

Available online at www.sciencedirect.com**ScienceDirect**

Procedia Engineering 162 (2016) 545 – 552

**Procedia
Engineering**www.elsevier.com/locate/procedia

International Conference on Efficient & Sustainable Water Systems Management toward Worth Living Development, 2nd EWaS 2016

Groundwater deterioration: the simultaneous effects of intense agricultural activity and heavy metals in soil

Emmanouella Remoundaki^{a,*}, Eleni Vasileiou^b, Angeliki Philippou^a, Maria Perraki^c,
Pavlina Kousi^a, Artin Hatzikioseyan^a and Georgios Stamatis^d

^aLaboratory of Environmental Science and Engineering, School of Mining and Metallurgical Engineering, National Technical University of Athens (NTUA), Heroon Polytechniou 9, 15780 Zografou, Greece

^bLaboratory of Engineering Geology & Hydrogeology, School of Mining and Metallurgical Engineering, National Technical University of Athens (NTUA), Heroon Polytechniou 9, 15780 Zografou, Greece

^cLaboratory of Mineralogy, Petrology and Economic Geology, School of Mining and Metallurgical Engineering, National Technical University of Athens (NTUA), Heroon Polytechniou 9, 15780 Zografou, Greece

^dLaboratory of Mineralogy and Geology, Department of Natural Resources Management & Agricultural Engineering, Agricultural University of Athens (AUA), Iera Odos 75, 11855 Athens, Greece

Abstract

Groundwater deterioration due to agricultural activity is mainly attributed to intense fertilization, groundwater overpumping and seawater intrusion being more pronounced in coastal areas. Irrigation return water is one of the main sources of aquifers enrichment and it is expected to become the main source due to the simultaneous reduction of the amount/frequency of precipitation for many areas in Greece and the Mediterranean. The reduction of groundwater quantity and the simultaneous deterioration due to enhanced concentrations of fertilizer residues, such as nitrates, is well documented. Moreover, heavy metals of both anthropogenic and natural origin may be present in soils where agricultural activity takes place. As a result, groundwater is enriched in soluble species of heavy metals and this enrichment is a serious problem added on top of the above mentioned problems of groundwater deterioration. The relationship between heavy metals mobilization from soils to groundwater and the content of irrigation return water in solutes that influence the generation rates and mobility of heavy metals soluble species are discussed in this work. Data from groundwater samples taken in Psachna, Evia, a region characterized by elevated geogenic Cr in soils and intense agricultural activity, are presented. Two aspects of the problem are discussed: 1. The intense use of ammonium fertilizers: The pH reduction from the nitrification of ammonium fertilizers may be a serious factor influencing Cr(III) mobility. 2. The role of the ionic strength of the water (enhanced concentrations of cations due to seawater intrusion in the aquifer) in the mobility of Cr(III) by mechanisms of cation exchange.

*Corresponding author. Tel.: +30 210 7722271; fax: +30 210 7722173.

E-mail address: remound@metal.ntua.gr

© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the organizing committee of the EWaS2 International Conference on Efficient & Sustainable Water Systems Management toward Worth Living Development

Keywords: groundwater; fertilizers; ammonium; heavy metals; chromium.

1. Introduction

Groundwater deterioration due to agricultural activity is mainly attributed to intense fertilization, groundwater overpumping and seawater intrusion being more pronounced in coastal areas. The recharge of aquifers occurs through atmospheric precipitation and irrigation return water. In many regions, the quantity of water recharging aquifers, originating from atmospheric precipitation, has been significantly reduced and more than half of groundwater quantity can be attributed to irrigation return water [1]. The reduced recharge of groundwater with fresh water from atmospheric precipitation and groundwater overpumping for irrigation are main reasons for the elevated NO_3^- concentrations in groundwater. Thus, the observed deterioration of groundwater due to enhanced concentrations of fertilizer residues, such as nitrates, is well documented for many regions where agriculture is a main activity.

