4	It does not occur naturally but it represents an short-live intermediate that influence the rate of reduction of the Cr(V) form. Chromium (IV) compounds are not common.
Pentavalent Cr	Tetraper–oxochromate CrO_4^{3-}, potassium perchromate	It does not occur naturally and represents an important intermediate that influence the rate of reduction of the Cr(VI) form. Chromium (V) species are derived from the anion $CrO4^{3-}$ and are long-lived enough to be observed directly. However, there are relatively few stable compounds containing Cr(V).
Hexavalent Cr	$(NH4)_2CrO_4$, $BaCrO_4$, $CaCrO_4$, K_2CrO_4, $K_2Cr_2O_7$	It is the second most stable oxidation state of Cr. Even though, Cr(VI) rarely occurs naturally, but is produced from anthropogenic sources. It occurs naturally in the rare mineral crocoite ($PbCrO_4$)

Source: NIEBOER and JUSYS (1988); SYRACUSE RESEARCH CORPORATION (1993); KATZ and SALEM (1994).

1.3 The hydro-geological characteristics of the Thiva – Tanagra – Malakasa Basin

The Thiva – Tanagra – Malakasa basin (central and north part of the studied area) (Fig. 4), is located at the southern part of the Eastern Sterea Hellas. At the south there are the Pastra and Parnis mountains and at the north there are some hills dividing the Thiva – Tanagra – Malakasa basin from the Viotikos Kifisos basin. At the east there is the Aerois divide and at the west is the South Evoikos gulf. The drainage of the basin discharges to South Evoikos gulf via Asopos River. The basin is 718 square kilometers in area.

According to I.G.M.E. (1996) the surface drainage coefficient was estimated to 0.19 and the percolation coefficient to 0.25. The estimated average annual discharge is 70.1 hm^3.

In the Thiva – Tanagra – Malakasa basin (central and north part of the studied area) (Fig. 4), there are the wells for the water supply of the municipalities of Oropos, Inofyta, Thiva and Schimatari. Those wells are sited on a thick Neogene formation (up to over 600 m thick), consisted by intercalations of marls, sands, clays and limestones. The aquifer is porous and is consisted of several sub-aquifers, as the clay intercalations are impermeable by the water.

The wells for the urban water supply of those municipalities have a depth between 200-220 m and those which are used for the agriculture in that area, have a depth between 20-300 m.

At the southeast of this basin there are the Mavrosouvala wells (Fig. 4). Those are sited in middle Triassic to middle Lias, limestone formation (up to over 500 m thick) which is the north extension of the thick Parnis Mountain limestone formation. These wells are pumping water from a karstic aquifer. The source of groundwater recharge is the Parnis limestone. The water is being used for the municipal water supply of the city of Athens and some of the surrounding towns and villages in the area.

METHODS AND MATERIALS

2.1 Sampling

The water sampling areas are shown in Figure 4. A total of 63 ground and surface water samples were collected from September to December 2008, (20 groundwater samples from the municipality of Oropos, 3 from the municipality of Inofyta, 3 from the municipality of Schimatari, 15 from the municipality of Thiva, 17 from the Mavrosouvala wells, and 5 surface water samples from Asopos River). The sampling sites of water samples presented in table 2 are shown in Figure 5.

2.2 Field work

Some physical and chemical parameters of the water samples (i.e. pH, Eh, conductivity and TDS) were measured in the field using a portable Consort 561 Multiparameter Analyzer. The samples were collected, divided in two portions and each one was stored in polyethylene containers at 4° C in a portable refrigerator. The second portion of each sample was acidified by addition of concentrated HNO_3 acid and stored at 4° C as well.

2.3 Analytical Methods

Chemical analyses for Cr(VI) were performed by the 1,5-diphenylcarbohydrazide colorimetric method, within 24 hours after sampling, using a HACH DR/4000 spectrophotometer. The estimated detection limit of the method was determined at 4 mg/L.

The analyses of calcium and magnesium were performed by flame AAS (Perkin Elmer 603). The estimated detection limit of the method was determined at 50 mg/L and 20 mg/L respectively.

The analyses of total chromium were performed by GFAAS (Perkin Elmer 1100B). The estimated detection limit of the method was determined at 1 mg/L.

