**REGULAR ARTICLE** 



# The organ level atmospheric element signatures of native *Pistacia atlantica* in semi-arid forests linked to the Ilam Gas Refinery, Iran

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Received: 16 December 2021 / Accepted: 26 February 2022 / Published online: 8 March 2022 © The Author(s), under exclusive licence to Springer Nature Switzerland AG 2022

#### Abstract

*Aims* The Ilam Gas Refinery (IGR) emitting atmospheric trace elements affect soils and Baneh trees (*Pistacia atlantica* Desf.) of semi-arid Zagros forests. Therefore, the seasonal concentrations of Pb, As, Cu, Cr, Mn, Zn, Ni, and S were analyzed in soils, barks, and leaves of trees located at various distances (1000, 1500, 2000, 2500, and 10,000 m (control) from the refinery.

*Methods* The seasonal changes, source distance, soil physicochemical properties (i.e., pH, electrolyte conductivity (EC), and texture), and organ-level atmospheric element deposition were detected in the study.

*Results* The season×distance effects on the soils, barks, and leaves revealed that the summer and autumn seasons and distances up to 2500 m from the IGR had higher element concentrations than spring and control distance. The total element trends were in decreasing order; soil>leaf>bark. High pollution was defined as soils with a pollution load index

Responsible Editor: Juan Barcelo.

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(PLI) of 5.3, with sulfur having the highest concentration. Leaves and barks with metal accumulation index (MAI) of 12.51 and 11.18, enriched by elements in particular with S and Cu.

*Conclusions* The Baneh trees might be ideal for atmospheric element remediation and be employed among practical techniques for reducing IGR pollution in Zagros forests. In addition, since the organisms that feed on these trees might be a hub for pollution dispersion across the food web, it is recommended that pollutant levels in the aerial organs and soils in the region be monitored regularly.

Keywords Pistacia trees  $\cdot$  Season-distance effects  $\cdot$  Zagros forests  $\cdot$  Bioaccumulation  $\cdot$  Metal contamination

#### Introduction

Anthropogenic factors (e.g., industrial operations) and natural activities are one of the primary sources of trace elements (TEs) enrichment and contamination (Lee et al. [20]; Li et al. [23]). Low concentrations of TEs are long-lasting and indestructible in a variety of environments where plants and humans have been exposed (Milicevic et al. [28]; Cao et al. [8]). The higher TE concentrations may negatively affect the air and soil quality, aquatic or terrestrial habitats, and food chain. Therefore, TEs have gained significant attention in recent years (Li et al. [23]).

Sulfur is a macronutrient needed for plant growth, metabolism, and environmental stress response. Sulfate, sulfur dioxide, and hydrogen sulfide are the forms in which sulfur could be accumulated in soils and leaves, respectively (Leustek and Saito [22]; Mutia et al. [30]). However, sulfur accumulation is controlled by the number of different forms deposited in the environment, and rising quantities would not help sensitive terrestrial ecosystem components (Kravitz et al. [19]).

Industry's impact on pollution and the risk of TEs accumulation in the ecosystems has grown in recent years (Ramachandra et al. [35]). Several methods are widely used to evaluate TE concentrations in soils, such as enrichment factor (EF), geo-accumulation index ( $I_{geo}$ ), pollution load index (PLI), and potential ecological risk index (RI; Liu et al. [26]). The bioaccumulation factor (BF) is also a pollution indicator in ecosystems that measures plants' tendency to take and translocate TEs from soils into their biological systems (Baker [5]).

There is a scarcity of studies on the potentially TEs contamination in forest soils vs. urban and agricultural soils (Turtscher et al. [43]). So far, only a few studies have been performed on biomonitoring of TEs in ecosystems components such as soils, trees, and their various organs in the areas near the gas refinery and petrochemical plants in Iran (Safari et al. [38]). Leitgeb et al. ([21]) evaluated different soil properties, S, and potentially TEs (As, Mn, Cu, Cr, Ni, Pb, and Zn) concentrations in forest soils of Singapore and discovered that anthropogenic activities had little impact on soils.

Baneh trees, also known as wild pistachio trees (Pistacia atlantica subsp. Mutica), are the second indigenous deciduous tree species in Iran's Zagros woodlands, where they coexist irregularly with the various oak trees. The indigenous people of Zagros get multiple benefits from using different components of Baneh trees in agriculture, trade, and industry. However, in addition to living on drought stress conditions in semi-arid Zagros climate (Sheikh-Hassani et al. [40]), these trees are confronted with another lousy situation due to the aforementioned (i.e., anthropogenic, natural) activities. Air pollution emitted from the industrial stationery resources, such as Ilam Gas Refinery (IGR) in Ilam province forests, is a safety issue addressed in this research. The IGR source, emitting toxic gaseous pollutants from the two different chimneys, affects the Zagros ecosystem, including the soils and tree species (e.g., pistachio).

In Iran, the medicinal and therapeutic qualities of Baneh trees have been examined in various studies. However, little analysis has been performed on the impacts of environmental and abiotic stress on the Zagros forests ecosystem, such as air pollution from industrial sources. In this context, we look at the concentrations of sulfur and other TEs in Baneh trees due to refinery pollution and the impacts of pollution on tree leaves, barks, and soil samples collected at different periods of the year with varying distances from the pollution source. The toxic concentration of elements is critical for animals that feed on these plants and people using the trees for pharmaceutical purposes. For instance, cattle, sheep, and goats that feed on Baneh trees in this particular air polluted region may be susceptible to Baneh poisoning. Besides, the toxicity of elements such as sulfur can cause injury symptoms, including necrosis and colored spots in the leaf organs. To the best of our knowledge, this is the first study on the effects of air pollution on Baneh trees in Iran's Zagros region.

The objectives of this research were (i) to investigate the seasonal and distance effects of Ilam Gas Refinery on the concentration of sulfur and TEs (ii) quantification and assessment of various pollution indices of elements in soil samples, barks, and leaves of Baneh trees (iii) analyze the relationship between sulfur and different TEs through principal component analysis (PCA) in soils and Baneh tree components which affected by the gas refinery (iv) provide a perspective and a basis to assess the effects of polluted soils and trees on the food chain in an ongoing process. We hypothesize that: (i) the concentration of S and TEs in the soil samples and Baneh tree components will be affected by seasonal and distance changes from the gas refinery (ii) barks and leaves of trees will react in different ways to the pollution (iii) sulfur and different TEs in tree components mainly accumulated from the atmospheric portions.

