

Assessment of groundwater contamination by hexavalent chromium and its remediation at Avlida area, Central Greece*

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ABSTRACT: Trivalent chromium [Cr(III)] is an essential trace element involved in stimulation of enzymes, peripheral action of insulin and lipid metabolism. In contrast, hexavalent chromium [Cr(VI)] is toxic, carcinogenic and teratogenic, since Cr(VI) can enter the body when people breathe air, eat food, or drink water. In the present study, which is part of my M.Sc. Thesis, some analytical data concerning the contamination of the groundwater at the area of Avlida are given, as well as the results of the remediation testing, aiming to the assessment of the contamination in groundwater at that area, and propose ways for the water remediation.

There is a wide variability in Cr concentration in groundwater from domestic, irrigation and municipal wells, ranging from 13 to 160 $\mu\text{g L}^{-1}$ and a heterogeneous distribution, although sampling locations are close to each other spatially. Relatively, high concentrations of Na and B, Li, As and Se in groundwater and a high positive correlation between the latter elements and Na reflect sea water intrusion into the Avlida aquifer. The remediation testing using high-Si and relatively low pH fly ash from Megalopolis confirmed that this material is very efficient for uptaking Cr (VI) from water. Also, the present study demonstrated the ability of EDC-M to directly reduce Cr(VI), suggesting that it may provide a significant contribution for in situ remediation of water and soil contaminated by Cr(VI).

Key words: Groundwater contamination, hexavalent chromium, Avlida, Greece.

ΠΕΡΙΛΗΨΗ: Το τρισθενές χρώμιο [Cr(III)] είναι ένα ιχνοστοιχείο απαραίτητο για την δράση των ενζύμων και τον μεταβολισμό της γλυκόζης και των λιπιδίων. Αντίθετα, το εξασθενές χρώμιο [Cr(VI)] είναι τοξικό, καρκινογόνο και δημιουργεί τερατογενέσεις, διότι το Cr(VI) μπορεί να εισχωρήσει στον ανθρώπινο οργανισμό με τον αέρα, την τροφή ή το νερό. Στην παρούσα μελέτη, η οποία αποτελεί μέρος της Διπλωματικής Εργασίας Ειδίκευσης, δίνονται αρκετά αναλυτικά δεδομένα σχετικά με την αποτίμηση του βαθμού ρύπανσης στον υδροφόρο ορίζοντα της περιοχής της Αυλίδας, καθώς επίσης τα αποτελέσματα από δοκιμές χρησιμοποιώντας ιπταμένη τέφρα και το οργανικό υλικό EDC-M για την απομάκρυνση του Cr(VI) από το νερό, ώστε να προταθούν τρόποι για την αποκατάσταση του υδροφόρου ορίζοντα.

Τα αποτελέσματα έδειξαν ότι υπάρχει μεγάλη διακύμανση στην συγκέντρωση του χρωμίου στο νερό από γεωτρήσεις του Δήμου, ύδρευσης και άρδευσης που κυμαίνονται από 13 έως 160 ppb, και μία ανομοιογενής κατανομή παρ' όλο που μπορεί να βρίσκονται σε γειτονικά σημεία της περιοχής. Οι σχετικά μεγάλες συγκεντρώσεις Na, B, Li, As και Se που προσδιορίστηκαν στον υδροφόρο ορίζοντα της Αυλίδας, και η καλή θετική σχέση μεταξύ των τελευταίων στοιχείων με το νάτριο υποδηλώνουν διεισδυση θαλασσινού νερού στον υδροφόρο ορίζοντα. Οι δοκιμές με ιπτάμενη τέφρα από την Μεγαλόπολη, η οποία χαρακτηρίζεται από σχετικά μεγάλη περιεκτικότητα πυριτίου και χαμηλό pH επιβεβαίωσαν την πολύ αποτελεσματική της δράση στην απομάκρυνση του Cr (VI) από το νερό. Επίσης, οι δοκιμές με το EDC-M έδειξαν ότι επετεύχθη η αναγωγή του Cr(VI) στο νερό, σε μικρό χρονικό διάστημα, και ότι θα μπορούσε να χρησιμοποιηθεί για in situ δοκιμές στο νερό και το έδαφος που έχουν ρυπανθεί από Cr(VI).

Λέξεις κλειδιά: υδροφόρος ορίζοντας, ρύπανση, εξασθενές χρώμιο, αποκατάσταση, Αυλίδα, Ελλάδα.