All the above analyses were performed at the Laboratory of Economic Geology and Geochemistry in the Faculty of Geology and Geoenvironment of University of Athens.

The other elements (Al, As, B, Ba, Cu, Fe, K, Li, Mn, Na, Ni, P, S, Se, Si, V and Zn), were analysed, in the acidified portion of the samples, by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS) at the ACME Analytical Laboratories in Canada.

RESULTS

The chemical analyses of representative water samples are presented in Table 2. In the majority of the analyzed water samples, some tens of μg/L of hexavalent chromium were detected.

The water samples were classified into 3 groups according to their origin and chemical composition: The groundwater samples from the municipalities of Oropos, Inofyta, Schimatari and Thiva, the groundwater samples from the Mavrosouvala wells and the surface water samples from Asopos River.

In Table 3 the correlation coefficients between all the chemical compounds and the physical parameters that had been measured, are presented.

Significant hexavalent chromium concentrations were found in the wells used for the urban water supply and the agriculture of Oropos town ranging from 3 up to 80 μg/L Cr(VI).

In the wells used for the urban water supply of Inofyta town the Cr(VI) ranged from 41 up to 53 μg/L.

High concentrations of Cr(VI), ranging from 5 to 33 Cr(VI), were also found in the groundwater that is used for the urban water supply of the town of Thiva (NW).

High As content, up to 34 μg/L, along with high Cr(VI), up to 40 μg/L, were detected in the urban water