#### Material and methods

Description of the study area

The Ilam Gas Refinery  $(33^0 42' \text{ N}, 46^0 13' \text{ E})$ , which is operating gas conversion, is located along the edge

of the mountains of Zagros forests. The refinery was founded in 2007 and primarily supplies gas to Iran's western provinces with its two chimneys, which release waste gases into the atmosphere. Based on random analysis of exhaust emissions, sulfur dioxide and hydrogen sulfide concentrations were detected, the highest among the other pollutants emitted from the refinery (Aghdash et al. [1]). In addition, Baneh trees in Zagros forests around the refinery are exposed to various air contaminants (different elements) from this source. The sampling points have an average altitude of about 1000-1200 m and less than 25% slope. The climate of the region is semi-arid and influenced by Mediterranean winds. The predominant wind direction is west and southwest (http://www.ilammet. ir).

## Sample collection and analysis of different elements in soils and tree components

Different distances (1,000, 1,500, 2,000, 2,500, and 10,000 m [control]) in an easterly direction from the facility (Fig. 1) was studied. Based on different articles on SO<sub>2</sub> pollution sources (Cicek and Koparal [9];

Mutia et al. [30]) and the Iranian environmental science reports (modeling, predicting, and assimilating air pollutants from various sources), 10 km from the gas refinery was selected as the control distance. In the late spring, summer, and autumn seasons of 2019, soils, barks, and leaves were sampled at each distance. Because of more prevalent spring rains, summer was hotter and drier, and autumn led to leaf senescence and wind velocity. In this research, seasonal changes' effects on element accumulations in the soil and trees were assayed.

Two soil samples were obtained with a plastic gardening shovel from a depth of 0–20 cm at each distance, and roughly 25 g of healthy barks were sampled by cutter from the middle of the tree trunk and at about 100 cm above the ground. After the bark sampling, the Baneh trees with special adhesives were protected from microorganism infection. Twenty healthy and mature leaves were taken from a particular height (around the middle of the canopy) of the outer canopy of two Baneh trees. The trees with an average height of 4 m and a diameter of 35 cm at breast height were chosen randomly.

The samples were placed into polyethylene bags and transported to the lab. for analysis (Estefan et al.

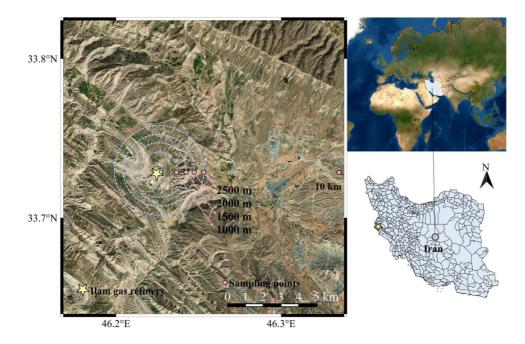


Fig. 1 The location of sampling sites of soils, barks, and leaves of Baneh trees at distances of 1000, 1500, 2000, 2500, and 10,000 (control) meters from the Ilam Gas Refinery

[12]). The soil, bark, and leaf samples were dried for ten days until they reached a constant weight at lab temperature. The leaves were then grounded, soils were sieved with ASTM mesh with a diameter of 2 mm and homogenized. To determine the pH and electrical conductivity (EC) of soils samples, 2 g of the soil samples were shaken in 10 ml of ddH<sub>2</sub>O with a ratio of 1:5. After an hour, the pH and electrical conductivity (EC) of the solution were measured by a digital pH (Fan Azma Gostar Company, Iran) and EC meter (Sartorius, PT-20, USA; Pen-Mouratov et al. [33]). The soil particle sizes were analyzed using the hydrometer method, and texture class was determined with a soil texture triangle (Palmer and Troeh [32]).

The soil and leaf samples were prepared and digested according to different U.S.EPA protocols modified by the following references. In the soil, leaf, and bark samples, the concentration of sulfur (S), arsenic (As), chromium (Cr), copper (Cu), lead (Pb), zinc (Zn), manganese (Mn), and nickel (Ni) were measured via inductively coupled plasma mass spectrometry (ICP-MS, 7500 CS, Agilent, US).

According to Da Silva et al. ([10]), approximately 0.5 g of dry soil sample was digested with 10 mL of HCl on a hot plate at ~ 180 °C until the solution was reduced to 3 ml. Approximately 5 mL of HF (40%, w/w), 5 mL of HNO3 (63%, w/w), and 3 mL of HClO4 (70%, w/w) were then added, and the solution was digested. This process was continued by adding 3 mL of HNO3, 3 mL of HF, and 1 mL of HClO4 until the silicate minerals disappeared. This solution was transferred to a 25 mL volumetric tube, and 1% HNO3 was added to bring the samples up to a constant volume. After filtering the digested samples, the concentrations of studied elements were measured via an ICP-MS device (7500 CS, Agilent, US). The procedures of quality assurance and quality control (QA/ QC) were performed. External standards with calibration levels were used to quantify element contents from soil samples. The precision and the repeatability of the analysis were tested on the instrument by analysing three replicate samples.

According to Liang et al. ([24]), 0.5 g of dry bark and leaf samples were acid digested, sieved powder samples were placed in the acid-washed tubes, and 10 mL of 65% nitric acid was added. The solutions were placed at room temperature overnight (12 h) and 100 °C for an initial 4 h and then another 4 h at 140 °C until the solutions` color was clear. After cooling, the solutions were diluted by deionized water to 50 mL and then passed through Whatman filter paper until 25 mL of the filtrate volume was obtained. Each sample was digested three times, and the average measurements were recorded. Total elements were measured by using the ICP-MS. A control sample was also used beside each sample to determine the background contamination during digestion. To confirm the methodology's accuracy and ensure the extraction of TEs, the standard solution of each studied element was used.

## Pollution range of different elements in soils and tree components

For assessment of contamination levels (concentrations) of different elements in soils and trees, standard indices of pollution including geoaccumulation index ( $I_{geo}$ ), pollution indices (PI), pollution load indices (PLI), enrichment factor of plants ( $EF_{plant}$ ), bioconcentration factor (BCF) and metal accumulation index (MAI) were used.

 $I_{geo}$  was calculated using the following equation:

$$I_{geo} = \log_2 \left[ C_n / 1.5 B_n \right] \tag{1}$$

where  $C_n$  is the measured concentration of the element n,  $B_n$  is the geoaccumulation background for this element, and 1.5 is a constant coefficient used to eliminate potential variations in the baseline data (Solgi et al. [41]). The I<sub>geo</sub> classifies samples into seven grades: <0 for practically unpolluted; 0–1 for unpolluted to moderately polluted; 1–2 for moderately polluted; 2–3 for moderately to strongly polluted; 3–4 for strongly polluted; 4–5 for strongly to extremely polluted; and >5 for extremely polluted (Qing et al. [34]).