INTRODUCTION

Heavy metal impact on the ecosystems is dependent on their concentration and speciation. The various chemical and biological changes that chromium undergoes in the environment depend on the conditions that govern its speciation and other activities. The solubility and adsorption by soil and sediments depend on the form of chromium species. Within the ranges of redox potentials and pH commonly found in soils, chromium exists predominantly as oxyanions of Cr(III) and Cr(VI). Chromium is an essential trace element involved in stimulation of enzymes, peripheral action of insulin, lipid metabolism and possibly in the stabilization of nucleic acids (ANDERSON *et al.*, 1983; ANDERSON, 1998; VINCENT, 2000). Trivalent chromium [Cr(III)] occurs naturally in rocks, soil, plants, animals, and volcanic emissions. Chromium is used in

the manufacture of alloys, corrosion inhibitory paints, wood preservatives, mordants and fixatives for dyes and tanning, photographic sensitizers and pigment for rubber and ceramics, and as anticorrosive in cooking systems and boilers (COTMAN *et al.*, 2004). High concentrations of chromium are toxic, carcinogenic and teratogenic. Cr(VI) can enter the body when people breathe air, eat food, or drink water. Cr(VI) is also found in house dust and soil. Certain Cr(VI) compounds have been found to be carcinogenic in humans, in particular into the lung and that it is dependent on high exposures (ASMATULLAH *et al.*, 1998). Hexavalent chromium compounds are emitted into the air, water, and soil by a number of different industrial activities, for instance during metal finishing processes. In the air, chromium compounds are present mainly as fine dust particles that eventually settle over the land and water. The U.S. Environmental Protection

* Αποτίμηση της ρύπανσης του υδροφόρου ορίζοντα στην περιοχή της Αυλίδας, Κεντρική Ελλάδα, από εξασθενές χρώμιο και η αποκατάστασή του

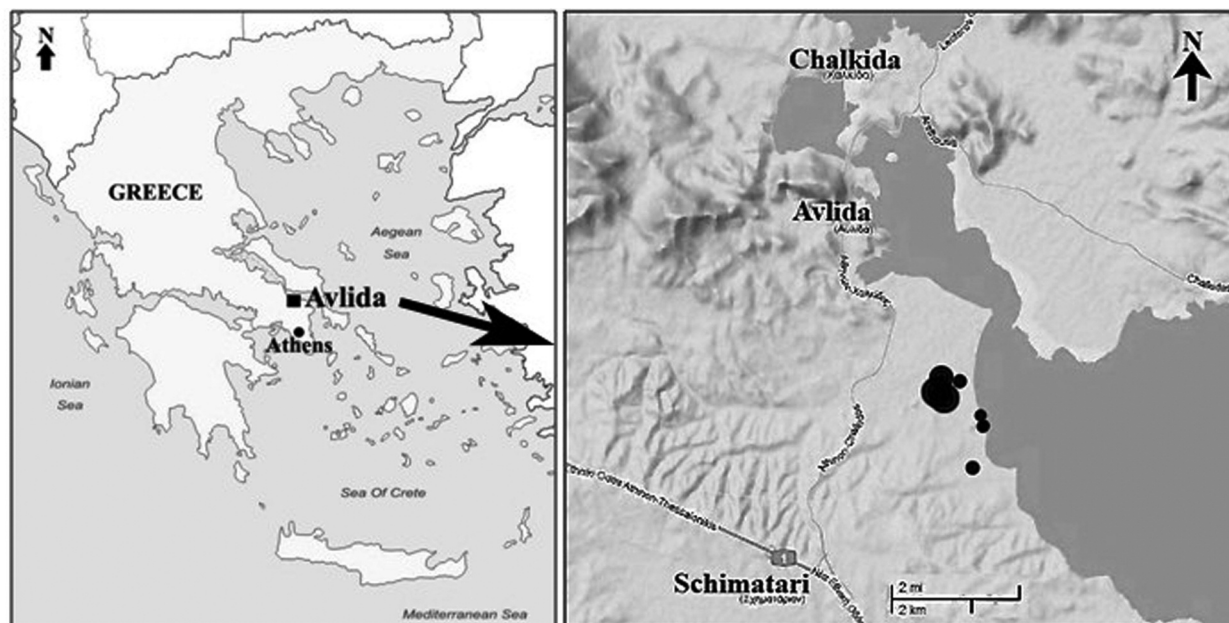


Fig. 1. Sketch map showing the sampling locations.

Agency (USEPA) regulates chromium releases into the environment. Directive 98/83/EC has established a maximum permissible limit of 50 mg / l or ppb for total chromium in drinking water, likewise the World Health Organization.

The crucial environmental problem in the Assopos basin, due to intense industrial activity in the area since 1969 is well known since 2007. The detected hexavalent chromium reaches levels of more than 150 $\mu\text{g/L}$ in drinking water - over 3 times the European Union's 50- $\mu\text{g/L}$ limit for total chromium in a groundwater monitoring well. Research on Cr(VI) in the Assopos basin (covering an area of approximately 700 km^2) and central Euboea is ongoing at the University of Athens, Department of Geology and Geoenvironment (MEGREMI, 2010; VASILATOS *et al.*, 2008, 2010; ECONOMOU-ELIOPOULOS *et al.*, 2010). Also, more efforts are being made by the above research team, either itself, or in cooperation with other researchers for experimenting in some low cost remediation techniques (ITSKOS *et al.*, 2010a, b, KOUKOUZAS *et al.*, 2010).

In the present study some analytical data concerning the contamination of the groundwater at the area of Avlida are presented, as well as the results of remediation testing aiming at the assessment of the groundwater and soil contamination, the determination of Cr-hosts, at the Avlida area, as a contribution to the effective influence of industry versus natural process, and the ways for water remediation.