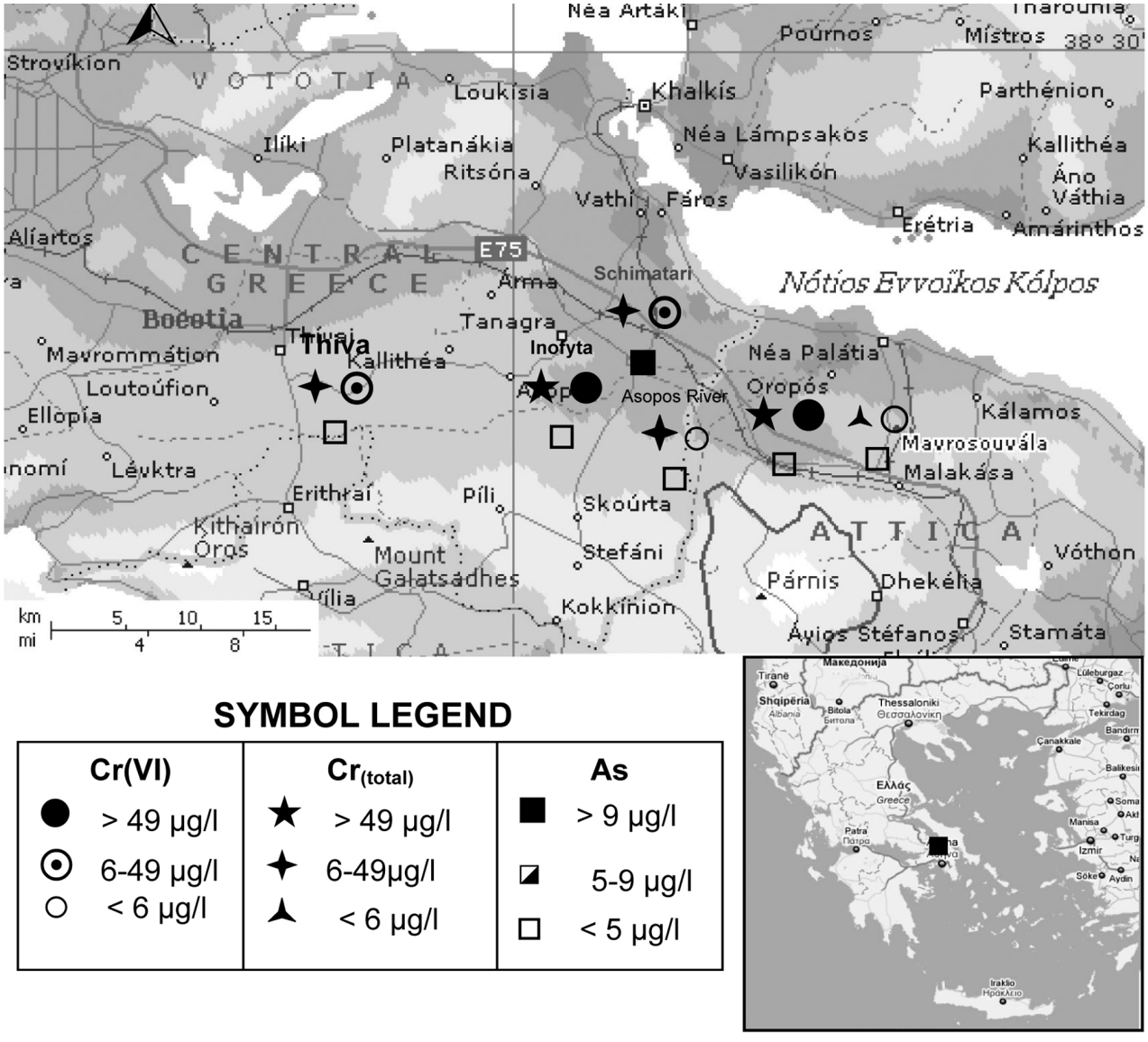

Fig. 4. Location map of the studied area, showing the distribution of the determined toxic element values [Cr(VI), Cr(total), As].

supply of municipality of Schimatari.

In the water samples from the Mavrosouvala wells the hexavalent chromium ranged from "below detection limit" (<4 µg/L) up to 5 µg/L and the total chromium was between "below detection limit" (<1 µg/L) and 6 µg/L.

In the Asopos River, total chromium ranged from 1 to 13 µg/L and hexavalent chromium from 'below detection limit' to 5 mg/L. The other toxic element concentrations were low.

The distribution of the toxic element [Cr(VI), $Cr_{(total)}$ and As] values in the Thiva – Tanagra – Malakasa basin is presented in Fig. 4.

DISCUSSION

Concentrations over the maximum acceptable level for total Cr in drinking water (50 µg/L), according to the EU Directive (EC, 1998), were found in several groundwater samples from Thiva – Tanagra – Malakasa basin.

The contamination of groundwater by Cr(VI) that was found in the majority of groundwater samples in the Thiva – Tanagra – Malakasa basin has been related to the widespread industrial activity for the last 40 years and the usage of hexavalent chromium in various processes.

With the exception of As, the Pb, Ni, Cu, Cd, Hg, Sb and Fe concentrations in ground and surface water samples, that are representative of all water types, were lower than maximum permeable limits for human usage (EC, 1998).