Heavy metals of both anthropogenic and natural origin may be present in soils where agricultural activity takes place. The metals may be present in soils under different insoluble forms, such as metal oxides, hydroxides, carbonates and phosphates, or may be adsorbed in soils by inorganic colloids, such as clays, and other insoluble metal species. The metals may then be mobilized forming soluble species and redistributed between soil and water. Main parameters influencing the formation of soluble species are: soil type, metal speciation, metal concentration, soil pH, solid/solution mass ratio and contact time [2, 3]. In general, greater metal retention and lower solubility occur at high soil pH [4, 5, 6].

Heavy metals mobilization from soils to groundwater appears to be significantly influenced by agricultural activity [1, 7, 8]. Both ammonium- and phosphate-based fertilizers have been shown to increase the mobility of Cr(VI) in ultramafic areas [1, 3, 8]. Field and laboratory simulations data are very recent, appearing in literature during the last decade. The elucidation of the mechanisms responsible for hexavalent chromium mobilization from soils is actually subject of international effort of high priority due to Cr(VI) toxicity.

Studies on the properties of ophiolites and associated metal mobility in different regions in Greece have been recently published [9, 10, 11, 12]. Recent data on ophiolitic aquifers in Vergina (northern Greece) [13], where agriculture is the main anthropogenic activity, have shown that there is a relationship between fertilization and the enhanced Cr(VI) concentration in groundwater.

The present paper focuses on Cr(VI) content in groundwater in Psahna plain in Central Evia, a region characterized by ophiolitic formations and alluvial deposits of elastic ophiolite material, where agriculture is the main activity. The paper reports preliminary results on the investigation of the relationship between Cr mobilization from soils to groundwater and the content of irrigation return water in solutes originating from intense fertilization. Apart from intense fertilization, seawater intrusion in the aquifer, resulting from groundwater overpumping, is evident in the region. The influence of seawater intrusion on Cr mobilization is also discussed.

2. Methodology

2.1. Sampling

Two data sets of groundwater are included in the present study. The first set (samples P1 to P19) corresponds to the November 2012-April 2013 period whereas the second set (samples M1 to M11) corresponds to April 2015. Three sample types are included in the present work: samples from irrigation drills, drills and springs. Two samples were also taken from mining pits. The sampling positions are presented in Table 1 and Figure 1. Three different samples were taken from each sampling position: one sample was used for the determinations of anions and cations; another for the determinations of heavy metals (after filtration and acidification of the sample by nitric acid) and another for

the determinations of hexavalent chromium (after its separation by ion exchange using IC-Alltech). In situ measurements of temperature, pH, electric conductivity, redox potential (with Ag/AgCl, 3M KCl) and dissolved oxygen were also carried out.

2.2. Determinations

The concentrations of Cr(tot) and Cr(VI) were determined by ICP-MS Thermo X series II. The concentrations of Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, NH₄⁺, Ca²⁺, Mg²⁺ were determined by ion chromatography (IC) and/or titrimetric (for Cl⁻ in the first data set) and colorimetric methods (for NO₃⁻, SO₄²⁻, Ca²⁺, Mg²⁺ in the first data set). Ions were determined by a Metrohm 732 IC Separation Center connected to a 732 IC conductivity detector and 753 Suppressor Module for anions determination as described in [14]. Bicarbonate ions were determined by titration (H₂SO₄, 1.6 N).

3. Results

Table 1 presents the overall picture of the determined parameters for both data sets.