The first PI is expressed as Eq. 2:

$$PI = C_i / S_i$$
<sup>(2)</sup>

where  $C_i$  is the concentration of element i in the soil (mg kg<sup>-1</sup>) and  $S_i$  is the soil quality standard or reference value for the element i (mg kg<sup>-1</sup>). The PLI for different elements is calculated via the following equation:

$$PLI = (PI_1 \times PI_2 \times PI_3 \times \dots \times PI_n)^{1/n}$$
(3)

The PLI of soils is classified as follows: PLI < 1 is unpolluted, 1 < PLI < 2 is unpolluted to moderately polluted, 2 < PLI < 3 is moderately polluted, 3 < PLI < 4 is moderately to highly polluted,

4<PLI<5 is highly polluted, and PLI>5 is very highly polluted.

Plant EF is calculated as:

$$EF_{plant} = C_{plant} / C_{control}$$
(4)

where  $C_{plant}$  and  $C_{control}$  are element concentrations (mg kg<sup>-1</sup>) in tree leaves or barks at the polluted and the control sites, respectively. A value of EF>2 indicates that the tree is enriched with a specific element (Mingorance et al. [29]). BCF, which indicates the ability of plants to accumulate different elements from the soil (Alahabadi et al. [2]), is computed as follows:

$$BCF = \left( [C]_{L,B} / [C]_{s} \right)$$
(5)

where  $[C]_{LB}$  and  $[C]_{S}$  are the concentration of different elements in leaf and bark and soil samples, respectively. Values of BCF>1, BCF<1, and BCF=1 imply that the trees are accumulators, excluders, and indicators for different elements, respectively (Liang et al. [24]).

The ability of Baneh tree leaves and bark to accumulate atmospheric elements differed. In this context, MAI was calculated as follows:

$$MAI = 1/n \sum_{j=1}^{n} Ij$$
(6)

where n is the total number of studied elements, and Ij is the sub-index of variable j, calculated by dividing each element's mean concentration (x) by its standard deviation (Liu et al. [25]; Hu et al. [13]).

#### Data analysis

The normality of the data distribution was checked by SAS software using Shapiro-Walk and Kolmograph-Smirnov tests before employing analysis of variance. The logarithmic conversion was used to normalize the data. The concentration of Pb, As, Cu, Cr, Mn, Ni, Zn, and S in soils, barks, and leaves of Baneh trees along with pH and EC in soils for two factors including seasons in three levels (spring, summer, and autumn) and distance in five levels (1,000, 1,500, 2,000, 2,500, 10,000) were analyzed with three replicates in a completely randomized design. Twoway ANOVA was performed, and the comparisons of means were conducted with Duncan's test at p < 0.05. Principal components analyses for different elements were performed by SAS software.

#### Results

The seasonal and distance effects of IGR on different elements concentration of soil samples and Baneh tree components

Season×distance effects on pH and EC of soil samples revealed no significant (p>0.05) differences between spring and autumn seasons at various distances from the IGR. Soils in summer at a distance of 1000 had the lowest pH (8.32) among the studied distances (Fig. 2a). While soil samples in spring at 1500 and 2000 m had the highest EC with 0.39 and 0.13 ds.m<sup>-1</sup>, the highest EC (with 0.32 and 0.25 ds.m<sup>-1</sup>) in summer was 1000 m and 10 km. Soil sampled from 1500 m showed the lowest EC among the other distances tested (Fig. 2b). The soils exhibited a loam clay texture at 1000 and 1500 m and a loam texture at other distances. Clay, silt, and sand percentages were 40.6%, 25%, and 34.4% respectively, at various distances from the IGR.

Season×distance effects on different elements concentration of soil samples revealed that Cr, Cu, Mn, Ni, Pb, and Zn elements had a substantially greater concentration in different seasons, at distances up to 2500 m from the IGR, than control distance soils (p < 0.05; Table 1).

Soil samples in spring at distances of 1000 and 1500 m showed lower Cr, Cu, Mn, Ni, Zn, and Pb concentrations than 2000 and 2500 m from the pollution source. Compared to 1500, 2000, and 2500 m distances from the source, soils at 1000 m had the lowest Cr, Cu, Mn, Ni, Zn, and Pb concentrations during the summer and autumn seasons. The amount of arsenic (As) in soil samples collected during the spring and summer seasons at 2500 m distance from the IGR was not significantly different from control distance soils. However, soil samples in the autumn season at different distances (1000, 1500, 2000, and 2500 m) showed higher As concentrations than control soils (Table 1).

S concentrations in soils were significantly higher (p < 0.05) in different seasons at distances up to 2500 m from the IGR than the control distance. Furthermore, the highest S concentrations were found in

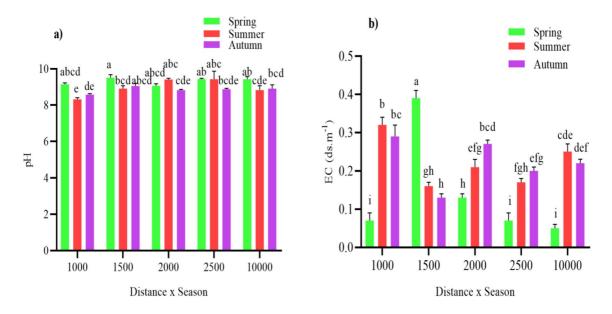


Fig. 2 The season × distance effects on pH (a) and EC (b) of soil samples. The means with different letters are significantly different (two-way ANOVA with Duncan post-hoc, p < 0.05)