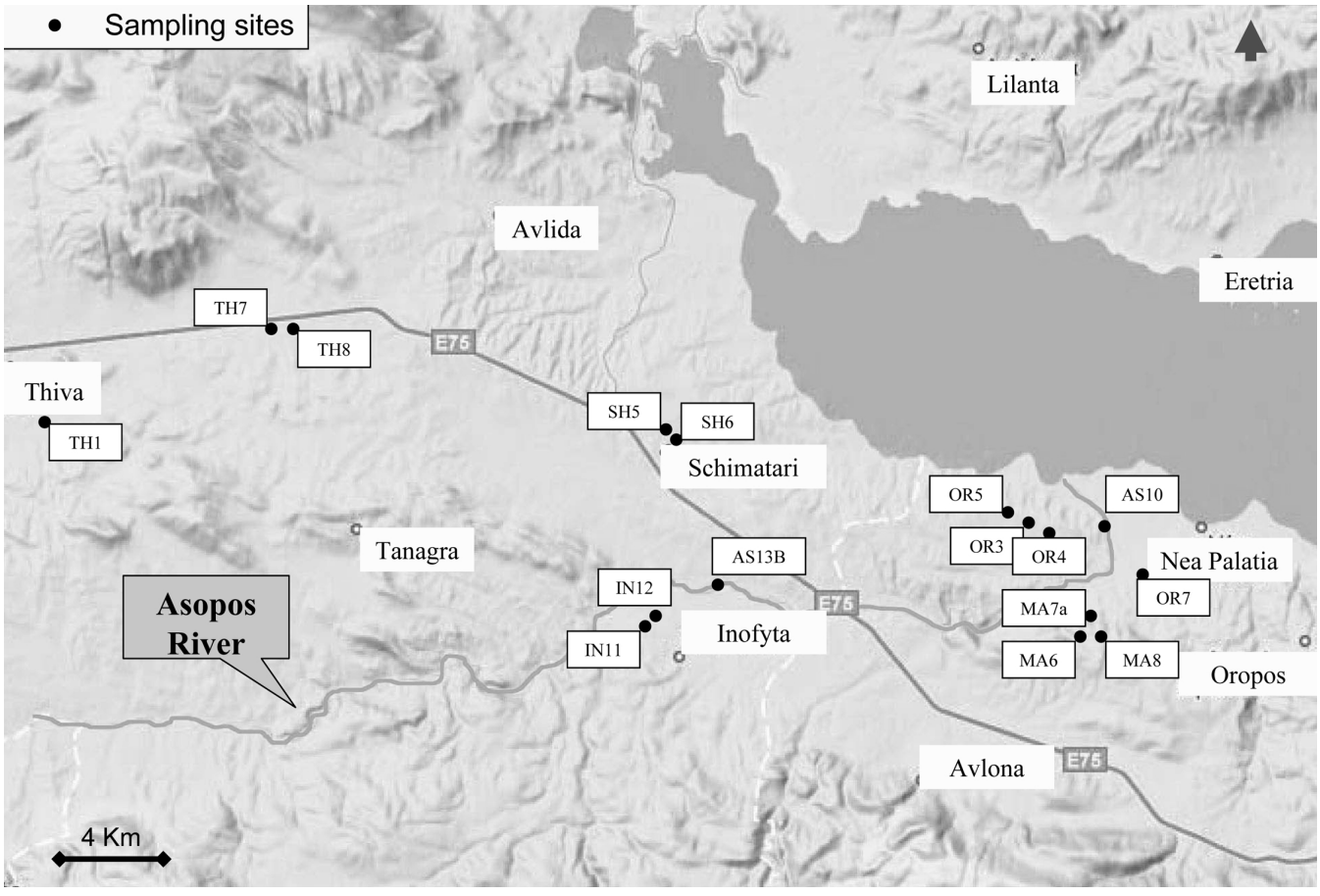

Fig. 5. Location map with the sampling sites of water samples presented in table 2.

High As content along with Cr(VI) was detected in the urban water supply of Schimatari. Its composition makes it unsuitable for human usage as the As content exceeds over 3.4 times the maximum acceptable limit (10 μg/L) for human usage (EC, 1998).

The chemical composition of the water samples from the Mavrosouvala wells presented a good quality for drinking water.

The discrimination between water samples form the Thiva – Tanagra – Malakasa basin and from the Mavrosouvala wells according to the differences of their chemical composition are presented using the Mg–Ca binary diagram (Fig. 6a) and the triangular plots of Fe-Ca-Mg (Fig. 6b) Mg-Ca-Cr(VI) (Fig. 6c) and Fe-Ca-Cr(VI) (Fig. 6d). The water samples from Mavrosouvala wells were characterized by higher Ca/Fe and lower Mg/Ca ratios compared to those coming from the Thiva – Tanagra – Malakasa basin, due probably to the different mineralogy and the chemistry of the rocks that host the aquifers. The marl, the sand and the clay rocks of the Thiva – Tanagra – Malakasa basin are containing minerals with high Fe and Mg compounds such as chlorite [$(Mg, Al, Fe)_{12}(Si, Al)_8O_{20}(OH)_{16}$], micas [$(K, Na, Ca)_2 (Al, Mg, Fe)_{4-6}(Si,Al)_8O_{20}(OH,F)_4$], smectites [$(Na,Ca)_{0.5} A_{l2}(Si_{3.5} Al_{0.5}) O_{10}(OH)_2 \bullet n(H_2O)$], e.t.c. In contrast, the limestone is composed mainly by calcite [$CaCO_3$]. The absence of hexavalent chromium in the samples from the Mavrosouvala wells is attributed to the insignificant industrial activity in the surrounding area of the wells and to the different hydro-geological characteristics of the aquifer: it is hosted in a karstic limestone formation with tremendous water potential and the source of ground-water recharge is the thick Parnis Mountain limestone formation at the southwest of the basin.

