

## Application of Some Statistical Procedures on Heavy Metal Status in Agricultural Land Around Aluminum Industrial Compound

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**Abstract:** {Based on the specific ecological condition in Markazi province, agriculture is one of the most important crafts, which is in the third priority of the industry, has particular place in province. In late decade with development of technology, global consumption of chemical ingredients especially in progressing countries has considerable growth. In such a way from 1940s to early 1980s production of different chemical industrial ingredients becomes 340 folded and million tons of materials that weren't in existence all at once release in the environment} Please transfer this part to the introduction. This study we attempt to identify the concentration of heavy elements around the soil of Iralko complex Markazi province with element resource, bioavailability and intense of pollutant chemically analyzed. The screen 3 software was used and modeling the contamination of air was done and at the end the places under contamination were distinguished. Elements in anthropogenic portions didn't have any significant relation, that this matter expresses different manners in sulfides,organo-metalic,loosely bonded ions and resultant of this portions which is known as anthropogenic porions that is exposed to changes in mentioned grafts. Bioavailability also just mark the existence of elements for absorbance (but this is the plant that decide to absorb or not???). According to the rate of the concentration of elements in bioavailability portions, Sn allocates the maximum concentration to itself.In this way considerable effect of metal contamination in soils of Iralko factory wasn't observed that index of Ipoll confirmed it. PLEASE, REWRITE THE ABSTRACT AGAIN TO BE MORE INFORMATIVE AND CLEAR, ALSO AVOID TO MENTION THE UNNESSARY PARTS IN THIS ABSTRACT).

**Key words:** Heavy metals • Iralko • Soil • Ipoll

### INTRODUCTION

The accumulation of heavy metals in agricultural soils is of increasing concern due to the food safety issues and potential health risks as well as its detrimental effects on soil ecosystems. These metals have peculiar characteristics including that [1] they do not decay with time [2]. They can be necessary or beneficial to plants at certain levels but can be toxic when exceeding specific thresholds, [3] they are always present at a background level of non-anthropogenic origin, their input in soils being related to weathering of parent rocks and

pedogenesis and [4] they often occur as cations which strongly interact with the soil matrix, [consequently, heavy metals in soils can become mobile as a result of changing environmental conditions THIS IS NOT TRUE}.. Sources of these elements in soils mainly include natural occurrence derived from parent materials and human activities. Anthropogenic inputs are associated with industrialization and agricultural activities deposition, such as atmospheric deposition, waste disposal, waste incineration, urban effluent, traffic emissions, fertilizer application and long-term application of wastewater in agricultural land [3, 5]. Apart from the source of heavy

metals, the physicochemical properties of soil also affect the concentration of heavy metals in soils. Organic matter and pH are the most important parameters controlling the accumulation and the availability of heavy metals in soil environment [6]. It is necessary then to evaluate the relationship among these parameters and heavy metal accumulation in soil.

The Knowledge of the heavy metal accumulation in soil, the origin of these metals and their possible interactions with soil properties are priority objectives in environmental monitoring. Statistical analysis procedures, as powerful tools, can provide such knowledge and assist the interpretation of environmental data [7-9]. In recent times, the statistical methods (univariate or multivariate) have been applied widely to investigate heavy metal concentration, accumulation and distribution in soils. This is documented by a large number of reported studies which apply statistical methods to heavy metal accumulation in soils, e.g. Modak and others (1992), Arakel and Hangjun (1992), Ratha and others (1993), Chakrapani and Subramanian (1993), Ntekim and others (1993), Henburg and Bruemer (1993) and Cambier (1994) studied the behavior and distribution of heavy metals in soils using multivariate statistical methods [10]. In environmental monitoring and assessment strategies, these methods can be used to predict or estimate the variability of heavy metals and its controlling factor (s) and to highlight the influence of human activities on heavy metal contents of soils [11, 12]. Therefore, statistical analysis of heavy metals in soil can offer an ideal means through which to monitor not only the heavy metal accumulation in soil but also the quality of the overall environment as reflects in soil.