Season	Distance	Cr (mg.kg <sup>-1</sup> )	Cu (mg.kg <sup>-1</sup> )	Mn (mg.kg <sup>-1</sup> )	Ni (mg.kg <sup>-1</sup> )	Pb (mg.kg <sup>-1</sup> )	As (mg.kg <sup>-1</sup> )	Zn (mg.kg <sup>-1</sup> )
Spring	1000	$31.55^{h} \pm 1.44$	$16.48^{d} \pm 0.85$	$249.53^{i} \pm 3.93$	$50.35^{\text{g}} \pm 0.87$	$2.98^{e} \pm 0.11$	$140.58^{f} \pm 4.4$	$39.71^{\text{g}} \pm 1.52$
	1500	$28.31^{\rm hi}\pm1.32$	$16.97^{d} \pm 0.72$	$208.77^{j} \pm 1.55$	$42.28^{h} \pm 1.16$	$3.06^{e} \pm 0.15$	$208.26^{cd} \pm 5.71$	$38.36^{\text{gh}} \pm 1.08$
	2000	$44.33^{\text{ef}} \pm 0.68$	$23.89^{\circ} \pm 0.9$	$409.8^{\rm f}\pm1.75$	$65.33^{d} \pm 3.07$	$3.79^{\rm d} \pm 0.04$	$233.5^{\circ} \pm 7.01$	$57.87^{e} \pm 1.36$
	2500	$58.51^{d} \pm 0.75$	$21.76^{\circ} \pm 1.9$	$290.8^{h} \pm 1.09$	$64.59^{d} \pm 0.51$	$1.96^{f} \pm 0.15$	$55.32^{ij} \pm 5.71$	$70.49^{d} \pm 1.01$
	10,000	$12.2^{k} \pm 1.01$	$5.86^{f} \pm 0.74$	$39.81^{\text{m}} \pm 1.7$	$8.05^{j} \pm 1.38$	$0.25^{h} \pm 0.05$	$9.17^{j} \pm 2.39$	$16.40^{j} \pm 0.93$
Summer	1000	$41.87^{\rm  fg} \pm 0.37$	$21.79^{\circ} \pm 1.54$	$325.72^{\text{g}} \pm 1.78$	$57.77^{ef} \pm 1.21$	$4.67^{\circ} \pm 0.25$	$167.56^{ef} \pm 4.65$	$52.41^{f} \pm 1.29$
	1500	$58.04^{d} \pm 0.94$	$35.59^{a} \pm 1.11$	$678.25^{a} \pm 5.65$	$116.19^{a} \pm 1.25$	$7.1^{a} \pm 0.55$	$186.87^{de} \pm 5.03$	$92.05^{b} \pm 1.05$
	2000	$80.27^{b} \pm 1.15$	$28.66^{\rm b}\pm1.44$	$469.26^{d} \pm 7.14$	$83.01^{\circ} \pm 1.33$	$4.83^{\circ} \pm 0.29$	$268.84^{b} \pm 10.02$	$69.09^{d} \pm 1.03$
	2500	$55.51^{d} \pm 0.72$	$32.31^{ab}\pm1.98$	$429.91^{e} \pm 2.32$	$62.84^{de} \pm 0.75$	$3.96^{d} \pm 0.05$	$329.68^{a} \pm 25.34$	$67.34^{d} \pm 1.78$
	10,000	$26.1^{ij} \pm 2.63$	$10.71^{e} \pm 1.19$	$135.69^{k} \pm 3.09$	$21.01^{i} \pm 0.89$	$1.01^{\text{g}} \pm 0.02$	$38.32^{ab} \pm 1.22$	$23.83^{i} \pm 1.28$
Autumn	1000	$39.61^{\text{g}} \pm 0.71$	$17.21^{d} \pm 1.09$	$249.24^{i} \pm 2.54$	$53.32^{\text{fg}} \pm 0.45$	$4.89^{\circ} \pm 0.02$	$76.72^{hi} \pm 5.03$	$51.73^{f} \pm 1.5$
	1500	$47.72^{e} \pm 0.61$	$28.17^{b} \pm 0.93$	$251.03^{i} \pm 1.47$	$67.02^{d} \pm 2.87$	$4.24^{cd} \pm 0.14$	$100.55^{\text{gh}} \pm 9.17$	$84.91^{\circ} \pm 1.43$
	2000	$71.33^{\circ} \pm 2.22$	$32.25^{ab}\pm1.53$	$509.29^{\circ} \pm 0.95$	$110.93^{b} \pm 1.71$	$5.99^{b} \pm 0.02$	$109.64^{g} \pm 8.97$	$82.58^{\rm c}\pm1.52$
	2500	$86.75^{a} \pm 0.95$	$34.05^{a} \pm 1.51$	$558.52^{b} \pm 2.62$	$107.06^{b} \pm 1.54$	$5.97^{b} \pm 0.05$	$140.64^{\rm f} \pm 13.23$	$109.87^{a} \pm 4.53$
	10,000	$23.69^{j} \pm 2.24$	$11.27^{e} \pm 1.16$	$107.14^{1} \pm 2.54$	$25.12^{i} \pm 3.22$	$1.81^{\rm f}\pm0.14$	$25.39^{j} \pm 2.32$	$33.35^{h} \pm 0.88$

Table 1 The season  $\times$  distance effects on Cr, Cu, Mn, Ni, Pb, As, and Zn elements of soil samples (Data show the Mean  $\pm$  SE)

According to the Duncan test, the means with different letters are significantly different (p < 0.05)

soils at distances of 1000, 1500, and 2000 m, respectively (Fig. 3a).

The season×distance effects on different element concentrations of bark samples indicated that Cr in spring and autumn had no significance among the investigated distances from the IGR. Also, barks sampled up to 2500 m showed higher Cr than control distance. Cu concentrations were considerably higher (p < 0.05) in the spring and autumn seasons at distances up to 2500 m from the source than in control

40

20

(

1000

1500

2000

Distance x Season

2500

10000

S (mg.kg<sup>-1</sup>)

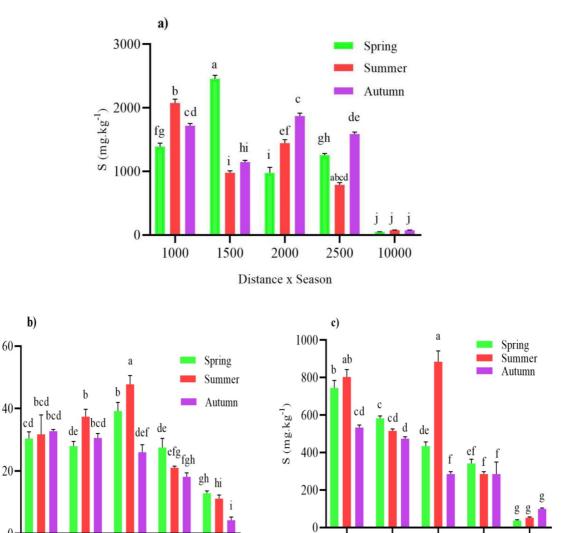


Fig. 3 The season × distance effects on S concentration of soil (a), bark (b), and leaf (c) samples of Baneh trees. The means with different letters are significantly different (two-way ANOVA with Duncan post-hoc, p < 0.05)

1000

1500

distance barks. Also, 2500 and 10,000 m from the pollution source had lower Cu than other distances in the summer. Mn, and As in different seasons, was found in significantly (p < 0.05) higher concentrations than control distance barks sampled up to 2500 m from the IGR. In the spring and autumn, there was no significant difference in Ni concentration; however, in the summer, the concentration was lower at the control distance than at the other distances. Compared to control, the Zn content of barks in three seasons at varied distances had the highest concentration. Barks in spring and summer with 13.35 and 9.33 mg.kg<sup>-1</sup> at 1000 m and in autumn with 16.33 mg.kg<sup>-1</sup> at 2500 m showed the highest Pb concentrations (Table 2).