Table 1. Sample types and the determined parameters

Sample ID	Sample type	pH	EC μS/cm	DO mg/L	Temp °C	Redox mV	Cr(tot) μg/L	Cr(VI) μg/L	Cl ⁻ mg/L	NO ₃ ⁻ mg/L	SO ₄ ²⁻ mg/L	Na ⁺ mg/L	K ⁺ mg/L	Ca ²⁺ mg/L	Mg ²⁺ mg/L	HCO ₃ ⁻ mg/L	Ions SUM meq/L
P1	Spring	7.7	358	9.94	15.8	205.0	8.00	3.00	20.50	7.70	8.00	10.90	0.80	68.08	12.64	270.84	10.26
P2	Spring	7.9	389	9.24	15.3	180.0	8.00	3.00	34.20	3.70	0.00	16.90	0.50	38.85	32.32	339.16	11.97
P3	Drill	7.6	672	9.56	18.1	188.0	27.00	21.00	29.50	35.40	18.00	21.30	2.10	57.27	61.24	457.50	18.22
P4	Irrig. drill	7.2	744	9.36	17.9	190.0	11.00	10.00	48.00	17.00	20.00	19.70	2.70	101.72	49.09	527.04	20.79
P5	Pit lake	9.0	503	9.84	22.9	180.0	10.00	5.00	17.00	4.30	0.00	11.80	2.30	22.03	43.01	295.24	10.65
P6	Drill	8.0	555	9.87	15.4	198.0	10.00	8.00	31.00	5.20	8.00	11.10	0.60	21.63	57.83	370.88	13.60
P7	Irrig. drill	7.5	1855	9.88	19.0	192.0	146.00	146.00	75.00	387.50	98.00	33.20	1.60	84.50	147.99	484.34	36.39
P8	Irrig. drill	7.5	1875	9.82	17.8	190.0	68.00	66.00	103.00	324.00	315.00	55.40	2.60	82.50	159.89	387.96	40.98
P9	Spring	7.6	1810	9.64	16.3	172.0	36.00	33.00	294.00	55.00	120.00	186.80	10.80	96.12	50.79	481.90	37.02
P10	Irrig. drill	7.6	1599	9.66	17.1	164.0	68.00	63.00	191.00	116.00	130.00	168.80	11.60	67.28	61.72	390.40	32.51
P11	Irrig. drill	7.5	634	9.65	13.2	185.0	32.00	29.00	26.00	34.50	29.00	17.30	7.10	88.11	14.82	257.42	12.69
P12	Irrig. drill	7.4	695	9.63	14.9	183.0	34.00	31.00	26.00	45.30	44.00	22.10	1.00	89.31	21.14	273.28	14.07
P13	Irrig. drill	7.3	1210	9.66	17.3	191.0	85.00	84.00	39.00	103.90	94.00	28.30	1.50	113.34	73.39	478.24	25.63
P14	Irrig. drill	7.4	1687	9.58	16.4	187.0	62.00	62.00	59.00	404.00	210.00	43.40	1.30	145.77	95.74	314.76	34.90
P15	Spring	7.1	881	8.19	16.8	171.0	28.00	26.00	27.80	66.30	71.00	21.60	0.70	121.75	36.94	923.54	28.60
P16	Spring	7.2	886	7.53	17.9	175.0	48.00	40.00	25.80	43.80	47.00	24.20	1.60	96.12	44.71	451.40	19.44
P17	Pit lake	7.7	500	8.92	17.4	186.0	4.00	2.00	48.70	7.40	15.00	17.50	2.40	86.50	7.78	406.26	14.26
P18	Spring	6.8	818	8.25	18.3	185.0	25.00	20.00	22.70	8.50	15.00	21.60	0.70	147.38	15.55	691.74	22.05
P19	Spring	7.6	1098	8.15	18.3	178.0	44.00	37.00	8.00	36.40	12.00	19.90	3.60	51.26	104.98	976.00	29.33
M1	Irrig. drill	7.3	800	9.18	19.3	156.8	24.43	21.64	36.48	55.84	30.77	20.13	6.07	77.72	47.33	270.84	15.87
M2	Irrig. drill	7.3	887	9.28	18.2	165.2	57.09	52.84	39.71	86.45	39.72	23.71	1.10	91.25	55.06	345.26	19.21
M3	Irrig. drill	7.0	948	8.70	18.3	174.2	15.98	12.76	57.27	51.45	30.99	35.15	2.29	129.85	31.55	211.06	17.26
M4	Irrig. drill	7.3	1265	8.79	18.4	173.8	73.52	69.81	79.02	183.83	87.84	38.69	2.82	115.68	85.17	355.02	27.48
M5	Irrig. drill	7.4	981	9.21	18.8	174.3	63.51	63.43	145.20	32.25	15.98	38.54	4.25	67.66	64.49	281.82	20.11
M6	Irrig. drill	7.2	1522	7.47	19.3	193.9	45.45	41.10	110.79	106.98	228.00	51.39	1.73	114.24	120.21	367.22	33.63
M7	Irrig. drill	7.4	1739	9.15	18.6	171.1	48.87	38.91	159.25	176.23	294.00	59.31	1.48	132.09	141.74	325.72	39.83
M8	Irrig. drill	7.2	2370	9.11	18.9	179.7	92.22	88.68	199.72	452.12	268.58	92.50	5.28	197.58	155.97	280.60	50.16
M9	Drill	7.0	1204	7.31	19.2	196.0	34.90	34.27	112.25	46.00	96.72	50.25	1.57	112.41	75.58	353.80	25.87
M10	Drill	7.0	910	8.60	19.4	178.7	6.40	5.00	93.46	26.00	20.17	47.15	2.43	105.53	30.24	297.68	18.26
M11	Drill	7.2	1529	9.95	19.3	187.6	69.48	63.58	72.18	341.64	86.12	34.41	2.35	113.07	123.53	309.88	31.92