In the Asopos River, that crosses the Thiva – Tanagra – Malakasa basin, although total chromium is up to 13 μg/L, hexavalent chromium less than 5 mg/L and the other toxic element concentrations were relatively low during our research, their values suggest their relation with the industrial activity in the area. Since hexavalent chromium is a strong oxidizing agent it may react with organic matter or other reducing agents to form Cr(III), (SCHROEDER & LEE, 1975; BARTLETT & KIMBLE, 1976; JAMES & BARTLETT, 1983). Thus, in the river water, rich in organic content (Fig. 7), Cr(VI) will exhibit a much shorter lifetime (natural bioremediation). It is well known that, bioremediation may be effective for the removal of Cr(VI) from groundwater, as many aerobic and anaerobic

TABLE 2
Chemical and physical analytical data for representative samples from Thiva – Tanagra – Malakasa Basin

Samples		MA7a	MA6	MA8	IN11	IN12	OR3	OR4	OR5
Location		Mavrosouvala wells	Mavrosouvala wells	Mavrosouvala wells	Municipality of Inofyta	Municipality of Inofyta	Municipality of Oropos	Municipality of Oropos	Municipality of Oropos
Type of sample		Groundwater	Groundwater	Groundwater	Groundwater	Groundwater	Groundwater	Groundwater	Groundwater
Cr	µg/L	<1	<1	<1	53	47	79	21	84
Cr(VI)	µg/L	<4	<4	<4	53	41	76	16	80
Ca	µg/L	91840	87600	90860	69610	57660	42580	30340	42650
Mg	µg/L	15350	21040	14300	96660	78530	67840	42750	65820
Fe	µg/L	<10	11	<10	<10	<10	<10	<10	<10
Al	µg/L	<1	1	<1	2	1	<1	<1	<1
As	µg/L	1.5	4	1.7	4	2	3	2	3
B	µg/L	10	18	9	47	39	116	141	114
Ba	µg/L	10.58	29	8.75	62	47	62	36	61
Cu	µg/L	0.3	2	2.4	0.6	0.5	1	1	0.8
K	µg/L	452	690	470	890	790	1380	2200	1310
Li	µg/L	0.9	3	1.1	10	9	25	21	23
Mn	µg/L	<0,05	0.9	<0,05	<0,05	<0,05	0.1	0.1	<0,05
Na	µg/L	9010	25090	8460	41010	33240	112420	102270	111420
Ni	µg/L	<0,2	0.6	<0,2	4	3	0.4	0.9	<0,2
P	µg/L	<20	<20	<20	<20	25	<20	<20	<20
S	mg/L	3	5	3	4	3	15	15	14
Se	µg/L	<0,5	0.5	<0,5	2	1	3	2	4
Si	µg/L	4180	5720	4150	20130	20460	10340	9290	10020
V	µg/L	0.6	0.7	0.6	6	6	3	2	3
Zn	µg/L	1.4	158	3.1	2	4	7	5	3
pH		7.33	7.34	7.43	7.31	7.44	7.43	7.61	7.43
Eh	mV	-15	-17	-22	-14	-22	-22	-33	-21
CND	mS/cm	0.538	0.654	0.536	1.19	0.94	1.21	0.93	1.19
TDS	g/L	0.287	0.347	0.284	0.63	0.50	0.64	0.49	0.63