## **MATERIALS AND METHODS**

Company of Aluminum Production of Iran (Iralko) is placed in 5<sup>th</sup> kilometer of Arak. In this Alumina (aluminum Oxide) is carried to the factory and in reduction hall in several stages it is change to aluminum metal and in moulding is changed into ingot and exit from the factory. In this study we use screen3 soft ware product of EPA America to choose the studying region according to the maximum concentration of the issued contaminants from point resource. According to the rate of the issued contaminants from the factory chimney, maximum concentration of Co, Nox and Sox in 500-1500 m distance was observed. The study region at this distance in direction of dominant wind by the angle of 75m from the

chimney was chosen. Soil samples in lands of Arak around Iralko complex all the samples were excavated from 0-25 depth. For this reason one stainless steel tube with entrance diameter about 4m and length of 1m equipped with piston was used to extract soil. To achieve comprehensive information about the contamination the sampling was done on land soil of 11 region and each 2 -3 samples were mixed together. Then their humidity, electric conduction and pH measured in the laboratory. All the samples were dried in 70°C and after isolation about 5 g from particles smaller than 63 micron powdered in agate mortar. HClO<sub>4</sub>, HF, HCl, HNO<sub>3</sub> in sand bath were used to assimilate in 125°C [31-34].

Acid ascetics, hydroxylamine, H<sub>2</sub>O<sub>2</sub> were used to assign the loosely, sulfides and organio-metalic bonded ions respectively. To study the bioavailability we use NaOH and Acid Ascetic. Then heavy elements in soil samples analyzed with Atomic Absorption [35].

Cluster analyses are one of the multi variate analysis that are used in this study to originate statistics of elements by Cluster software [37].

Coefficient of correlation which is one of the approaches of exploring software was used to achieve the similarity coefficient and dendogram. Cluster tree joins the treasure of the same weight with together to make bigger cluster [38]. Then it assigns the similarity of the samples. Finally by using Ipoll index compared with the intensity of the contamination the elements were analyzed (EXPLAIN IN DETAILS).

## **RESULTS**

Entrance parameters to Screen 3 software are followed (Table 1). Results of the entrance parameters are followed (Table 2). To be more accurate in these researches ternery diagram of soil texture (Figure 1) in sampling station were designed and results presented in Table (3).

Biavailability, anthropogenic, lithogenous portions and kind of elements grafting with soil and their average in 11 sampling stations around the Iralko complex is presented in Table (4). Static of these tables show that the average concentration of all the heavy metals compared to the average of earth crust are unstable. It is expected that Al is considered as the contamination index of the factory but according to the results of the chemical separation analysis Al is not present in anthropogenic portions in soils of Iralko so we use this element as an lithogenous index to analyse the dominant relation on elements.

Table 1: Input parameters for modeling software Screen3 Iralko complex air pollution

Unit Name	The old anode baking Manufactory	New anode baking Manufactory
Stack length (m)	60	60
Chimney diameter (m)	5	5
Number of chimney	1	1
Average ambient temperature K°	284	284
So2 (ppm)	0	160.5
NOx (ppm)	21	32
CO (ppm)	1.2	3.79
Exhaust Gas speed (m/s)	16.8	4.1
Gas temperature Output K°	343	342.6
Air Stability Class	4	4
Pollutant (g/s) So2	0	0.035
Pollutant (g/s)nox	0.003	0.005
Pollutant (g/s)CO	0.0025	0.170

Table 2: Result analysis from the software Screen3

	Min distance (m) 585	Max distance (m) 1115
Max concentration Nox Anode baking old	0.003	
Max concentration Nox New anode baking		142
Max concentration Co Anode baking old	0.0219	
Max concentratin Co New anode baking		0.4828
Max concentration Sox New anode baking	0.099	