Figure 1 presents hydro lithological maps of the sampling region, together with the concentration levels of Cr(VI) (ppb, $\mu\text{g/L}$), electric conductivity EC ($\mu\text{S/cm}$), NO_3^- (mg/L) and Cl^- (mg/L).

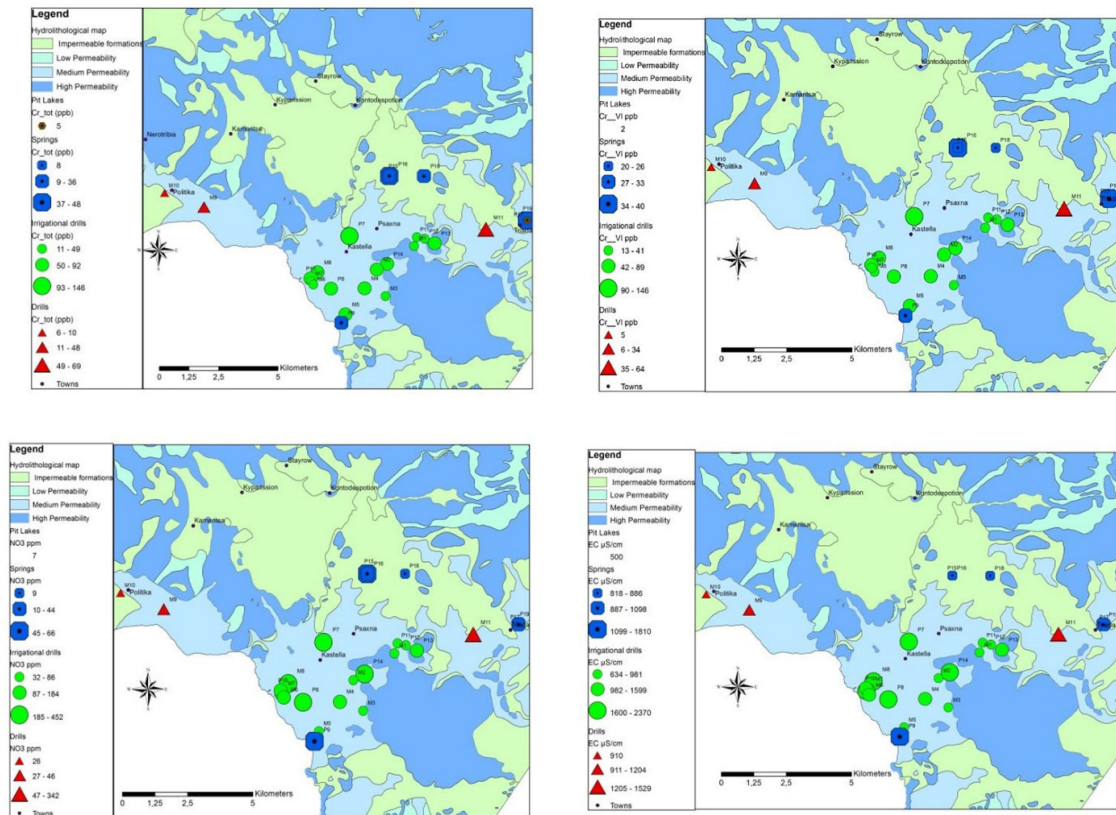


Fig. 1. Hydro lithological maps of the region: the concentrations of Cr(VI) (ppb, $\mu\text{g/L}$), electric conductivity EC ($\mu\text{S/cm}$), NO_3^- (mg/L) and Cl^- (mg/L) are shown for the different sampling points.