2000

Distance x Season

2500

S concentrations were significantly higher (p < 0.05) in different seasons at distances up to 2500 m from the IGR than in control distance barks. The barks showed the highest S concentrations in spring and summer at 2000 m and had the lowest concentrations in 2500 m and control distances

10000

Season	Distance	Cr (mg.kg <sup>-1</sup> )	Cu (mg.kg <sup>-1</sup> )	Mn (mg.kg <sup>-1</sup> )	Ni (mg.kg <sup>-1</sup> )	Pb (mg.kg <sup>-1</sup> )	As (mg.kg <sup>-1</sup> )	Zn (mg.kg <sup>-1</sup> )
Spring	1000	$2.19^{ab} + 0.3$	$9.16^{de} + 0.27$	$23.36^{\text{def}} + 0.73$	$2.96^{\text{ef}} + 0.38$	$13.35^{a} + 1.9$	$336.91^{a} + 37.42$	$11.75^{a} + 0.86$
spring	1500	$1.49^{abc} + 0.28$	$8.2^{\text{ef}} + 0.95$	$37.15^{a} + 2.69$	$1.3^{e} + 0.44$	$7.43^{bcd} + 0.49$	$152.1^{efg} + 12.67$	$5.34^{\text{def}} \pm 0.75$
	2000	$1.5^{abc} \pm 0.38$	$14.03^{a} \pm 0.27$	$20.47^{\rm f} \pm 0.82$	$1.25^{ef} \pm 0.25$	$4.8^{\text{ef}} \pm 0.43$	$139.11^{\text{fg}} \pm 17.25$	$6.46^{cde} \pm 0.97$
	2500	$1.57^{abc} \pm 0.1$	$7.9^{\text{ef}} \pm 1.21$	$20.82^{f} \pm 1.08$	$1.6^{\rm ef} \pm 0.42$	$5.41^{\text{def}} \pm 0.47$	$257.68^{b} \pm 6.71$	$5.27^{def} \pm 1.13$
	10,000	$1.03^{cd} \pm 0.17$	$4.78^{\text{g}} \pm 1.03$	$5.32^{i} \pm 2.08$	$0.87^{de} \pm 0.25$	$1.35^{g} \pm 0.31$	$31.24^{i} \pm 9.6$	$2.23^{hi} \pm 0.4$
Summer	1000	$2.32^{a} \pm 0.23$	$9.89^{\text{cde}} \pm 0.15$	$22.27^{\rm ef} \pm 1.08$	$2.09^{\rm d} \pm 0.24$	$9.33^{b} \pm 0.34$	$139.35^{fg} \pm 8.59$	$9.34^{b} \pm 0.61$
	1500	$1.80^{abc}\pm0.46$	$10.82^{bcd} \pm 0.42$	$26.42^{bc} \pm 0.8$	$1.5^{cd} \pm 0.07$	$6.83^{\rm cde} \pm 0.48$	$187.33^{de} \pm 5.47$	$5.96^{\rm cdef} \pm 0.77$
	2000	$1.73^{abc} \pm 0.3$	$11.67^{bc} \pm 0.88$	$21.92^{\rm ef} \pm 2.93$	$2.18^{d} \pm 0.07$	$6.37^{\rm cde} \pm 0.44$	$107.83^{\text{g}} \pm 4.82$	$4.11^{\text{fgh}} \pm 0.77$
	2500	$1.74^{abc} \pm 0.16$	$7.65^{ m ef} \pm 0.64$	$18.95^{\text{fg}} \pm 1.51$	$1.73^{d} \pm 0.37$	$4.04^{\rm f}\pm1.18$	$233.79^{bc} \pm 5.47$	$7.45^{bcd} \pm 0.37$
	10,000	$0.85^{cd} \pm 0.08$	$5.87^{fg} \pm 0.37$	$13.2^{h} \pm 0.86$	$0.73^{e} \pm 0.43$	$1.4^{\rm fg} \pm 0.26$	$63.17^{i} \pm 6.71$	$2.62^{ghi}\pm0.37$
Autumn	1000	$1.58^{abc} \pm 0.55$	$10.9^{bcd} \pm 0.26$	$26.5^{\rm cde}\pm0.85$	$2.04^{a} \pm 0.4$	$8.16^{bc} \pm 0.43$	$181.78^{def} \pm 8.59$	$7.74^{bc} \pm 0.39$
	1500	$1.33^{bcd} \pm 0.3$	$9.03^{de} \pm 0.26$	$27.38 {}^{cd} \pm 0.91$	$1.37^{\rm abc}\pm0.62$	$4.05^{f} \pm 0.11$	$190.49^{cde} \pm 8.78$	$4.73^{\rm efg} \pm 1.06$
	2000	$1.25^{\rm bcd} \pm 0.04$	$12.88^{ab}\pm1.08$	$32.46^{b} \pm 2.01$	$1.37^{ab} \pm 0.37$	$8.1^{bc} \pm 0.27$	$303.04^{a} \pm 22.75$	$4.32^{\text{efgh}} \pm 0.2$
	2500	$1.62^{abc} \pm 0.11$	$8.01^{\text{ef}} \pm 0.12$	$30.55^{bc} \pm 1.08$	$2.84^{ab} \pm 0.1$	$11.63^{a} \pm 1.16$	$213.3 ^{\text{cd}} \pm 4.81$	$8.76^{b} \pm 0.51$
	10,000	$0.52^{d} \pm 0.12$	$2.28^{h} \pm 0.7$	$15.27^{\text{gh}} \pm 0.46$	$0.65^{e} \pm 0.19$	$1.12^{g} \pm 0.11$	$38.93^{i} \pm 4.27$	$1.01^{i} \pm 0.21$

Table 2 The season  $\times$  distance effects on Cr, Cu, Mn, Ni, Pb, As, and Zn elements of bark samples (Data show the Mean  $\pm$  SE)

According to the Duncan test, the means with different letters are significantly different (p < 0.05)

(Fig. 3b). S element in different seasons at distances up to 2500 m from the IGR, significantly (p < 0.05) had higher concentration than control distance leaves. There was no discernible variation between seasons at a distance of 2500 m from the source (Fig. 3c).

The results of the season×distance effects on the concentration of different elements in leaf samples revealed that Cr element had significantly higher (p < 0.05) concentration than control distance tree leaves in the spring and summer seasons at distances up to 2500 m from the IGR. Also, at 1500 m from the source, the Cr concentration was the lowest compared to other distances.

Cu, Pb, Zn, and As concentrations were significantly higher (p < 0.05) than control distance leaf samples in different seasons at distances up to 2500 m from the source. There was no significant change in Mn concentrations between leaf samples collected in spring and fall at distances of 1500 and 2500 m compared to other distances. In comparison to the control distance, Mn concentrations were higher at various distances. Leaf samples in spring and autumn at distances of 2500 m had no significant difference in Ni concentration compared to other distances with control. However, there was a higher Ni concentration in different distances than the control distance (Table 3).