Table 3: Result analysis 11 soil samples in the study area

Sample Profile Description	Place Name	Depth cm	Saturation S. P.	Guidance Electrical ECX10 <sup>3</sup>	pH	Organic carbon%	CO <sup>-2</sup> 3	C.E.C Meq/100 Soil
Region 1	Iralko Vicinity	25	30.8	3.5	7.5	0.34	0.0	6.0
Region 2	Iralko Vicinity	25	31.8	3.2	7.5	0.38	0.0	14.0
Region 3	Iralko Vicinity	25	31.9	3.8	7.5	0.57	0.0	13.0
Region 4	Iralko Vicinity	25	32.2	3.3	7.4	0.65	0.0	8.0
Region 5	Iralko Vicinity	25	31.4	1.0	7.7	0.91	1.2	9.0
Region 6	Iralko Vicinity	25	32.6	2.6	7.4	1.5	1.5	12.0
Region 7	Iralko Vicinity	25	26.9	0.96	7.8	0.53	1.2	4.0
Region 8	Iralko Vicinity	25	41.6	0.62	7.8	0.61	0.8	6.0
Region 9	Iralko Vicinity	25	27.8	1.0	7.7	0.57	0.8	6.0
Region 10	Iralko Vicinity	25	31.9	0.59	7.8	0.53	1.2	12.0
Region 11	Iralko Vicinity	25	31.8	0.58	7.8	0.49	0.8	15.0

Table 4: Amounts of heavy metals,bioavailability,anthropogenic, lithogenous portions and the type of link elements in soil and their average soil

Day 11 sample	Cr	Ni	Sn	Zn	Cd	Al
Total concentration Ions	125	85	5	107	0.25	65137
Loosely bonded Ions	2.5	6.7	1.25	6.09	0.06	293.09
Sulfides bonded Ions	1.2	11.5	1.25	1.09	0.06	420
Organo-metalic Ions	1	1	1.25	1.7	0.06	15
Lithogenous Portions	120.6	65.7	1.25	88.8	0.07	4409.1
Anthropogenic Portions	4.8	19.18	3.75	8.09	0.18	728.5
Bioavailability	0.2	0.2	5	0.9	0.05	3
Minimum	71	55	5	79	0.25	43250
Maximum	159	168	5	121	0.25	92500

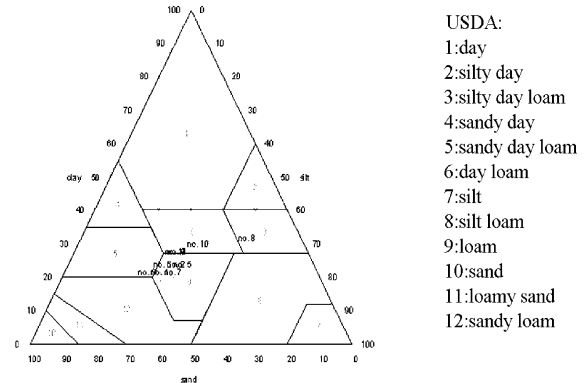
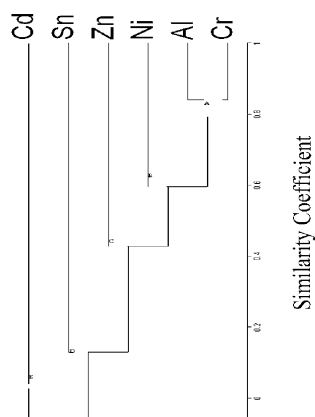
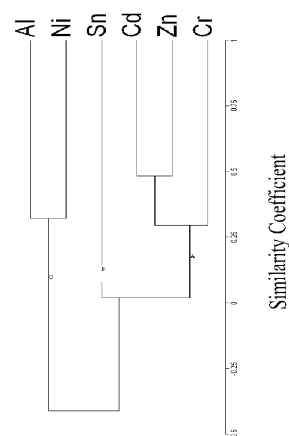


Fig. 1: Ternery diagram showing soil texture

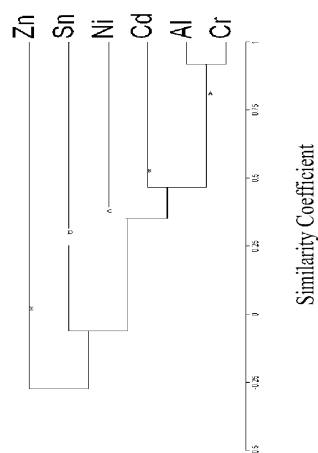
Coefficient correlation of heavy elements was used to static explanation of metals relation and origination of them, then coefficient correlation changed to cluster dendrogram and its name changed into similarity coefficient. Results of the cluster analysis present in chart. Dendrogram of cluster analysis has 5 distinct branches with the name A, B, C, D and E. In branch A, Al and Cr exist and these two elements under similarity coefficient that mentioned above connect each other. So we can say that Cr originate in the lithogeneous sources and Zn, Ni under mostly high similarity coefficient connect to the elements of branch A. {This fact shows that origin of Zn, Ni to some extent is equal with



