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# Spatial evaluation of environmental and Geomedical effects of heavy metals in Davijan 1:50000 geology sheet based on univariate analysis

Asal Farhadi<sup>\*</sup>, Mohammad-Reza Jafari

Department of Geology, Islamic Azad University, Tehran North Branch, Tehran, Iran

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#### ABSTRACT

Metals enter the life cycle of plants and organisms through water and soil, causing short-term and long-term effects which can endanger their biosystem. As heavy metals do not play a significant role in the biological and organic compounds of human body (and the majority of other plant and animal species), they would gradually be accumulated in specific areas in the body, ultimately leading to poisoning as well as physical and psychological disorders (Humans). Davijan Area is located in the southeast of Malayer 1:100000 Geological Sheet. Through conducting field, laboratory, and library studies in the vicinity of this sheet, as well as taking geochemical samples providing 2D and 3D maps of the area, we discovered that concentrations of certain elements like arsenic, nickel, and lead, in certain areas such as Lesavand Village, Zanganeh Paeen, Mishen and Aznavole were greater than the maximum standard limits recommended by international Organizations and institutions. This can be a significant reason for the high documented cancer statistics in the area. Therefore recommend that a more detailed investigation into the matter be conducted in the future works.

### 1. Introduction

Metals are elements with a shiny appearance which are good conductors of heat and electricity. In chemical reactions, metals are usually present in the form of positive ions or cations (Hajalilou and Vusuq, 2009). There are 84 known elements classified as metals, and thus, metals are prominent in nature and medical geology. If we classify metals from a medical geological perspective, then a number of metals (if regarded in balanced and specific amounts) are not only harmless, but also greatly needed for human metabolism (examples include iron, selenium, calcium, etc.). A number of other metals either have no particular effect on human body, or do not come in daily contact with human body due to their being rare, and, as such, their positive or negative effects on human health are not quite evident (e.g. zirconium the effects of which are not yet quite clear). And there is another group of metals which are potentially harmful for the body, e.g., lead, mercury, radioactive metals, and other specific elements (Hajalilou and Vusuq, 2009). Metals are introduced into the life cycle of plants and organisms through water and soil, causing short and long-term hazards which can pose a risk to their very life. Metal poisoning has been known to humans since ancient times. A heavy metal is defined as a metal with a specific weight of greater than 4.5 g/cm<sup>3</sup>. Heavy metals play no role in body compounds and gradually accumulate at specific places within the body, causing poisoning as well as physical and psychological disorders. Metal poisoning is dangerous because the high volumes of accumulated metal cannot easily be dispelled by the body and remains in the body in a stable condition, and this stability makes heavy metals harmful for human health. Upon entering the body, these metals are distributed to the majority of body tissues via blood circulation.

In line with environmental studies regarding environmental pollution due to the abnormal existence of different elements and metals, environmental logistic, environmental-geologist and climatologists, have focused on exploiting various statistical and mathematical methods to determine the environmental health of different areas.

In this research, The authors used the analysis results obtained from 243 geochemical samples from Davijan study area in order to examine and analyze this region from environmental and medical geological perspectives ,which ultimately obtained five 3D maps showing element concentration distributions as well as the corresponding dispersion curves (with regard to the standard environmental threshold given within the text). This is discussed in more detail in the following sections.

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<sup>\*</sup> Corresponding Author.

Email Address: a farhadi@iau-tnb.ac.ir (A. Farhadi)

### 2. Methodology

# 2.1. Single-Variable geochemical statistical studies

In the geochemical studies conducted in Davijan 1:50000 Sheet, 243 stream geochemical samples were taken and, upon due preparation, were sent on to the ASL laboratory (Canada) for ICP-OES analysis.

#### 2.2. Processing the geochemical data

Reliability of the results is the basis of all reports based on quantitative data. Consequently, data processing investigations act as instruments which facilitate the achievement of proper results. In this study, the raw data were filed and their distribution closely approximated by the normal distribution through the Box-Cox transformations using singlevariable statistical methods. A summary of the implemented method is presented below.