From Table 1, it can be seen that total chromium is in the form of hexavalent chromium. The concentrations of hexavalent chromium present high values in groundwater samples. The maxima of hexavalent chromium concentration are observed in groundwater samples from the irrigation drills in Psahna plain (Figure 1). Hexavalent chromium concentrations present lower values for water samples from springs and drills than those obtained for groundwater from irrigation drills. The presence of hexavalent chromium in groundwater in different regions in Greece is mainly attributed to the presence of ophiolitic minerals. The studies on the properties of ophiolites and associated chromium mobility in regions of central Greece point out the problem of groundwater contamination with hexavalent chromium [9, 10, 11]. These studies include regions where contamination of groundwater with hexavalent chromium is also due to industrial activity. There is little data on chromium release from Cr-rich rocks and soils where agricultural activity is almost the only anthropogenic influence. A recent work on the problem in Vergina points out the influence of agriculture in the release of hexavalent chromium in groundwater [13].

From Figure 1, it is clear that the maxima of nitrate concentration were observed in groundwater samples from the irrigation drills in Psahna plain. It is evident that high values of nitrate concentration in groundwater originate from fertilization. In the following paragraphs, the relation between hexavalent chromium and nitrate will be discussed. Electric conductivity (EC) also presents high values in Psahna plain with maxima for the samples corresponding to the coastal zone (Figure 1). Chloride, a tracer of seawater intrusion, shows trends very similar to electric conductivity,

as expected. The results reported in Table 1 and Figure 1, clearly show that groundwater is characterized by a strong ionic content and this is more pronounced for the samples corresponding to the plain and the coastal zone. Thus, groundwater sampled in the plain and the coastal zone is characterized by a heavy ionic matrix and a simultaneous enrichment in nitrate (originating from intense fertilization) and in hexavalent chromium.

Table 2 shows the correlation matrix for the determined parameters. Apart from the high correlations among EC and most of the ionic species as well as the sum of equivalents of anions and cations, which are expected and confirm the quality of the determinations, the highest correlations are obtained between Cr(VI) and NO_3^- , Cr(VI) and Mg^{2+} , Cr(VI) and EC. A significant correlation is also obtained between Cr(VI) and SO_4^{2-} . These results are also shown in Figure 2. The correlation between Cr(VI) and NO_3^- , observed in this work, was also obtained for similar cases for other regions in the world and is attributed to the residues of fertilizers [1, 7]. This correlation is consistent with the leaching of Cr(VI) generated in the vadose zone by irrigation return water containing high levels of NO_3^- .

In addition to providing increased leaching of Cr(VI) from the vadose zone, the solutes contained in irrigation return water may influence Cr(VI) generation rates and mobility. Nitrification of ammonium fertilizers results in soil acidification as it can be seen from reaction (1):



Complete nitrification of a typical application of ammonium fertilizer (approx. 100 mg N per kg soil) results in the input of about 14 mmole H^+ per kg of soil [1]. Incubation experiments of soils have shown increased mobility of heavy metals in soils after the addition of ammonium fertilizers [15, 16]. Furthermore, Cr(III) can be oxidized by Mn oxides before it re-partitions into the solid phase. Manceau and Charlet [17] demonstrated that Cr(III) oxidation occurs after dissolved Cr(III) sorbs onto solid Mn oxides, where it oxidizes and is released back into solution. Fertilizer application may have a much more pronounced effect on Cr mobility and toxicity than on other geogenic trace elements in the soil (e.g. Ni, Co). The exchange of H^+ - Cr^{3+} results in enhanced Cr(VI) generation [1]. The correlation between NO_3^- and SO_4^{2-} observed in this work is due to the fact that ammonium fertilizers applied in soils are in the form of ammonium sulfate justifying the correlation between Cr(VI) and SO_4^{2-} . The correlations between Cr(VI) and EC/Sum of equivalents of ions and, mainly, between Cr(VI) and Mg^{2+} are in agreement with the findings of Mills *et al.* [1] after soil incubation laboratory experiments. According to Mills *et al.* [1], cationic constituents in irrigation return water may accelerate Cr(VI) production. A possible mechanism of increased Cr(VI) production may be the exchange of cations, such as Mg^{2+} and Ca^{2+} , for sorbed Cr(III) and the subsequent oxidation of Cr(III) by Mn oxides present in soil. We should point out here that, it is clear from our results that groundwater is enriched with cations originating from seawater intrusion.