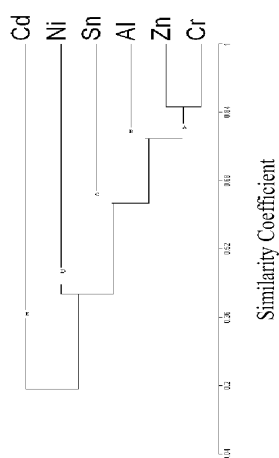
Scheme 1: Dendrogram of cluster analysis for metals in total concentration Ions



Scheme 3: Dendrogram of cluster analysis for metals in anthropogenic portions



Scheme 2: Dendrogram of cluster analysis for metals in bioavailability



Scheme 4: Dendrogram of cluster analysis for metals in lithogenous portions

the originate of the branch A, Cd, Sn exist in branch D and E that under insignificant similarity coefficient connect to branches A, B, C. So we can not state directly. But approximately we state that originate of these elements are from lithogeneous sources (Scheme 1).} REWRITE THIS PARAGRAPH MORE CLEARLY TO BE EASILY UNDERSTOOD.

In dendrogram of bioavailability, 5 branches are presented. In branch A Cr, Al, in branch B, Cd exist that these elements under similarity coefficient of the above connect to Al. This fact shows that these elements. originate from lithogenous sources. Ni, Zn, Sn form C, D and E branches that under the following similarity coefficient connect to A and B branches. So we can approximately state that origin of these elements is not equal with the origination of A and B branches (Scheme2). Elements in anthropogenic portions have no significant relation (Scheme3).

This shows that elements treat differently in loosely, sulfides and organio-metalic portions and their resultant is known as anthropogenic portions which is exposed to changes in the mentioned bonds.

In identifying the dendrogram of the lithogenous portions is emphasized on lithogenous ogination of Zn, Sn and Cr while this relation is not seen for Ni and Cd (scheme 4).

Result and discussion (WHAT DO YOU MEAN BY THIS PART ? Is trhis discussion for the previous part?)

In statistical finding of the heavy elements origination elements like Al and Fe are considered as lithogenous indexes. According to the chemical separation we can come to conclusion that Cr, Ni, Zn originates from lithogenous sources and about other elements we can state directly.

Table 5: The result of research and based formula and the average Ipoll concentration and severity of the shell elements in soils around Iralko

Elements	Cr	Ni	Sn	Zn	Cd	Al
Poll	0.04	0.36	2	0.27	1.83	0.15
Average element in 11 samples(mg/kg)	125	85	5	107	0.25	6.5%
Severity element region	N.P	N.P	L.P	N.P	L.P	N.P
ee&yao1970(mg/kg)	110	89	-	94	0.2	-
Taylor1964(mg/kg)	100	75	2	70	0.2	8.2%
AlinaKabata2007(mg/kg)	100	20	2.5	70	0.1	-

N.P: No pollution L.P: Low pollution

To assign the contamination intensity of the mentioned region we use Ipoll geochemical index which is based on formulation(36):

$$I_{Poll} = \log_2 \left[ \frac{Cn}{Bn} \right]$$

**Ipoll:** geochemical index or intensity of contamination in sediments.

**Cn:** concentration of the heavy and poisonous elements in sediments with less than 63micron in diameter.

**Bn:** concentration of heavy metals in lithogenous portions.

Based on the Ipoll formulation and according to the average concentration of elements in crust and contamination of the Iralko around soils are calculated and compared with each other (Table5).

According to this, contamination intensity is defined 0-5 which 0 and 5 express no and high level of contamination respectively. And other digits express the low, medium, high and severe rate of contamination.