# 2.3. Calculation of statistical parameters and plotting raw data histograms

Obtaining statistical parameters is the first and most comprehensive option provided for data processors. This information demonstrates the distribution of data around the mean value as well as the skewness and kurtosis of sample concentrations and the degree of their similarity to a corresponding normal distribution. The mean, median, and mode quantities show the degree and quality of the tendency towards the center of data. Standard deviation and variance demonstrate data dispersion form the mean value. Skewness and kurtosis show data symmetry around the mean and the distribution curve height respectively. If skewness and kurtosis approach 0 and 3 respectively, then the studied distribution would be close to the normal distribution. The information obtained from Davjan study area is presented in Tables 1 and 2.

		Со	As	Cr	Ni	Pb
NT	Valid	243	243	243	243	243
Ν	Missing	0	0	0	0	0
Mean		19.80	18.99	112.16	78.35	65.07
Std. Error of Mean		.221	.676	1.794	.871	14.778
Median		19.00	16.00	108.00	77.00	23.00
Std. Deviation		3.448	10.539	27.966	13.578	230.371
Skewness		.742	2.749	.673	.748	7.170
Std. Error of Skewness		.156	.156	.156	.156	.156
Kurtosis		2.348	9.785	.919	2.606	53.552
Std. Error of Kurtosis		.311	.311	.311	.311	.311
Minimum		11	6	40	39	11
Maximum		36	80	210	136	2080

Table 2: Calculated statistical parameters for Heavy metals in Davijan study area after using box-cox transform

		Co_BoxCox	As_BoxCox	Cr_BoxCox	Ni_BoxCox	Pb_BoxCox
N	Valid	243	243	243	243	243
	Missing	0	0	0	0	0
Mean		4.00018	1.53943	10.42804	7.77994	.93803
Std. Error of Mean		.019513	.006821	.066668	.032140	.001056
Median		3.94856	1.53312	10.35979	7.76180	.93679
Std. Deviation		.304183	.106332	1.039246	.501015	.016462
Skewness		.016	029	.019	.024	.232
Std. Error of Skewness		.156	.156	.156	.156	.156
Kurtosis		1.503	.517	.731	1.745	055
Std. Error of Kurtosis		.311	.311	.311	.311	.311
Minimum		3.039	1.202	6.804	5.941	.892
Maximum		5.139	1.830	13.416	9.536	.976

For more detailed studies in Davijan study area, histograms were provided for showing sample frequencies corresponding to a specific concentration (or a concentration range) relative to the original concentration. These histograms yield three important characteristics, namely, position (with respect to the population mean, median, and mode), dispersion, and shape of the distribution curve.

The probability distribution diagram was also used to further study Davjan region. Through these curve, one can determine the following data characteristics: normality, probable populations in the data, and the boundary of abnormal populations (if any) with the general background.

The histograms and probability distribution diagram for the five studied elements in the region are presented in the following section. These diagrams and statistical parameter tables can be used to observe the approximate normalization or deviation from normal distribution of the raw data obtained for different elements (Fig. 1).



Fig. 1: The histograms of datasets and The histograms of transformed datasets by box-cox method

# 2.4. Normalizing raw data and normal data statistical parameters

IN most statistical calculations and methods, it is required to determine data distributions as well as study the similarity thereof with normal distributions. In this study, first the similarity of the data to normal element distributions was determined. Upon studying the skewness and kurtosis of the element distributions in Davjan, it was observed that there was a great difference between these and the normal distributions. For this reason, the Box-Cox transformations were implemented.

Since normalized data are required in most statistical calculations and methods; in this study, first addressed is the problem of data normalization. The relatively normalized data were investigated via their raw or logarithmic data, and the other data were normalized by through multi-variable logarithmic transform or the Box-Cox transformations.

This transformation can better approximate data with their normal distribution and is formulated as:

$$Z = \begin{cases} \frac{x^{\lambda} - 1}{\lambda} & (\lambda \neq 0), X > 0\\ \ln(X) & (\lambda \neq 0), X > 0 \end{cases}$$

Where X: represents the data to be normalized,  $\lambda$ : is a real number, and Z: shows the transformed values.

The data distribution function in this case is:

$$f(x) = \frac{x^{\lambda} - 1}{\beta\sqrt{2\pi}} e^{-\frac{1}{2} \left[\frac{x^{\lambda} - 1}{\lambda} - \alpha\right]^2}$$

Where  $\alpha$  and  $\beta$  are the mean and standard deviation of the transformed data respectively. All the above calculations and data processing methods were implemented in the studied area in Davijan.