GEOLOGICAL CHARACTERISTICS OF THE STUDY AREA

The Neogene Assopos basin, is mainly composed of more than 400 meters thick Tertiary and Quaternary sediments, covering an area of approximately 700 km^2 . The uppermost

formations comprise continental sediments consisting of conglomerates with small intercalations of marl, marl limestone, metaclastic schist, sandstone, clays and flysch. The lowest parts of the basin consist of alternations of yellow lake marls and marl limestones hosting thin black lignite horizons (PAPANIKOLAOU *et al.*, 1988; CHATOUPIS & FOUNTOULIS, 2004). This sequence is dominant in the region of Oropos-Sykamino-Chalkoutsis-Avlona-Avlida, although there is variation of the thickness of both conglomerates and the lake to shallow sea fine-grained sediments. Although peridotites, as dismembered parts of ophiolite complexes are rare throughout the Assopos basin the presence of chromite and other Cr-bearing minerals may be present.

The Vathi-Faros aquifer at the area of Avlida is located within continental sediments consisting of conglomerates with small intercalations of marl, marly limestone, metaclastic schist, sandstone, clays and flysch (GIANOULOPOULOS, 2008). The ground water samples were representative of domestic, irrigation and municipal wells (of a depth ranging between 150 and 200 meters) of the Avlida area (Fig. 1).

MATERIALS AND METHODS

Groundwater and soil samples were collected from the Avlida area (Fig. 1) during November 2008. Ground water samples were representative of domestic, irrigation and municipal wells of this area. The physicochemical parameters of the water samples (pH, Eh, CND, TDS) were measured using a portable Consort 561 Multiparameter Analyzer. The hexavalent chromium was determined colorimetrically within 24h following the 1,5-diphenylcarbohydrazide method, using a HACH DR/4000 spectrophotometer (American Public Health Association *et al.*, 1989). The estimated

detection limit of the method was determined at 4 µg L⁻¹. The analyses of total chromium were performed using GFAAS (Perkin Elmer 1100B). Concentrations of Al, B, Ba, Cu, Fe, K, Li, Mn, Na, Ni, P, S, Se, Si, V and Zn, were measured by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS).

The soil samples were disaggregated mechanically and passed through a sieve of 2 mm mesh size. Mineralogical composition of soil was investigated by optical microscopy, X-ray diffraction (Siemens D5005 power diffractometer) and

phase mineral analysis from polished blocks. Microprobe analyses and SEM imaging were carried out at the University of Athens, Department of Geology and Geoenvironment, using a JEOL JSM 5600 scanning electron microscope, equipped with automated energy dispersive analysis system ISIS 300 OXFORD, with the following operating conditions: accelerating voltage 20 KV, beam current 0.5 nA, time of measurement 50 sec and beam diameter 1-2 µm.

For testing the remediation potential by using fly ash, representative samples which had been collected from the elec-

TABLE 1
Concentrations of trace elements (µg/L), and physical parameters of the groundwater samples from the Avlida area.

Element	Cr	Cr(VI)	As	B	Li	Co	Cu	Ni	Fe	Zn
B1 municipal	160	150	4.3	405	3	0.02	4.3	0.6	<10	41
B1D domestic	13	9	4.5	580	9.9	<.02	4.3	2.4	<10	5
B2 municipal	120	108	3.5	340	9	0.17	2.8	2.2	21	136
B3 municipal	54	48	5.4	570	44	0.04	5.8	1	<10	25
B4 municipal	116	110	2.3	220	31	0.04	1.9	2.1	16	100
B5 municipal	25	20	5.5	800	7	0.47	8.9	23	<10	10
B6 irrigation	56	40	5.4	710	1	0.18	9.1	14	<10	<.5
B7 irrigation	13	13	4.1	570	9.7	<.02	7.6	0.9	<10	37
B8 irrigation	52	50	3.8	160	23	0.13	2.2	4.4	<10	<.5
B9 municipal	93	92	2	210	27	0.1	2.5	2.1	42	2
B10 municipal	13	11	3.4	190	10	<.02	1.6	<.2	11	115
SRD	93		1.3	27	7.2	0.03	0.4	4.4	12	<.5
SRA	13		1.2	40	11	<.02	0.7	1.2	<10	<.5
STD WD6	661		286	932	<.1	814	182	1955	729	410

cont.											
Element	Pb	Mn	Cd	S	Sb	Se	Mg	Ca	Na	K	Si
B1	<.1	<.05	<.05	44	<.05	14.7	98	31	379	1.7	9.1
B1D	<.1	<.05	<.05	19	<.05	3.6	21	12	233	1.2	7.6
B2	0.1	20	<.05	35	0.33	14.7	139	42	25	1.3	9
B3	<.1	6.1	<.05	30	<.05	13.9	36	21	471	34	7.6
B4	<.1	0.5	<.05	10	<.05	5.9	103	36	168	0.8	12
B5	0.1	76	<.05	74	<.05	11.6	83	36	700	34	11
B6	<.1	0.12	<.05	83	<.05	10.9	99	42	690	33	12
B7	<.1	0.1	<.05	19	0.06	3.1	22	12	240	1.3	7.1
B8	<.1	<.05	<.05	41	<.05	8.6	186	75	167	2	11
B9	<.1	1.5	<.05	18	<.05	5.8	133	43	133	0.8	10
B10	<.1	0.25	<.05	15	<.05	4	8	22	118	1.1	11
SRD	<.1	0.19	<.05	4	0.08	1.1	37	76	24	0.7	7.7
SRA	<.1	<.05	<.05	6	<.05	1.4	55	76	36	0.8	9.9
STD WD6	851	671	545	<.1	790	1540	<50	<50	<50	<50	0.07