Table 2. Correlation matrix of the determined parameters

	pH	EC μS/cm	DO mg/L	Redox mV	Cr(tot) μg/L	Cr(VI) μg/L	Cl ⁻ mg/L	NO_3^- mg/L	SO_4^{2-} mg/L	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	HCO_3^- mg/L
EC (μS/cm)	-0.30													
DO (mg/L)	0.49	0.02												
Redox (mV)	0.09	-0.10	0.10											
Cr(tot) (μg/L)	-0.20	0.76	0.16	-0.03										
Cr(VI) (μg/L)	-0.21	0.74	0.17	-0.01	0.99									
Cl ⁻ (mg/L)	-0.13	0.71	0.05	-0.25	0.32	0.32								
NO_3^- (mg/L)	-0.18	0.82	0.25	0.07	0.77	0.77	0.33							
SO_4^{2-} (mg/L)	-0.20	0.85	-0.01	0.01	0.51	0.50	0.57	0.72						
Na^+ (mg/L)	-0.09	0.64	0.09	-0.33	0.27	0.27	0.91	0.24	0.46					
K^+ (mg/L)	0.05	0.34	0.20	-0.46	0.13	0.13	0.65	0.03	0.13	0.79				
Ca^{2+} (mg/L)	-0.73	0.57	-0.31	-0.07	0.33	0.33	0.32	0.52	0.53	0.22	-0.03			
Mg^{2+} (mg/L)	-0.09	0.84	0.05	0.09	0.73	0.72	0.40	0.81	0.79	0.24	0.01	0.30		
HCO_3^- (mg/L)	-0.15	-0.01	-0.35	-0.05	0.02	0.02	-0.19	-0.15	-0.13	-0.06	-0.08	-0.02	0.02	
SUM (meq/L)	-0.32	0.97	-0.06	-0.08	0.69	0.68	0.66	0.78	0.86	0.59	0.26	0.59	0.84	0.19