According to this contamination intensity, elements like Cr, Ni, Al and Zn are in range around 0-1 and Sn, Cd in range 1-2. Which are categorized uncontaminated and low contaminated respectively. Based on the above subjects the achieved concentration related to average land crust is variant but cluster analysis shows that origination of elements like Zn, Cr, Ni mainly are from lithogenous sources in the zone and we can not state directly about Cd and Sn. Element concentration in bioavailability portions have allocated the maximum rate of concentration.

## REFERENCES

- McLaughlin, M.J., D.R. Parker and J.M. Clarke, 1999. Metals and micronutrients-food safety issues. Field Crops Res., 60: 143-163.
- Facchinelli, A., E. Sacchi and L. Mallen, 2001. Multivariate statistical and GIS-based soils. Environ. Pollu., 114: 13-324.
- Bilos, C., J.C. Colombo, C.N. Skorupka and P.M.J. Rodriguez, 2001. Sources, distribution and variability of air borne trace metals in La Plata city are, Argentina. Environ. Pollu., 11: 149-158.
- McLaughlin, M.J., R.E. Hammon, R. McLaren, G. Speir and T.W. Rogers, 2000. A bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australian and New Zealand. Aust. J. Soil Res., 38: 1037-1086.
- Koch, M. and W. Rotard, 2001. On the contribution of background sources to the heavy metal content of municipal sewage sludge. Water Sci. Technol., 43: 67-74.
- Nyamangara, J. and J. Mzezewa, 1999. The effects of long-term sewage sludge application on Zn, Cu, Ni and Pb levels in clay loam soil under pasture grass in Zimbabwe. Agri. Ecosys. Environ., 73: 199-204.
- Tuncer, G.T., S.G. Tuncel, G. Tuncel and T.I. Balkas, 1993. Metal pollution in the Golden Horn, Turkey-Contribution of natural and anthropogenic components since 1913. Water Science and Technol., 28: 50-64.
- Sena, M.M., R.T.S. Frighetto, P.J. Valarini, H. Tokeshi and R.J. Poppi, 2002. Discrimination of management effects on soil parameters by using principal component analysis: A multivariate analysis case study. Soil and Tillage Res., 67: 171-181.
- Einax, J.W. and U. Soldt, 1999. Geostatistical and multivariate statistical method for the assessment of polluted soils; Merits and limitations. Chemometrics Intell. Lab., 46: 79-91.
- Salman, S.R. and Y.H. Abu Rukah, 1999. Multivariate and principal component statistical analysis of contamination in urban and agricultural soils from north Jordan. Environmental Geol., 38: 256-270.