cont.				
Parameter	pH	Eh(mV)	CND(mS/cm)	TDS(g/lt)
B1	7.39	-0.027	2.31	1.23
B1D	7.62	-0.039	1.11	0.59
B2	7.24	-0.018	2.11	1.12
B3	7.57	-0.036	2.32	1.24
B4	7.38	-0.026	1.54	0.82
B5	7.33	-0.022	3.44	1.85
B6	7.31	-0.021	3.61	1.93
B7	7.57	-0.037	1.15	0.61
B8	7.14	-0.012	2.09	1.12
B9	7.2	-0.015	1.56	0.83
B10	7.74	-0.047	0.96	0.52

TABLE 2
Correlation matrix for selected major and trace element data from the groundwater samples of the Avlida area (Table 1).

	Cr	Ni	Cu	Co	As	B	Ba	Ca	K	Li	Mg	Mn	Mo	Na	S	Se	Si	U
Cr	1																	
Ni	-0.26	1.00																
Cu	-0.35	0.69	1.00															
Co	-0.12	0.92	0.49	1.00														
As	-0.38	0.54	0.79	0.38	1.00													
B	-0.37	0.65	0.94	0.47	0.85	1.00												
Ba	0.07	-0.09	-0.09	0.11	0.01	0.01	1.00											
Ca	0.32	0.23	-0.26	0.37	-0.21	-0.41	-0.16	1.00										
K	-0.26	0.71	0.75	0.59	0.78	0.75	0.33	-0.03	1.00									
Li	0.54	0.48	0.36	0.55	0.37	0.35	0.27	0.32	0.62	1.00								
Mg	0.48	0.07	-0.46	0.27	-0.43	-0.60	-0.15	0.94	-0.23	0.30	1.00							
Mn	-0.17	0.80	0.45	0.91	0.39	0.51	0.29	0.06	0.51	0.42	0.00	1.00						
Mo	-0.44	-0.32	-0.06	-0.43	-0.13	0.05	-0.36	-0.67	-0.51	-0.81	-0.62	-0.20	1.00					
Na	-0.10	0.80	0.87	0.65	0.83	0.86	0.05	-0.04	0.90	0.70	-0.21	0.57	-0.41	1.00				
S	-0.02	0.83	0.71	0.74	0.70	0.63	-0.22	0.35	0.73	0.69	0.19	0.52	-0.53	0.88	1.00			
Se	0.56	0.26	0.22	0.39	0.44	0.25	0.33	0.29	0.48	0.90	0.28	0.34	-0.73	0.56	0.57	1.00		
Si	0.12	0.48	-0.12	0.45	-0.18	-0.25	-0.30	0.65	0.15	0.27	0.66	0.20	-0.47	0.15	0.40	0.04	1.00	
U	0.79	-0.13	-0.32	0.14	-0.35	-0.29	0.19	0.22	-0.24	0.54	0.46	0.14	-0.38	-0.09	0.02	0.58	0.05	1.00
Zn	0.30	-0.39	-0.50	-0.22	-0.42	-0.44	0.09	-0.14	-0.40	0.00	0.11	-0.06	0.09	-0.40	-0.41	0.05	0.06	0.55

trostatic precipitators of three different lignite-fired power plants of Greece at Ptolemais, Kardias, and Megalopolis thermal power stations, were used. In order to test their capacity of uptaking the hexavalent chromium from wastewater, an aqueous solution of about 1300 ppb Cr(VI) was prepared. The solutions also contained, 200 ppb of Cr(total), Cu, Ni, Pb, Zn (each) and 20 ppb Cd. The experiment involved filling a series of glass tubes with 50ml of solution, adding 10g of each fly ash type to them and then implementing mechan-

ical stirring at 200 rpm for 24h. At the end of this procedure, the supernatant solution was filtered and subjected to GFAAS, for the determination of the remaining concentration of Cr(total), and spectrophotometer for Cr(VI).

The commercial material EDC-M (Electron Donor Compound-Metals) was used in the present study for testing metal detoxification potential by using microorganisms. This material is manufactured by EcoCycle Corporation of Toyama, Japan, and was kindly donated by Mr. Makis Tsismenakis