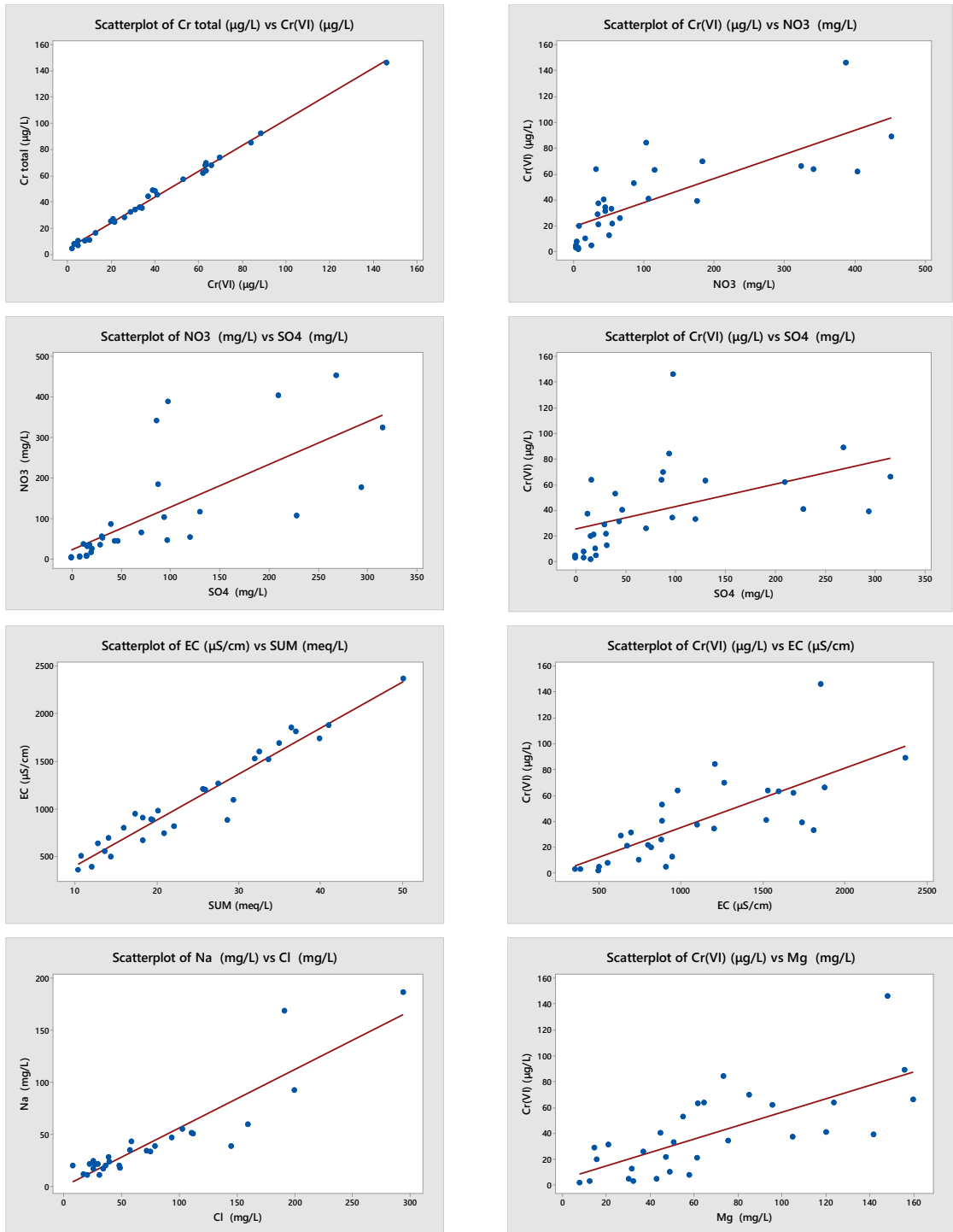


Fig. 2. Scatter plots

The results presented in this work provide evidence that agriculture significantly contributes in the enhancement of Cr mobility and toxicity by direct and indirect processes. Direct processes are associated with intense fertilization. The present work focused on the role of ammonium fertilizers. The role of phosphate fertilizers was also investigated in other studies [8] but it is not possible to be discussed in the present paper due to space limitations. The indirect process appears to be seawater intrusion in the aquifer due to overpumping of groundwater for irrigation. This process results in a significant enrichment of groundwater with cations among which magnesium appears to play an important role in Cr(VI) generation.

4. Conclusions

In Central Evia, in the region of Psahna, groundwater quality is significantly affected by agriculture which is a main anthropogenic activity in the region. The presence of Cr in groundwater, originating from the weathering of ultramafic rocks, in concentrations much higher than the limit of 50 µg/L (for total Cr) and in the form of Cr(VI) is a serious problem added on top of the usual problems of groundwater deterioration due to agriculture: Fertilizer residues, such as nitrates, in groundwater (and, as a consequence, in irrigation water and irrigation return water) are present in high concentrations. Moreover, groundwater is characterized by a heavy ionic matrix due to seawater intrusion originating from groundwater overpumping.

The results presented confirm and support the findings of previous works and the proposal of a major mechanism of increased Cr(VI) production: pH reduction due to nitrification of ammonium provides H⁺ which favor the release of sorbed Cr(III) and the subsequent oxidation of Cr(III) by Mn oxides. Dissolved Cr(III) sorbs onto solid Mn oxides, where it oxidizes and is released back into solution. Moreover, cationic constituents, such as Mg²⁺ and Ca²⁺, in groundwater (and, as a consequence, in irrigation water and irrigation return water) may accelerate Cr(VI) generation rates.

Future work should focus on further elucidation of the underlying mechanisms. The implementation of remediation processes seem to be of priority in order to avoid related dangers for public health.