The following formula was used to calculate the kurtosis coefficient for the X1... X243 raw data in the studied area:

$$\sigma^{4} = (\sigma^{2})^{2} = \left[\frac{\sum_{i=1}^{n} (X_{i} - \bar{X})^{2}}{n}\right]^{2}$$
$$\mu^{4} = \frac{\sum_{i=1}^{n} (X_{i} - \bar{X})^{4}}{n}$$

Where  $\mu^4$  is the third order central moment. The moment coefficient of skewness was calculated from the following formula:

$$S = \frac{\mu^{3}}{\sigma^{3}}$$

$$\sigma^{3} = (\sigma^{2})^{\frac{3}{2}} = \left[\frac{\sum_{i=1}^{n} (X_{i} - \bar{X})^{2}}{n}\right]^{\frac{3}{2}}$$

$$\mu^{3} = \frac{\sum_{i=1}^{n} (X_{i} - \bar{X})^{3}}{n}$$

Where  $\mu^3$  is the third order central moment. If S>0, the skewness is positive and the skewness diagram is to the right, whereas for S<0, the skewness diagram is negative and towards the left. For symmetrical diagrams, we have S=0.

#### 2.5. The Shapiro-Wilk test

After investigating skewness and kurtosis of statistical distribution of each dataset, The Shapiro–Wilk test is applied for finding that the normality distributions of each dataset for elements.

The Shapiro–Wilk test was published in 1965 by Samuel Sanford Shapiro and Martin Wilk.

$$(a_1, \dots, a_n) = \frac{M^{T_V - 1}}{\left(m^{T_V - 1_V - 1}m\right)^{1/2}},$$
  

$$W = \frac{\left(\sum_{i=1}^n a_i X_{(i)}\right)^2}{\sum_{i=1}^n (X_i - \bar{X})^2},$$
  

$$m = (m_1, \dots, m_1)^2,$$
  

$$\bar{X} = (X_1, \dots, X_n)/n$$

Where,  $x_{(i)}$  is the smallest data and  $\overline{x}$  is the mean of data set.

# 2.6. Single-Variable geochemical statistical analysis results

Due consideration of the above as well as interpretation of the obtained results lead Authors to the following conclusions: elements Ni (Nickel), Cr (Chromium), As (Arsenic), and Co (Cobalt) showed negligible skewness since, upon subjecting the data Box-Cox transformations: thev vielded to distributions normal/symmetrical akin to distributions. Of course, considering the kurtosis and skewness obtained for these elements, we would expect As to have a higher deviation (as compared to other elements) from the environmental standards, and thus, further investigation must be conducted in this regard in Davihan to determine the environmental harm resulting from surplus amounts of As. In the section dealing with environmental effects, we address this problem in more specialized terms. Regarding Ni, we can conclude that the difference between kurtosis of this element and the normal distribution is relatively large. Thus, perhaps more environmental investigations would be needed in the region regarding Ni also. However, this element (Ni) showed a favorable distribution in terms of symmetry and it is only the considerable kurtosis difference with the normal distribution (i.e., the standard environmental concentration of Ni) which would make further field investigation necessary. Due to the existence of lead and zink mines in the region around Davijan including Ahangaran Mine, we expected to find much higher lead concentrations (as compared with other elements) in the studied region which comprised both rural and urban Davjan areas. This expectation was confirmed upon subjecting the obtained data to Box-Cox transformations with normal distribution since the skewness and kurtosis results for lead bespoke of a considerable difference between environmental concentration distributions of this element with the normal distribution, revealing the existence of higher than standard amounts of lead in the studied region. Although the environmental concentration of this element is not very high, further investigation in this regard must be conducted in the region.

Furthermore, according to The Shapiro–Wilk test, and after using Box-Cox transformations, it seems that Cr, Pb and <u>As</u> distributions are abnormal (Table 3). For more investigation QQ-plots are also drow. The QQ-plots results shows that Pb and As elements have the maximum value of the standard error of mean (Fig. 2).