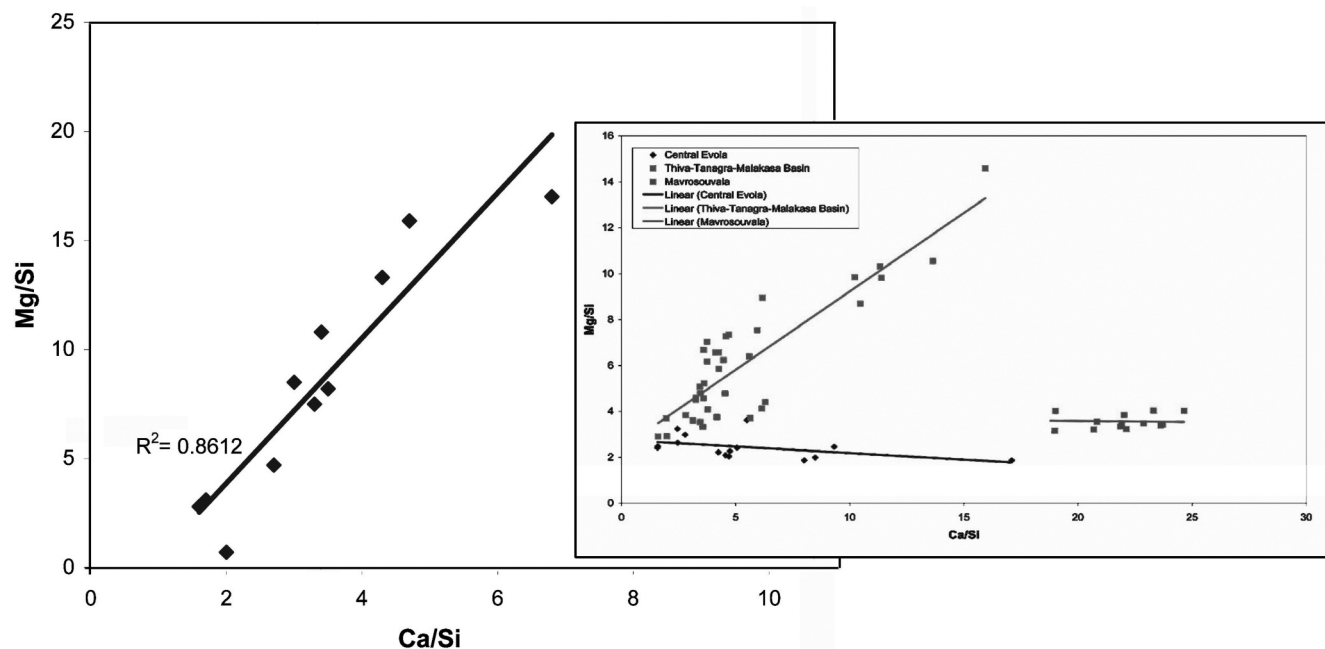


Fig. 2. Variation of Mg/Si versus Ca/Si ratios in groundwater boreholes. Present data from Table 1 and after VASILATOS *et al.*, 2010 and MEGREMI, 2010 (right part).

(Eco Chem – Hellas). It was used for laboratory testing of contaminated water treatment. Three samples of contaminated natural water from the Assopos basin, containing Cr(VI) at concentrations ranging from 112 to 140 ppb were used for this experiment. The EDC-M material was dissolved in water (400 to 1000 g/m³) and was added into glass bottles full with contaminated water. Solutions were maintained at a temperature ranging between 17 and 18 °C and concentration of Cr(VI) as well as water pH were recorded over a period of one month after application.

RESULTS

Chromium concentration in groundwater

There is a wide variation in the Cr(VI) contents in groundwater samples throughout the Avlida area. Although samples

were collected from a similar aquifer horizon, and neighbouring geographical locations the total chromium content varied widely, ranging from 13 to 160 µg L⁻¹ (Table 1). The range of pH (7.2 to 7.6) and Eh (-0.012 to -0.047 mV) measurements indicate alkaline and almost neutral redox conditions in the aquifer. The good positive correlations ($r > 0.6$) between B, Li, Se, and Na (Table 2), coupled with the positive correlation plots of the elements B, Li, Se and As versus Na (Fig. 2), all of which are elevated in the sea water, reflect sea water intrusion into the Avlida aquifer. Also, the lack of any significant correlation between Cr and Mg or Ni concentrations in the water samples (Table 2) coupled with the variation of the Mg/Si versus Ca/Mg ratios (Fig. 5) suggest that the contamination source is related to anthropogenic activity rather than the influence of ophiolitic rocks by natural processes.