Samples:		OR7	SH5	SH6	TH1	TH7	TH8	AS13B	AS10
Location		Municipality of Oropos	Municipality of Schimatari	Municipality of Schimatari	Municipality of Thiva	Municipality of Thiva	Municipality of Thiva	Asopos River	Asopos River
Type of sample		Groundwater	Groundwater	Groundwater	Groundwater	Groundwater	Groundwater	Surface water	Surface water
Cr	µg/L	51	22	42	27	37	29	13	5
Cr(VI)	µg/L	44	20	40	25	33	24	5	4
Ca	µg/L	68010	38580	41270	19000	24300	26700	49450	125770
Mg	µg/L	69600	56670	77610	46300	61500	59500	40730	126060
Fe	µg/L	<10	<10	<10	<10	29	<10	34	<10
Al	µg/L	<1	13	<1	<1	<1	1	2	1
As	µg/L	3	28	20	2	34	3	5	15
B	µg/L	59	76	84	136	81	46	62	124
Ba	µg/L	115	53	70	41	60	55	33	76
Cu	µg/L	0.4	0.5	2	1	34	1	10	1.5
K	µg/L	960	1380	1280	2080	1510	830	6650	10550
Li	µg/L	18	51	33	18	58	10	13	17
Mn	µg/L	0.4	<0,05	0.1	0.1	0.1	0.2	0.1	1.2
Na	µg/L	49970	64800	74820	104360	76190	38040	664620	174190
Ni	µg/L	3.6	0.2	1.4	<0,2	2.2	5	9	11
P	µg/L	<20	<20	<20	<20	<20	<20	1311	183
S	mg/L	7	10	9	17	12	3	111	56
Se	µg/L	2	2	3	2	2	1	2	2
Si	µg/L	19680	19410	20970	9260	23030	19840	10430	11700
V	µg/L	4	3	7	2	4	6	9	3
Zn	µg/L	7	2	5	5	58	177	15	0.7
pH		7.26	7.66	7.51	7.78	7.27	7.55	8.16	7.67
Eh	mV	-11	-36	-27	-61	-32	-49	-64	-35
CND	mS/cm	1.02	0.814	0.986	0.513	0.91	0.90	3.27	2.15
TDS	g/L	0.54	0.431	0.524	0.272	0.48	0.48	1.76	1.15