11. Kelly, J., I. Thornton and P.R. Simpson, 1996. Urban Geochemistry: A study of the influence of anthropogenic activity on the heavy metal content of soils in traditionally industrial and non-industrial areas of Britain. *Applied Geochemistry*, 11: 363-370.
12. Lin, Y.P., T.P. Teng and T.K. Chang, 2002. Multivariate analysis of soil heavy metal pollution and landscape pattern in Changhua county in Taiwan. *Landscape and Urban Planning*, 62: 19-35.
13. Karbassi, A.R. and R. Amirnezhad, 2004. Geochemistry of heavy metals and sedimentation rate in a bay adjacent to the Caspian Sea. *Int. J. Env. Sci. Tech.*, 1(3): 199-206.
14. Lee, S.V. and A.B. Cundy, 2001. Heavy metal contamination and mixing processes in sediments from the Humber Estuary, Eastern England. *Estuarine Coastal and Shelf Sci.*, 53(5): 619-636.
15. Alina Kabata-Pendias and Arun B. 2007. Mukherjee Trace Elements from Soil to human.
16. Bin Li, Qiuquan Wang, Benli Huang and Shuping Li, 2001. Evaluation of results from a Quasi-Tessier's sequential extraction procedure for heavy metal speciation in soils and sediment by ICP-MS. *Analytical sciences*, Vol. 17 supplement.
17. Boukhalifa, C., 2007. Heavy metals in the water and sediments of Oued Es-Souk, Algeria, a river receiving acid effluents from an abandoned mine. *African J. Aquatic Sci.*, 32(3): 245-249.
18. Brummner, G.W., J. Herth and U. Herms, 1986. Heavy metals species, mobility and availability in soils. *Z. Pflanzenernahr Bodenkd*, 149: 382-398.
19. Brumelis, G., D.H. Brown, O. Nikodemus and D. Tjarve, 1999. The monitoring and risk assessment of Zn deposition around a metal smelter in Latvia. *Environmental Monitoring and Assessment*, 58(2): 201-212.
20. Cortes, O.E.J., L.A.D. Barbosa and A. Kiperstok, 2003. Biological treatment of industrial liquid effluent in copper production industry. *Tecbahia Revista Baiana de Tecnologia*, 18(1): 89-99.
21. Clemente, R., N.M. Dickinson and N.W. Lepp, 2008. Mobility of metals and metalloids in a multi-element contaminated soil 20 years after cessation of the pollution source activity. *Environmental Pollution*. (in press).
22. Devkota, B. and G.H. Schmidt, 2000. Accumulation of heavy metals in food plants and grasshoppers from the Taigetos Mountains, Greece. *Agriculture, Ecosystems and Environment*, 78(1): 85-91.
23. De Vries, W., P.F. Romkens and G. Schutze, 2007. Critical soil concentrations of cadmium, lead and mercury in view of *health effects on humans and animals*. *Reviews of Environmental Contamination and Toxicol.*, 191: 91-130.
24. Freedman, B. and T.C. Hutchinson, 1981. Sources of metal and elemental contaminants of terrestrial environments. In: Lepp NW, editor. *Effect of heavy metal pollution on plants: Metals in the environment*, London and New Jersey: applied Sci., 11: 35-94.
25. Meissner, K., T. Lippert, A. Wokaun and D. Guenther, 2004. Analysis of trace metals in comparison of laser-induced breakdown spectroscopy with LA-ICP-MS" Elsevier, 316-322.
26. Korashy, H.M. and A.O.S. El-Kadi, 2008. Modulation of TCDD-mediated induction of cytochrome P450 1A1 by mercury, lead and copper in human HepG2 cell line. *Toxicology in vitro*, 22(1): 154-158.
27. Lagisz, M. and R. Laskowski, 2008. Evidence for between-generation effects in carabids exposed to heavy metals pollution. *Ecotoxicol.*, 17(1): 59-66.
28. Pandey J. and U. Pandey, 2008. Accumulation of heavy metals in dietary vegetables and cultivated soil horizon in organic farming system in relation to atmospheric deposition in a seasonally dry tropical region of India. *Environmental Monitoring and Assessment*, 1-14.
29. Stimpfl, E., M. Aichner, A. Cassar and C. Thaler, 2006. Andreass O, Matteazzi A. The state of fruit orchard soils in South Tyrol (Italy). *Laimburg J.*, 3(1): 74-134.
30. Albanese, S. and C. Cuneo, 2003. Heavy metals in coastal sediments of the Ligurian sea off Vado Ligure. *J. de Phys.*, IV 107(1): 159-162.
31. Malo, B.A., 1977. Partial extraction of metals from aquatic sediments. *J. Env. Tech.*, 11: 277-282.
32. Gibbs, R.J., 1973. Mechanisms of trace metal transport in rivers. *Sci.*, 180: 71-72.
33. Gupta, K.S. and K.Y. Chen, 1975. Partitioning of trace metals in selective chemical fractions of near shore sediments, *Environ. Lett.*, 10: 129-159.
34. Chester, R. and R.M. Hughes, 1967. A chemical technique for the separation of ferromanganese minerals, carbonate minerals and adsorbed trace elements from Pelagic Sediments, *Chem. Geol.*, 2: 249-262.
35. Karbassi, A.R., 1989. Geochemical and Magnetic Studies of Marine, Estuarine and riverine Sediments. Ph.D. Thesis, Mangalore University, India.

36. Karbassi, A.R. *et al*, 2008. Metal pollution assessment of sediment and water in the Shur river. *J. Environ. monit Assess*, 147: 107-116.
37. Davis, J.C., 1973. *Statistics and Data Analysis in Geology*. Wiley International, New York.
38. Anazawa, K. *et al*. 2004. Heavy Metal Distribution in River Waters and Sediments around a "Fire Fly Village". Shikoku, Japan: Application of Multivariate Analysis. *J. Analytical Sci.*, 20: 79-84.