## Multivariate analysis of different elements in soil samples and tree components

The results of principal components analysis (PCA) in the soil samples showed that the first and second main components with Eigenvalues of 6.09 and 1.61, respectively, explained a total of 77.09% of the total variance of the components (the first component equals 60.94% and the second component was 16.15%). The first component has a positive and significant correlation with the elements of Ni (0.97), Cu (0.96), Mn (0.95), Cr (0.94), Pb (0.93), and Zn (0.92). The second component, which represents soil properties, includes 16.15% of the variance, which was positively and negatively correlated with the EC (0.87) and pH (-0.60), respectively. This component is thought to reflect soils with high salt and low acidity (Table 4).

In the bark samples, the first and second components had Eigenvalues of 4.69 and 1.19, respectively, and accounted for 73.58% of the total variance (the first component was 58.69%, and the second component was 14.88%). The PCA results for bark showed a high and positive correlation for the first component of Pb, Zn, Ni, As, and Cr. In addition, a positive correlation was observed based on the second component of Cu and S elements. According to the

Table 3 The season  $\times$  distance effects on Cr, Cu, Mn, Ni, Pb, As, and Zn of leaf samples (Data show the Mean  $\pm$  SE)

Season	Distance	Cr	Cu	Mn	Ni	Pb	As	Zn
		(mg.kg <sup>-1</sup> )	(mg.kg <sup>-1</sup> )	(mg.kg <sup>-1</sup> )	(mg.kg <sup>-1</sup> )	(mg.kg <sup>-1</sup> )	$(mg.kg^{-1})$	$(mg.kg^{-1})$
Spring	1000	$3.8^{d} \pm 0.49$	$6.85^{ m ef} \pm 0.12$	$24.65^{\circ} \pm 0.53$	$5.1^{de} \pm 024$	$4.53^{bcd} \pm 0.35$	9.9 <sup>bcd</sup> ±1.17	$21.49^{bcde} \pm 1.45$
	1500	$4.02^{\rm cd} \pm 0.44$	$10.1^{ab} \pm 0.92$	$19.79^{cde} \pm 091$	$6.7^{cd} \pm 1.48$	$4.52^{bcd} \pm 0.12$	$16.31^{a} \pm 1.41$	$25.51^{ab} \pm 1.88$
	2000	$4.9^{bcd} \pm 0.66$	$6.1^{fg} \pm 0.13$	$18.76^{\rm cde} \pm 1.25$	$9.42^{b} \pm 0.88$	$3.2^{de} \pm 0.32$	$7.43^{\mathrm{def}} \pm 0.45$	$15.4^{cde} \pm 0.9$
	2500	$6.4^{ab} \pm 0.37$	$4.9^{g} \pm 0.51$	$14.8^{\text{efg}} \pm 1.84$	$2.94^{\rm ef}\pm0.16$	$3.61^{cde} \pm 0.51$	$11.2^{bc} \pm 0.9$	$20.32^{de} \pm 0.81$
	10,000	$1.01^{e} \pm 0.08$	$0.91^{i} \pm 0.72$	$9.58^{g} \pm 0.53$	$1.17^{f} \pm 0.16$	$0.9^{f} \pm 0.11$	$3.21^{gh} \pm 0.26$	$6.07^{h} \pm 0.33$
Summer	1000	$3.7^{d} \pm 0.91$	$7.9^{de} \pm 0.13$	$33.63^{b} \pm 0.81$	$6.05^{\rm d} \pm 1.28$	$7.28^{a} \pm 0.33$	$11.79^{b} \pm 0.31$	$27.12^{a} \pm 1.9$
	1500	$4.89^{\mathrm{bcd}} \pm 0.14$	$11.9^{a} \pm 1.12$	$18.68^{cde} \pm 0.74$	$5.04^{de} \pm 1.22$	$3.63^{cde} \pm 0.32$	$15.15^{a} \pm 0.87$	$18.72^{\rm ef} \pm 0.26$
	2000	$5.81^{abc} \pm 0.54$	$7.78^{\text{def}} \pm 0.54$	$19.35^{cde} \pm 2.23$	$8.02$ <sup>cd</sup> $\pm 1.22$	$7.46^{a} \pm 1.39$	$14.78^{ab} \pm 1.28$	$11.94^{\text{g}} \pm 1.87$
	2500	$6.4^{ab}\pm0.91$	$4.97^{g} \pm 0.73$	$17.55^{\mathrm{def}} \pm 0.84$	$2.28^{\rm ef}\pm0.08$	$3.2^{de} \pm 0.54$	$9.11^{cde} \pm 0.79$	$33.34^{abcd} \pm 1.03$
	10,000	$1.01^{e} \pm 0.08$	$2.68^{h} \pm 0.2$	$9.38^{g} \pm 1.36$	$8.57^{f} \pm 0.2$	$1.03^{\rm f} \pm 0.66$	$2.44^{h} \pm 0.31$	$5.74^{h} \pm 0.5$
Autumn	1000	$4.9^{bcd} \pm 0.1$	$8.8^{cd} \pm 0.16$	$50.19^{a} \pm 5.37$	$14.88^{\mathrm{a}} \pm 1.38$	$5.28^{bc} \pm 0.14$	$14.5^{a} \pm 0.8$	$25.15^{abc} \pm 2.08$
	1500	$4.17^{cd} \pm 0.23$	$4.95^{g} \pm 0.22$	$11.6^{\text{fg}} \pm 1.6$	$5.03^{\rm de}\pm0.73$	$3.77^{\rm cde} \pm 0.66$	$6.96^{\rm ef} \pm 0.48$	$13.2^{\text{g}} \pm 1.94$
	2000	$7.04^{a} \pm 0.54$	$9.76^{bc} \pm 0.43$	$23.82^{cd} \pm 1.08$	$11.44^{b} \pm 0.54$	$6.09^{ab} \pm 0.36$	$10.1^{\rm bc} \pm 0.58$	$17.4^{\text{ef}} \pm 0.53$
	2500	$4.02^{ab} \pm 0.09$	$5.08^{e} \pm 0.35$	$15.75^{d} \pm 0.56$	$3.03^{ab}\pm0.81$	$2.57^{abc}\pm0.37$	$5.25^{fg} \pm 0.66$	$21.14^{cde} \pm 0.56$
	10,000	$1.25^{a} \pm 0.07$	$2.72^{f} \pm 0.29$	$8.6^{f} \pm 2.74$	$2.01^{\rm f} \pm 0.86$	$0.99^{g} \pm 0.22$	$0.87^{h} \pm 0.21$	$5.12^{h} \pm 1.07$