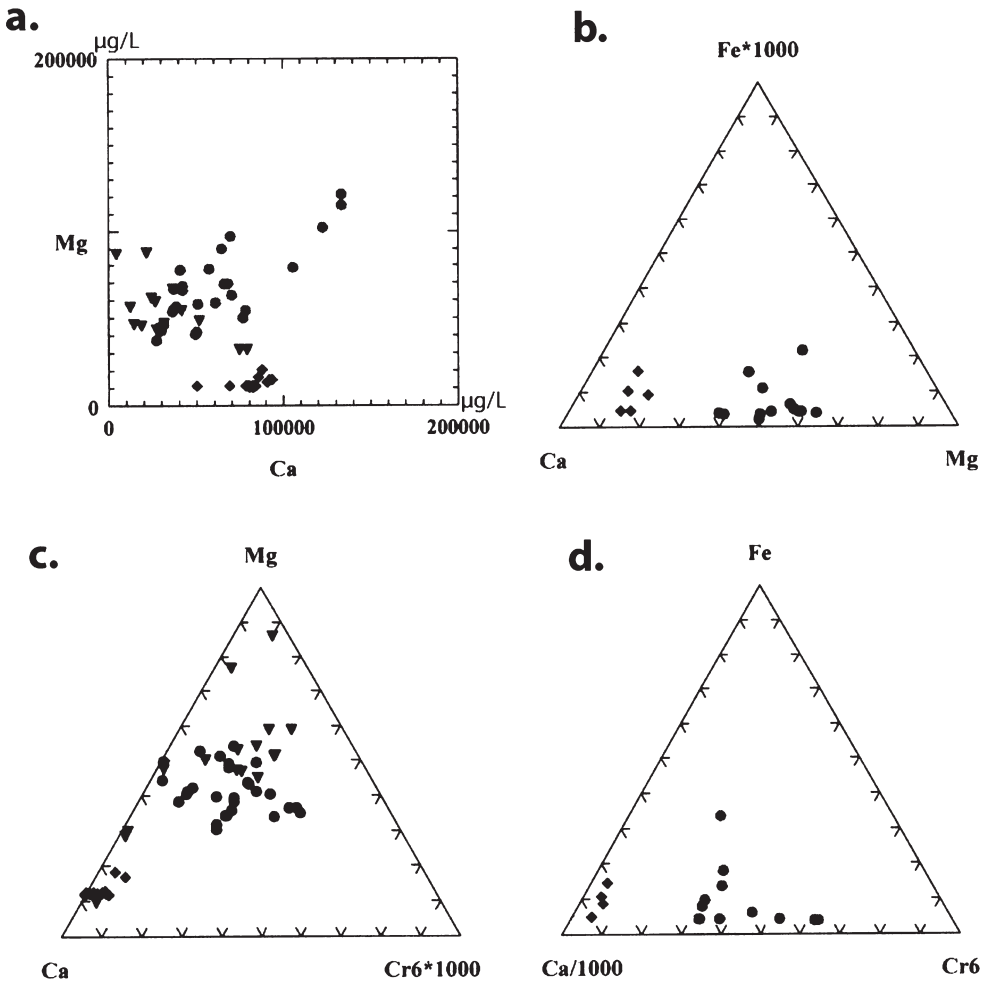

Fig. 6. Discrimination diagrams for the water samples on the basis of their chemical compounds.
(●): samples from Oropos, Inofyta and Schimatari, (▼): samples from Thiva, (♦): samples from Mavrosouvala wells.
a. Mg –Ca binary diagram, b. Fe-Ca-Mg triangular plot, c. Mg-Ca-Cr^{6}+ triangular plot and d. Fe-Ca-Cr^{6}+ triangular plot, for the water samples from Thiva – Tanagra – Malakasa basin.

Fig. 7. Asopos River is rich in plantation and organic matter.

micro-organisms reduce Cr(VI) to Cr(III) (MULLIGAN *et. al*., 2001, VANKAR & BAJPAI, 2008, WEERASINGHE *et. al*., 2008). The lower Cr(VI) contents in the Asopos River, than those recorded in groundwater samples, may suggest that the industrial wastes containing hexavalent chromium are probably being injected directly into the aquifer through percolated waste cesspits or inert water boreholes.

The observed red color of the water of the Asopos River is attributed to the presence of organic pollutants into the river rather than to hexavalent chromium (Fig. 7)

The absence of any significant correlation between Cr(VI) and Mg, Fe or Si is consistent with the anthropogenic origin of the hexavalent chromium in that area (MEGREMI *et al*., 2008).

The ratio of Cr(VI)/Cr(total), ranging between 0.7 to 1 and their excellent correlation (0.99), as it is shown in table 3, suggests that hexavalent chromium is the predominant form of chromium in the natural waters.

Further research is being carried out in order to investigate the trends in time of the Cr(VI) and the other

TABLE 3
Correlation coefficients of the measured chemical and physical parameters for the groundwater samples from Thiva – Tanagra – Malakasa Basin (excepttsose from the Mavrosouvala wells).