References

- [1] C.T. Mills, J.M. Morrison, M.B. Goldhaber, K.J. Ellefsen, Chromium(VI) generation in vadose zone soils and alluvial sediments of the southwestern Sacramento Valley, California: A potential source of geogenic Cr(VI) to groundwater, *Appl Geochem*. 26 (2011) 1488–1501.
- [2] D.B. Kent, R.H. Abrams, J.A. Davis, J.A. Coston, D.R. Le Blanc, Modeling the influence of variable pH on the transport of zinc in a contaminated aquifer using semiempirical surface complexation models, *Water Resour Res*. 36 (2000) 3411–3425.
- [3] H.B. Bradl, Adsorption of heavy metal ions on soils and soils constituents, *J Colloid Interf Sci*. 277 (2004) 1–18.
- [4] E. Semu, B.R. Singh, A.R. Selmer-Olsen, Adsorption of mercury compounds by tropical soils, *Water Air Soil Poll.* 27 (1986) 19–27.
- [5] N.J. Barrow, V.C. Cox, The effects of pH and chloride concentration on mercury sorption. II. By a soil, *J Soil Sci*. 43 (1992) 305–312.
- [6] Y. Yin, H.E. Allen, Y. Li, C.P. Huang, P.F. Sanders, Adsorption of Mercury(II) by Soil: Effects of pH, Chloride and Organic Matter, *J Environ Qual*. 25 (1996) 837–844.
- [7] J.A. Izbicki, J.W. Ball, T.D. Bullen, S.J. Sutley, Chromium, chromium isotopes and detected trace elements, western Mojave desert, USA, *Appl Geochem*. 23 (2008) 1325–1352.
- [8] T. Becquer, C. Quantin, M. Sicot, J.P. Boudot, Chromium availability in ultramafic soils from New Caledonia. *Sci Total Environ*. 301 (2003) 251–261.
- [9] I. Megremi, Distribution and bioavailability of Cr in central Euboea, Greece, *Cent Eur J Geosci*. 2 (2010) 103–123.
- [10] D.G. Eliopoulos, M. Economou-Eliopoulos, A. Apostolikas, J.P. Golightly, Geo-chemical features of nickel-laterite deposits from the Balkan Peninsula and Gordes, Turkey: the genetic and environmental significance of arsenic, *Ore Geol Rev*. 48 (2012) 413–427.
- [11] E. Kelepertzis, E. Galanos, I. Mitsis, Origin, mineral speciation and geochemical baseline mapping of Ni and Cr in agricultural topsoils of Thiva Valley (central Greece), *J Geochem Explor*. 125 (2013) 56–68.
- [12] I. Panagiotakis, D. Dermatas, C. Vatsaris, M. Chrysochoou, N. Papassiopi, A. Xenidis, A. Vaxevanidou, Forensic investigation of a Cr(VI) groundwater plume in Thiva, Greece, *J Hazard Mater*. 281 (2015) 27–34.
- [13] D. Dermatas, T. Mpouras, M. Chrysochoou, I. Panagiotakis, C. Vatsaris, N. Linardos, E. Theologou, N. Boboti, A. Xenidis, N. Papassiopi, L. Sakellariou, Origin and concentration profile of chromium in a Greek aquifer, *J Hazard Mater*. 281 (2015) 35–46.
- [14] E. Remoundaki, P. Kassomenos, E. Mantas, N. Mihalopoulos, M. Tsezos, Composition and Mass Closure of PM_{2.5} in Urban Environment (Athens, Greece), *Aerosol Air Qual. Res*. 13 (2013) 72–82.
- [15] C.D. Tsadilas, N.A. Karaivazoglou, N.C. Tsotsolis, S. Stamatiadis, V. Samaras, Cadmium uptake by tobacco as affected by liming, N form, and year of cultivation, *Environ Pollut*. 134 (2005) 239–246.
- [16] J. Liu, C.Q. Duan, Y.N. Zhu, X.H. Zhang, C.X. Wang, Effect of chemical fertilizers on the fractionation of Cu, Cr and Ni in contaminated soil,

Environ Geol. 52 (2007) 1601–1606.

- [17] A. Manceau and L. Charlet, X-Ray absorption spectroscopic study of the sorption of Cr(III) at the oxide-water interface, I. Molecular mechanism of Cr(III) oxidation on Mn oxides, *J Colloid Interf Sci.* 2 (1992) 425–442.