According to the Duncan test, the means with different letters are significantly different (p < 0.05)

**Table 4** The eigenvectors and accumulative contributions of variance for the first two principal components (PCs) of different elements in soil, bark, and leaves of Baneh trees

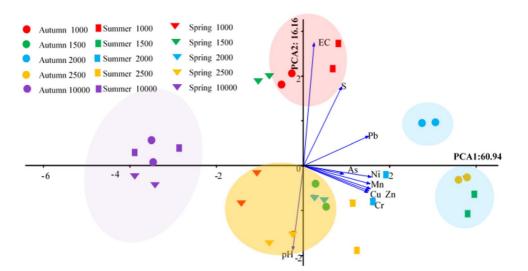
Parameters	Soil		Bark	Leaf	
	1	2	1	2	1
Pb	0.938	0.209	0.905	-0.234	0.877
Zn	0.922	-0.190	0.844	-0.385	0.768
Ni	0.973	-0.078	0.783	-0.344	0.764
As	0.581	-0.057	0.764	-0.159	0.893
Cr	0.942	-0.177	0.750	-0.134	0.697
Cu	0.963	-0.164	0.706	0.628	0.867
S	0.547	0.565	0.683	0.604	0.871
Mn	0.959	-0.129	0.664	0.260	0.777
EC	0.154	0.877			
рН	-0.154	-0.603			
Total	6.094	1.616	4.695	1.191	5.340
% of Variance	60.941	16.158	58.694	14.888	66.752
Cumulative %	60.941	77.099	58.694	73.581	66.752

The bold value indicates the significant correlation at P < 0.01

PCA results for the leaf samples, all elements except Cr had a positive correlation with the first component (Table 4).

In all three seasons, the control distance had the lowest concentration of TEs in the soil. The highest amount of soil EC was observed in the summer and autumn seasons near the IGR. Regardless of distance from the refinery, soils in spring showed the lowest acidity and salinity. The highest concentrations of Pb and S were observed in autumn at closer distances to the refinery (2000 m). In addition, the soils at various distances from the refinery (1500, 2000, and 2500 m) exhibited significant amounts of Zn, Cu, Cr, Mn, and Ni in the summer and autumn seasons (Fig. 4).

According to the PCA, the control distance had the lowest TE concentrations in the bark samples in all three seasons. The maximum concentrations of Pb, As, Zn, Ni, and Cr were found at a distance of 1000 m from the IGR in the spring, while the lowest concentrations of Cu, S, and Mn elements were found at a distance of 1000 m. This distance showed the highest Pb, As, Zn, Ni, and Cr concentrations in summer and autumn. The concentrations of Cr, S, and Mn were not affected by the season and were highest at 1500 and 2000 m. The lowest concentration of these elements was observed at 2500 m from the IGR (Fig. 5).



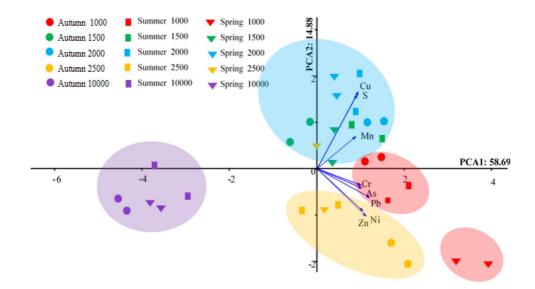
**Fig. 4** Principal Component Analysis (PCA) shows the multivariate variation among different parameters, including Pb, Zn, Ni, As, Cr, Cu, S, Mn, pH, and EC of soils in different seasons sampled from different distances the Ilam Gas Refinery,

# Pollution assessment of elements in soils and tree components

The mean element concentrations (mg  $kg^{-1}$ ) of Cr, Cu, Mn, Ni, S, and As were higher than specified in

Iran. Vectors indicate the direction and strength of each studied parameter to the overall distribution. The first and second principal axes in soils explained 60.94% and 16.15% of the variances, respectively

the soil quality standards of the Department of Environment of Iran. Also, Ni, Cr, Pb, S, and As were detected higher than the world soil standards (Cicek and Koparal [9]; Alloway [4]). The mean concentrations of the elements examined in Baneh bark



**Fig. 5** Principal Component Analysis (PCA) shows the multivariate variation among elements including Pb, Zn, Ni, As, Cr, Cu, S, and Mn in barks in different seasons sampled to varying distances from the Ilam Gas Refinery, Iran. Vectors indi-

cate the direction and strength of each studied parameter to the overall distribution. The first and second principal axes in barks are explained by 58.69% and 14.88% of the variances, respectively

samples were As > S > Mn > Cu > Pb > Zn > Ni > Crin decreasing order. The mean element concentrations in leaves were 446.19 for S, 19.75 for Mn, 17.18 for Zn, 9.27 for As, 6.41 for Cu, 5.63 for Ni, 4.23 for Cr, and 3.67 for Pb; (S > Mn > Zn > As > Cu > Ni > Cr > Pb) (Table 5).

The different pollution metrics, including  $I_{geo}$ , PI, PLI, BCF, EF, and MAI, were calculated for various elements in the soil, bark, and leaf samples across different seasons and distances around the Ilam gas refinery. The mean PI and  $I_{geo}$  values for S, Cr, Cu, Mn, Ni, Pb, As, and Zn were S > As > Pb > Mn > Ni > Cu > Zn > Cr. S and Zn elements were found to have the highest and lowest pollution levels in soil samples, respectively. The mean PLI in all soils was 5.09 (Table 6). The mean EF values of leaf samples for S, Cr, Cu, Mn, Ni, Pb, As, and Zn, was S > As > Pb > Cr > Cu > Ni > Zn > Mn in decreasing order. The mean EF values of bark samples for S, Cr, Cu, Mn, Ni, Pb, As = Sn > S > Mn > Cu > Ni > Cr (Table 6).

 Table 5
 The mean concentration of toxic elements (TEs) and
 S
 for soil, leaf, and bark
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Studied element (mg kg <sup>-1</sup> )	Leaf	Bark	Soil	Iranian soil standards <sup>a</sup>	World soil standards <sup>b</sup>
Cr	4.23	1.5	47.05	0.4	42
Cu	6.41	8.87	24.46	14	63
Mn	19.75	22.81	327.52	-	418
Ni	5.63	1.63	62.32	50	18
Pb	3.67	6.23	3.77	300	25
S	446.19	26.56	1192.59	-	418
AS	9.27	171.76	139.27	17	4.7
Zn	17.18	5.81	59.33	200	62

a According to the data of the Iran Department of Environment b (Cicek and Koparal [9]; Alloway [4]) The leaf samples had mean BCF values of 0.36 for S, 0.08 for Cr, 0.29 for Cu, 0.06 for Mn, 0.07 for Ni, 0.94 for Pb, 0.19 for As, and 0.40 for Zn: Pb>Zn> S>Cu>As>Cr>Ni>Mn. The mean BCF values of bark samples were 0.02 for S, 0.03 for Cr, 0.36 for Cu, 0.07 for Mn, 0.03 for Ni,1.65 for Pb, 1.23 for As and 0.10 for Zn; thus, as follows: Pb>As>Cu>Cu >Zn>Mn>Cr=Ni>S (Table 6). The findings of the mean metal accumulation sub-index and MAI of the elements examined in tree leaves and barks revealed that the concentrations were in decreasing order, S> Cu>Zn>Mn>Cr=As>Pb>Ni and Cu>Mn>A s>S>Pb>Zn>Ni>Cr respectively. The MAI of leaves and barks were 12.51 and 11.18, respectively (Fig. 6).