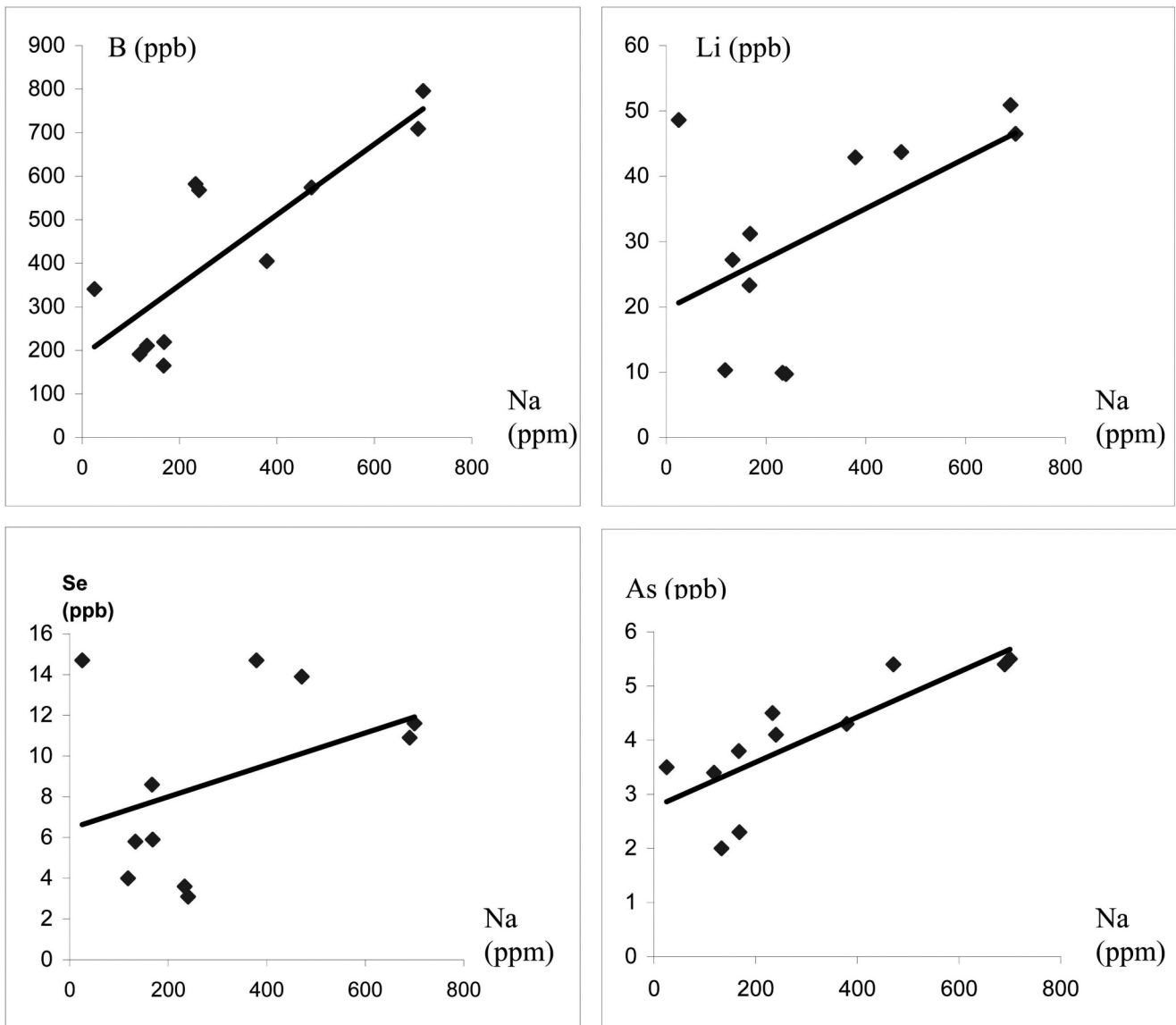


Fig. 3. Binary plots of B, Li, As and Se versus Na concentrations in groundwater boreholes. Data from Table 1.