	Cr	Cr(VI)	Ca	Mg	Fe	Al	As	B	Ba	Cu	K	Li	Mn	Na	Ni	P	S	Se	Si	V	Zn	pH	Eh	CND	TDS
Cr	1,00																								
Cr(VI)	0,99	1,00																							
Ca	-0,18	-0,15	1,00																						
Mg	-0,02	0,00	0,79	1,00																					
Fe	-0,13	-0,18	-0,05	-0,04	1,00																				
Al	-0,22	-0,21	-0,20	-0,14	-0,14	1,00																			
As	-0,30	-0,31	-0,33	-0,11	0,40	0,53	1,00																		
B	-0,10	-0,09	-0,45	-0,34	-0,16	-0,03	0,06	1,00																	
Ba	-0,01	-0,02	0,73	0,63	0,20	-0,19	-0,14	-0,34	1,00																
Cu	-0,06	-0,06	0,03	-0,27	0,07	-0,10	0,09	-0,27	-0,04	1,00															
K	-0,49	-0,48	0,19	0,16	0,08	-0,05	0,00	0,51	0,23	-0,27	1,00														
Li	-0,17	-0,19	-0,53	-0,33	0,37	0,51	0,93	0,32	-0,26	0,02	0,04	1,00													
Mn	0,07	0,09	0,04	-0,25	-0,16	-0,10	-0,14	-0,22	-0,25	-0,05	-0,30	-0,11	1,00												
Na	-0,15	-0,11	0,16	0,18	-0,18	-0,10	-0,01	0,75	0,12	-0,26	0,66	0,12	-0,21	1,00											
Ni	-0,26	-0,25	0,83	0,88	-0,06	-0,18	-0,16	-0,35	0,64	-0,14	0,21	-0,39	-0,21	0,19	1,00										
P	0,06	0,02	-0,06	0,06	-0,11	-0,03	-0,13	-0,27	-0,23	-0,08	-0,26	-0,20	-0,09	-0,30	0,07	1,00									
S	-0,36	-0,33	0,75	0,67	-0,08	-0,10	-0,10	0,21	0,55	-0,17	0,62	-0,16	-0,19	0,72	0,68	-0,19	1,00								
Se	0,44	0,46	-0,12	0,09	-0,03	-0,06	0,18	0,56	0,15	-0,30	0,21	0,35	-0,12	0,60	-0,20	-0,35	0,28	1,00							
Si	-0,04	-0,08	-0,17	0,14	0,33	0,26	0,56	-0,55	0,04	0,03	-0,47	0,36	-0,16	-0,63	0,13	0,28	-0,45	-0,32	1,00						
V	0,18	0,17	-0,08	0,42	-0,05	0,05	0,24	-0,30	0,03	-0,30	-0,37	0,06	-0,31	-0,28	0,32	0,39	-0,22	-0,06	0,76	1,00					
Zn	0,21	0,23	0,04	-0,14	-0,12	-0,09	-0,14	-0,09	-0,22	-0,05	-0,22	-0,11	0,69	-0,04	-0,20	-0,11	-0,05	0,08	-0,30	-0,30	1,00				
pH	-0,23	-0,26	-0,83	-0,59	0,31	0,30	0,64	0,48	-0,66	-0,05	0,08	0,76	-0,13	-0,02	-0,61	0,04	-0,43	0,10	0,24	0,02	-0,12	1,00			
Eh	0,26	0,28	0,81	0,58	-0,29	-0,31	-0,66	-0,50	0,65	0,02	-0,10	-0,77	0,15	-0,01	0,61	-0,03	0,39	-0,11	-0,21	0,00	0,10	-1,00	1,00		
CND	-0,10	-0,06	0,83	0,85	-0,10	-0,22	-0,23	0,01	0,63	-0,27	0,46	-0,33	-0,18	0,60	0,82	-0,14	0,92	0,28	-0,32	0,01	-0,05	-0,62	0,59	1,00	
TDS	-0,10	-0,06	0,83	0,86	-0,10	-0,22	-0,22	0,01	0,64	-0,26	0,45	-0,33	-0,19	0,60	0,82	-0,14	0,92	0,27	-0,31	0,01	-0,04	-0,61	0,59	1,00	1,00

toxic elements in the area.

In order to reduce the concentration of total chromium below the EC maximum contaminant level (50 μg/L) and eliminate the Cr(VI) compound, remediation strategies should focus on the reduction of Cr(VI) to the insoluble Cr(III), that is relatively stable and non-toxic. Although a more detailed study is in progress, our preliminary results showed that the removal of Cr(VI), using activated carbon filters or scrap iron filings, from both natural water and industrial wastes, are effective, simple and cost-effective methods.

CONCLUSIONS

Concentrations close to, and over the maximum acceptable level of total Cr in drinking water and high Cr(VI) values have been found in Thiva – Tanagra – Malakasa basin.

The ratio of Cr(VI)/Cr(total) (close to 1), and the excellent correlation between Cr(VI) and $Cr_{(total)}$, indicate that hexavalent chromium is the predominant form of dissolved chromium in the water samples.

High As content along with high Cr(VI) were detected in the municipal water of Schimatari.

According to their Fe, Ca, Mg and Cr(VI) content, there is a geochemical discrimination between the groundwater samples from the karstic aquifer of the Mavrosouvala wells, which are free of Cr(VI) and the samples from the clay – sand –marl – limestone porous aquifer in the rest of the basin, which have higher $Cr_{(total)}$ and Cr(VI) values.

The Mg–Ca binary diagram and the triangular plots of Fe-Ca-Mg, Mg-Ca-Cr(VI) and Fe-Ca-Cr(VI) have been successfully used for the discrimination and the identification of the origin (the aquifer) of the water samples from the studied area.

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