# 3. Environmental and medical geological studies based on results obtained from statistical tests

The studied Davjan region lies to the southeast of Malayer 1:100000 Geological Sheet. Through field,

laboratory, and library studies conducted within this sheet as well as the geochemical samples and the plotted maps, Authors managed, with due regard to the standard environmental limits and ranges, to provide a general Geo Medical and environmental overview of the Davijan region, and prepare five 3D maps for element concentration distribution as well as 2D distribution maps. These are discussed in the flowing section.

Table 3: Shapiro-Wilk Test for datasets of Heavy metals in Davijan study area

	Shapiro-Wilk				
	Statistic	df	Sig.		
cr	.993	241	.285		
ni	.966	241	.000		
pb	.980	241	.002		
as	.985	241	.015		
со	.971	241	.000		



Fig 2: The Detrended Normal QQ-plots of elements

#### 3.1. Arsenic

Arsenic (As), is one of the most toxic materials in nature and can enter the plant and organism's life cycle as well as human body through food, air, and water. Skin contact with contaminated soil or water can also induct Arsenic into the body. The amount of As detected in food is negligible since this substance is not added to food due to its high toxicity. However, high concentrations of As might be found in fish and sea food since fish can absorb the As dissolved in water. Due to the high levels of As absorption in rice and the suitable environment existing in rice fields for retaining As, rice can be contaminated with As, leading to various cancers or heart disease in human being. Arsenic has an undeniably destructive effect on human DNA, thus affecting the embryos in pregnant women. Arsenic mostly affects the following groups: workers who have to handle As and farm workers working on fields where fertilizers with high As levels are used. Direct contact with As can cause varying effects including stomach and bowel irritation, reduced red and white blood cell production, skin discoloration, and lung irritation. Absorbing high levels of inorganic As increases the risk of various cancers including skin, lung, liver, and lymph nodes cancer. In humans, As existing in the environment might account for the occurrence of various cancers including skin cancer and cancers affecting internal organs such as bladder, lung, and kidneys. Exposure to As can cause infertility and miscarriage in women, as well as skin irritation, reduced immunity to viruses, heart failure, and brain damage in both men and women. Arsenic is mostly scattered in the environment through copper producing plants. However, lead and zink producing plants as well as agricultural activities can also scatter As. Arsenic does not decompose upon being released into the environment. Therefore, the excess As released through various human activities can cause disease in humans and animals alike. If As enters a river drainage system, it can remain in water in the form of stable arsenide-cyanide compounds for a long time as a contaminating agent. Studies show that the maximum allowable As content in water is 10 ppm/lit. If As exceeds this threshold, it can lead to harmful effects (Hajalilou and Vosouq, 2009).

#### 3.1.1. Environmental effects of as in Davijan

The As concentrations obtained from the geochemical samples taken from Davijan Sheet revealed that in the northeastern, eastern (near

Lesavand, Zanganeh and Mishen Village), and southeastern areas, this concentration exceeded the highest allowable concentration (circa 20 ppm/lit). This can cause environmental problems in this area in the long run. Fig. 3 shows a 3D As-concentration map as well as a 2D As-distribution diagram obtained for Davijan Sheet. These maps were prepared via data processing and statisticalbiological analyses in the area. The relatively high concentration of As in the eastern and southeastern parts are marked in red color (color blue is used for allowable concentration levels, green for danger threshold concentrations, and red for concentrations exceeding the standard level). This study confirms the results obtained in the previous studies (these results were obtained when the area was scanned in 2004 for providing a medical geology atlas for this area) regarding the high mortality rates due to liver and the hepatobiliary system cancer, colon cancer, prostate cancer, and cervical cancer (shown in the maps as red areas). As mentioned above, As is a toxic element and can cause various diseases including cancer. For this reason, further more detailed studies must definitely be conducted in the region.



**Fig. 3:** 3D As-concentration map and 2D As-distribution diagram obtained for Davijan Sheet

#### 3.2. Cobalt

More than 30 kinds of inorganic cobalt have so far been identified including cobanite, Rameles-

Brigitt, and skutterudite. Cobalt has numerous applications in air industries as well as ceramic and glass production industries. In agriculture, suing small amounts of cobalt can play a significant role in human health since cobalt is essential in nitrogen fixation in soil. However, large concentrations of this element can lead to soil toxicity and plant destruction (Arzani, 2003). In air, cobalt can attach itself to other aerosols and take several days to settle on the ground. Cobalt can enter the environment through natural resources. This element cannot be destroyed and is merely converted from one form to another. If absorbed in amounts exceeding the allowable limits through drinking water or other means, cobalt can turn into a pathogen. Cobalt poisoning can lead to destructive effects on body tissues and heart and kidney function (Ataby, 2005). If absorbed in large amounts, cobalt can cause acute bronchitis. Skin contact with cobalt solutions or dust can lead to skin irritations. Many institutions around the world who study various cancers have announced cobalt as a possible carcinogen.