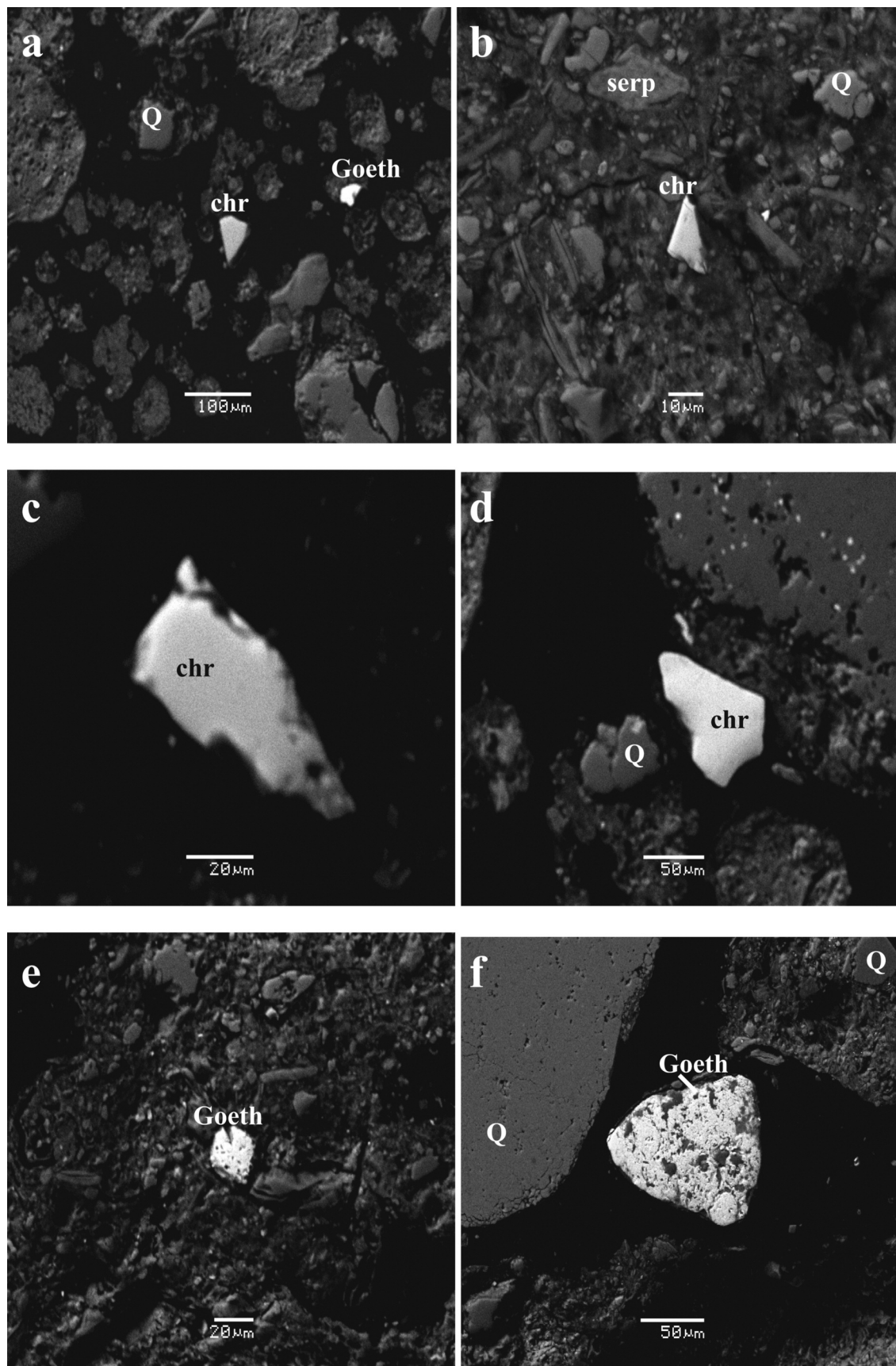


Fig. 4. Backscatter SEM images from soil of the Avlida area containing fragments chromite (a-d), goethite (e-f), quartz and silicates. Mineral compositions are given in the Table 3.

TABLE 3
Representative microprobe analyses (wt%) of oxides and silicates from the Avlida area.

Mineral	chr	chr	Fe-chr	Fe-chr	goeh	goeh	goeh	spt	spt
SiO ₂	n.d.	n.d.	1.02	0.92	2.87	0.61	3.36	43.93	40.2
Cr ₂ O ₃	44.09	48.17	23.96	29.58	1.8	n.d.	1.21	n.d.	n.d.
Al ₂ O ₃	25.59	22.66	3.19	1.88	1.61	n.d.	1.63	0.91	0.88
Fe ₂ O ₃	0.94	0.39	45.69	3.97	80.83	83.12	79.78		
FeO	16.97	18.99	11.41	54.12				3.97	6.49
MgO	12.29	8.28	12.79	7.52	0.36	1.16	n.d.	36.08	35.79
TiO ₂	0.24	n.d.	n.d.	n.d.	0.98	n.d.	0.76	n.d.	n.d.
MnO	n.d.	0.52	2.61	3.06	n.d.	0.61	n.d.	n.d.	n.d.
NiO	n.d.	n.d.	n.d.	n.d.	0.77	n.d.	0.69	0.39	0.31
Total	100.12	99.01	100.67	101.05	89.22	85.5	87.43	85.28	83.67

Abbreviations: *chr* = chromite; *Fe-chr* = iron chromite; *goeh* = goethite; *spt* = serpentine; *n.d.* = below detection limit

Cr-hosting minerals in soils

Given that the composition of water may be affected by the interaction with the hosting rocks the mineralogical composition of soils related to neighbouring rocks was investigated. They are mainly composed by quartz, calcite, serpentine, chlorite, chromite magnetite, ilmenite, and apatite. A portion of the chromium in soils from the Avlida area is hosted in chromite grains or fragments transported as a residual component inherited from the ophiolitic parent rocks, goethite and silicates (Fig. 4; Table 3).

Remediation of water

Fly ash

The removal efficiency of all the fly ash samples that had been used, for total chromium, from the aqueous solution, was better than 99.5 %. The results of uptaking ability for hexavalent and total chromium of the different fly ash samples are presented in Table 4. Hexavalent chromium was efficiently immobilized by the siliceous fly ash of Megalopolis.

Bio-remediation by micro-organisms

The results of the Cr(VI) measurements after injection of EDC-M into the separated water samples, during a period of one month, along with the pH of water, are summarized in the table and process diagram (Fig. 5). Based on the Data Summary a decreasing trend with time is obvious. This trend is consistent with the development of chemically reducing conditions. pH values, for initial groundwater samples ranged from about 7.3 to 7.64, whereas values for post-injection samples ranged from 6.68 to 7.66.

TABLE 4

The removal potential from aqueous media for the total and the hexavalent chromium by different fly ash types.