### 3.2.1. Environmental studies on Cobalt in Davijan

Study of the geochemical samples obtained from Davjan Sheet showed that, in all the studied areas, cobalt concentration was lower than the danger threshold predicted in standards (in Bijanabad, cobalt concentration was very near this threshold. Therefore, more exact studies are required in this area). Fig. 4 shows the 3D cobalt concentration distribution map as well as the 2D dispersion map for this element in Davijan Sheet.

## 3.3. Chromium

Geochemically, chromium is considered a lithophile element. The only economically viable chromium is Clark Chromium of the Spinnell (Chromte) family which occurs in association with ultramafic intrusive rocks such as dunite, peridotite and pyroxenite. The clark chromium concentration is 100 ppm. Chromium has numerous applications in metallurgical industries for producing ferrochromium alloys (Hajalilou and vosoug, 2009). So far, no evidence has been found regarding the possible negative effects of 3-valence chromium on workers or ordinary people who are exposed to this element in the regions containing chromium compounds. Moreover, 6-valance chromium is used in preparing anticancer drugs to treat lung cancer as well as treating various skin allergies. Recent research shows moderate levels of chromium added to animals diet has increased the longevity. The most prominent signs of chromium poisoning humans include skin irritation, skin allergies, and destructive effects on the respiratory system, gradual destruction of kidneys, liver, stomach, and the intestines, as well as various types of lung cancer. Chromium concentrations in excess of 5 mg/lit n sewage and waste materials can be highly dangerous.

# 3.3.1. Environmental study of Chromium concentration in Davijan

The chromium concentration levels obtained from the samples in Davijan Sheet were lower than the danger threshold. Fig. 5 shows the 3D Cr concentration map and the 2D distribution map obtained for this region.

# 3.4. Nickel

Due to its favorable chemical resistance, mechanical, and thermal properties, nickel has widespread applications in our daily lives.



Fig. 4: 3D Co-concentration map and 2D Co-distribution diagram obtained for Davijan Sheet



Fig. 5: 3D Cr-concentration map and 2D Cr-distribution diagram obtained for Davijan Sheet

Nickel can enter human body via air, drinking water, food, and smoking. Skin contact with contaminated soil or water can also lead to absorption of nickel into the body. Small amounts of nickel are essential for human health. However, high levels of this element can be dangerous. Such disorders are exhibited in the form of general weakness and metabolism slowness in fighting external pathogens, and increased number of celleating microbes. As a result of these, the body becomes prone to leukemia as well as brain and bone cancer, as well as local infections, inflammation, and death (Hajalilou and Vosouq, 2009). In addition to the irreparable damages caused through nickel absorption into the body, skin contact with nickel can also cause severe skin allergies, irritation, itching, and skin disease. Unfortunately, due to lack of public awareness regarding the negative effects of Ni, people do not heed the safety precautions issued with regard to this element.

Nickel compounds can, depending on their toxic properties and the time of contact with or closeness to the body, exhibit a wide range of toxicity. It must be noted that not all nickel compounds are toxic. The highest level of contamination due to Ni is caused via skin contact or inhalation of nickel in gaseous and powder forms. Inhaling nickel-contaminated air leads to acute irritation in the respiratory system and the mucous tissues thereof as well as severe irritation in the throat and respiratory tract. If nickel enters the body through inhaling, it might lead to throat, nose, and lung cancer. Presence of nickel in the circulations system through inhalation or consumption of ground water with high nickel concentrations (obtained from wells in the tropical regions, laterite terrains, etc.) can lead to immune system disorders as well as destruction of internal organs.

There is not much evidence regarding the harmful effects of nickel on living organisms besides that obtained for human beings. Scientists already know that high Ni concentrations in sandy soil can harm plants and high Ni concentrations in water can reduce the number of algae and slow their growth. Microorganisms also show reduced growth levels in the presence of Ni. However, they grow resistant to this element in time.

### 3.4.1. Environmental study of Ni in Davijan

The greatest Ni concentrations in Davijan Sheet obtained from the geochemical samples were found to be in the eastern (Lasavand, Ghale khan, Zangane paeen and Mishen), northeastern (Aznavale), southeastern (Biatan bala and Biatan paeen), and central parts (Bijan abad and East of Davijan). These concentrations were in excess of 80 ppm, i.e., they highest recommended level exceed the in international standards. This can lead to environmental problems in the area. Fig. 6 shows the 3D Ni concentration dispersion map and the 2D dispersion curve in Davijan. Nickel concentrations were higher in the eastern, northeastern, and southeastern regions as compared with other parts.

### 3.5. Lead

Occurring in natural concentration of 10-20 ppm, lead is one of the most abundant heavy metals in nature. Lead concentrations in excess of 100 ppm in soil are indicative of soil contamination with this element. The level of lead concentration in soils around metal producing industrial plants or roads with high vehicle traffic might be between 1 and 10 percent. As compared with other heavy metals, lead is less active chemically.

The amount of lead entering the environment from natural resources is negligible as compared with that introduced through man-made industrial and production activities. Lead dust exists in urban air. Although the level of lead entering human digestive system through food and water is much more than that inhaled through air in cities, the lead entering the respiratory system through inhalation can be much more easily absorbed.

Other important sources of lead contact include the lead used in drinking water pipes. Although using lead is discontinued in modern constructions technology, such piping systems can still be found in old houses.

In animals and humans, lead accompanied by strontium and calcium can accumulate in bones and interfere with the natural maturity of bone marrow. Lead can also prevent hemoglobin synthesis in cells. Most of the lead entering human body during its life time is accumulated in bones. Depending on an individual's age, lead concentrations might also be found in various degrees in the soft tissue and organs like liver, kidneys, and pancreas. Studies show that lead absorption leads to reduced immunity in the body and adversely affects the activity of many enzymes.

General symptoms of lead poisoning include anemia, stomach pains, and nervous disorders such as aggressive behavior, confusion, and loss of motor control (peripheral nervous system disorder). While some of the effects caused by lead poisoning can be cured, the damage to the brain and the nervous system, as well as the cancers that occur as a result of lead poisoning is almost impossible to treat.

#### 3.5.1. Environmental study of lead in Davijan

The Maximum lead concentrations (150 ppm) in Davijan Sheet occurred in the northeastern and eastern parts (Lasavand and Ghale khan). These were higher than the standard levels and, in the long run, can lead to environmental problems and health hazards in the region. As can be observed, the high concentration of this element in the northeastern and eastern parts is shown in the map with the color range green to red. As the geochemical samples demonstrated a higher concentration than the standard limits, the authors propose that a more detailed investigation should be conducted in the area. Fig. 7 shows the 3D Pb concentration dispersion map and the 2D dispersion curve in Davijan.

### 3.6. Conclusion and recommendations

From the results obtained from the geochemical samples taken from Davijan Sheet, we conclude that certain elements like Ni, Pb, and Ni have higher concentrations than the recommended standards. Long-term effects of such high concentrations can exhibit themselves in the form of skin and respiratory diseases and even cancer among the inhabitants of the region.



Fig. 6: 3D Ni-concentration map and 2D Ni-distribution diagram obtained for Davijan Sheet



Fig. 7: 3D Pb-concentration map and 2D Pb-distribution diagram obtained for Davijan Sheet

These results are in agreement with those obtained from the survey team dispatched via reputable government agencies to the same area for providing medical geological maps. Those studies also classified Davijan as a high-risk area.

For this reason, we recommend that more detailed investigations be conducted in this area and that, if necessary, soil amendment agents as well as inorganic and urban waste water treatment schemes be deployed in the region.

Needless to say, the costs associated with soil amendment in these regions shall be far less than those which will have to be paid in the long run to compensate for the harmful environmental and medical geological effects in this area.

Further studies are suggested to be carried out with higher precision and specifying standard ranges of environmental concentration of the area in question. It is also recommended that more extensive studies are carried out using chi-square test to systematically asses the concentration of these elements, hence their environmental impact. This helps achieving more precise and practical solutions.

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