	Cr(VI) %	Cr(total) %
Ptolemais fly ash	23.73	99.53
Megalopolis fly ash	100.00	99.99
Kardia's fly ash	64.99	99.88

DISCUSSION

The various chemical and biological changes that chromium undergoes in the environment depend on the conditions that govern its speciation and other activities. Remediation strategies are employed in order to minimize the risk of public exposure to chromium contaminated sites. Many potential remediation pathways are known for the chromate reduction, but the dominance of one pathway over another has not been established. Several common remediation strategies include excavation and removal of contaminated soil, pump and treat strategies, and soil solidification and stabilization. Reduction of Cr(VI) in soils depends on the presence of other electron acceptors such as iron, and manganese that can act as electron

Cr(VI)	12/5/2009	14/5/2009	20/5/2009	25/5/2009	9/6/2009
B1	138	90	23	20	0
DHM	142	63	17	17	0
B4	112	102	12	10	0

pH	12/5/2009	14/5/2009	20/5/2009	25/5/2009	9/6/2009
B1	7.64	7.66	6.71	7.17	7.70
DHM	7.30	7.35	7.52	6.68	7.68
B4	7.61	7.42	7.54	6.88	7.65

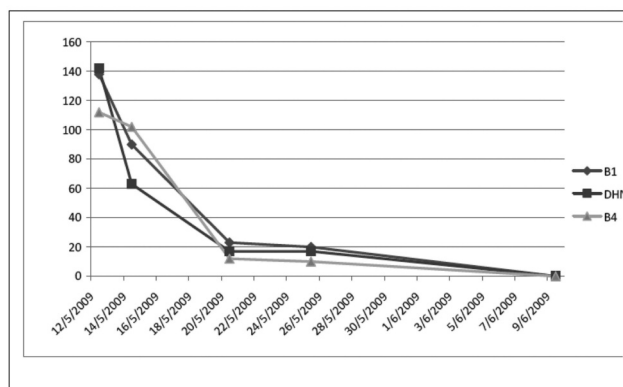


Fig. 5. The results of the Cr(VI) and pH measurements after post-injection of the EDC-M into three separated water samples, and process diagram showing the decreasing trend of the Cr(VI) concentration during the period of one month, along with the pH of water.

sinks and accept electrons from the reactive organic and inorganic electron sources (AISLABIE & LOUTIT, 1986). Traditional techniques for remediation of chromate contaminated water also involve reduction of Cr(VI) to Cr(III) by chemical means (usually with Fe²⁺) or electrochemical means at pH 5, followed by precipitation and filtration or sedimentation (EARY & RAI, 1988). The electrochemical Cr(VI) reduction process uses consumable iron electrodes and electrical current to generate ferrous ions that react with Cr(VI) to Cr(III). This method is often employed in combination with the pump and treats methods. Most of these methods take long time and the cost is very high.

With respect to the remediation strategies of the Cr(VI) the use of zero-valent iron metal [Fe(0)], which is one of the most abundant metals on the earth, as a reducer is of increasing interest:



The reduction rate of Cr(VI) by Fe(0) produces ferric ion (Fe(III)) and Cr(III), which may be removed through the precipitation or co-precipitation in terms of mixed Fe(III) and Cr(III) (JUNYAPOON & WEERAPONG, 2006).

All the fly ash samples from the lignite-fired power plants (Ptolemais, Kardias, and Megalopolis) have shown high uptake efficiency for the removal of total chromium from the aqueous solution. Ptolemais and Kardias fly ashes presented a poor removal potential for hexavalent chromium. Ptolemais and Kardias fly ashes have been characterized as high-Ca ashes and suffers higher pH values (ITSKOS *et al.*, 2010a, b). On the other hand, Megalopolis fly ash (that is a higher-Si fly ash, with lower pH value), proved to be very efficient in uptaking Cr (VI) from water. This is in agreement with the results of ITSKOS *et al.* (2010a, b) and indicates that high-Si ashes, remove Cr (VI) and Cr (total) more efficiently than high-Ca ashes.

Microorganisms have long been recognized for their ability to bring about the transformations of organic and inorganic compounds. The discovery of microorganisms that can reduce metals has led to applications in the bio-remediation which are potentially more cost effective than traditional methods. Although reduction of Cr(VI) to Cr(III) does not remove chromium from soils, it does limit the mobility and toxicity of chromium in the contaminated soils. Furthermore, coupled geochemical and microbiological processes have a potential to dominate the reduction of metals such as Cr(VI). The present study, also demonstrated the ability of EDC-M to directly reduce Cr(VI). The lower post-injection values of pH for groundwater samples compared to the initial values approaching neutrality have been attributed to organic acid fermentation products, as well as biogenic production of carbonic acid. Despite the post-injection decrease in pH, the values generally remained within the pH range considered conducive for microbial activity by adding sodium carbonate, which serves as a buffering agent to maintain pH near initial values (SCHAFFNER, *et al.*, 2010).

CONCLUSIONS

The composition of groundwater combined with the geological, geochemical and experimental data of the present study, lead to the following conclusions:

- There is a wide variability in the Cr-concentration in groundwater from domestic, irrigation and municipal wells, ranging from 13 to 160 ppb.
- Good positive correlations between Na and B, Li, As and Se in groundwater reflect salinization by the intrusion of the sea water into the Avlida aquifer.
- The lack of any significant correlation between Cr and Mg or Ni concentrations in the water samples, coupled with the variation of the Mg/Si versus Ca/Mg ratios suggest that the contamination source at the Avlida area, is related to anthropogenic activity rather than natural processes related to the ophiolitic rocks.
- The present study demonstrated the ability of EDC-M to directly reduce Cr(VI). These results suggest that EDC-M may be applied for *in situ* remediation of water and soil contaminated by Cr(VI).
- The usage of high-Si fly and relatively low pH ash from Megalopolis confirms that that it is very efficient in uptaking Cr (VI) from water.

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