#### Discussion

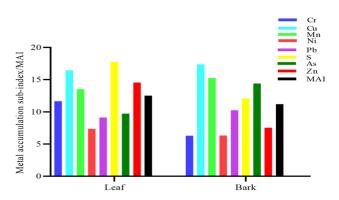
According to our findings, environmental variables such as soil characteristics, seasons of the year, and distances from the pollution source impacted the concentration of sulfur and TEs in soil, bark, and leaf samples of Baneh trees in Zagros forests. Also, the primary variables for pollutants transport and deposition in Zagros forest components were the height of the IGR flare gas exhaust tower and wind velocity.

Clay particles in soil samples exhibit the most remarkable ability for retaining sulfur and other elements in their structure (Rodriguez et al. [37]). Although the pH of the soils varied depending on the season and distance, they were all characterized by an alkaline state (pH>8.3). The presence of carbonate sodium, the entrance of calcareous matters, parent material rocks, and anthropogenic pollution sources might be the primary reasons soils were in alkaline condition (Solgi et al. [42]). However, the soil samples having an EC of < 1 were not salty in any way.

Pollution indices	Cr	Cu	Mn	Ni	Pb	S	As	Zn
PI <sub>Soil</sub>	2.73	2.86	4.81	4.69	6.55	21.22	9.26	2.85
Igeo <sub>soil</sub>	0.78	0.89	1.53	1.52	1.87	3.86	2.26	0.87
EF <sub>bark</sub>	2.20	2.75	2.77	2.49	5.77	3.93	5.15	4.04
BCF <sub>bark</sub>	0.03	0.36	0.07	0.03	1.65	0.02	1.23	0.10
EF <sub>leaf</sub>	4.65	4.51	2.23	4.27	4.7	10.15	6.39	3.56
BCF <sub>leaf</sub>	0.08	0.29	0.06	0.07	0.94	0.36	0.19	0.40

Table 6Different pollutionindices for S, Cr, Cu, Mn,Ni, Pb, As, and Zn elements

Fig. 6 Mean metal accumulation sub-index and MAI of different elements in the leaves and barks of Baneh trees



These characteristics resulted in soils with low conductivity for the elements examined.

Other studies have shown that our findings follow a similar pattern: in an assay of soils sampled from several industrial locations in Ahvaz (western Iran), Keshavarzi et al. ([17]) discovered that soils had an alkaline condition, low EC, and virtual clay fraction characteristics. In another work, the predominant texture of soils was loam, according to heavy metal monitoring in various soils of Bojnord, Iran. Furthermore, the soils were not saline (low EC) and had a neutral to alkaline pH range (Solgi et al. [42]). In essence, the significant variables that caused soils to have a higher ability to accumulate TEs were loam texture, alkaline pH, and low EC.

Soil samples from the furthest distances (1500, 2000, and 2500 m) exhibited greater sulfur and TEs contents than samples from the closest distance. Furthermore, soils sampled up to 2500 m from the IGR showed higher element concentrations than soils at a control distance. This refinery's exhaust output properties, such as size or height of the exhaust tower and output loads per unit of time, are the crucial factors to emit air pollution to surrounding ecosystem components. Certain studies have confirmed this data. For instance, Mutia et al.([30]) found that in Kenya, soils close to a pollution source (1000 m near) showed lower sulfur concentrations than soils sampled from a larger radius. Thus, the usual pattern was found in this study.

In terms of seasonal impacts on element concentrations in soils, in comparison to other seasons, the humidity and dispersed rainfall of the Zagros forests in spring cause significant amounts of air pollutants and elements to be washed and deposited in soils. However, due to the dryness of the air in subsequent seasons, pollutants accumulated into the soils at high concentrations. As a result, soils in the summer and autumn were subjected to drought stress or a lack of moisture in addition to air pollution. These circumstances resulted in increased element concentrations in the soils throughout these seasons.

Both seasons and distances from the IGR impacted S and TEs concentrations in tree barks and leaves. Furthermore, the concentration of studied elements at distances up to 2500 m was higher than that of the control distance. In line with our results, another work to analyze the impact of a pollution source on ecosystems in Turkey revealed that the concentrations of sulfur and TEs in tree leaves at the furthest distance (10 km) were the lowest among the other distances from the source (Cicek and Koparal [9]). However, due to dry weather and arid lands of these ecosystems, and a lack of rainy seasons, significant pollution accumulated in tree organs throughout the summer and autumn seasons compared to spring (Richardson et al. [36]).

Based on the PCA results, there were significant positive correlations between TEs in soil, bark, and leaves of trees directly impacted by the IGR's air pollution. The concentration of the elements tested was found proportional to their distance from the gas refinery. As a result, their quantities near the source (1500 to 2000 m) exceeded the control distance. The concentrations of Zn, Cu, Cr, Mn, and Ni were higher in barks located at different distances (1500, 2000, and 2500 m) from the source. Rather than the size of emitted particles. e.g., dust and smoke particles that carry TEs are essential factors in the differences of air pollution amounts in the nearest and farthest distances from the gas refinery.

In line with our results, various elements had a positive correlation in each portion of soils, barks, and leaves of trees, and all of them may have originated from IGR operations. De Nicola et al. ([11]), in their study of TEs monitoring of soils and oak trees (Ouercus ilex L.) growing in different locations, concluded that Mn and Cu concentrations of soil and leaves were correlated that it might indicate the same source of origin. Our data showed that the concentration of S and TEs in summer and autumn was higher than spring season. In the summer and autumn seasons, the concentration of TEs and S in leaves was higher also because the time of TEs accumulation was more prolonged than in spring when leaves appear on the trees and the trees just start to uptake water with elements more intensively after winter. Baneh trees at distances growing in 1000-2500 m from IGR were affected by the pollution, mainly As toxicity (morphological differences were such smaller leaves and necrosis in leaves) compared to control distance trees.

The mean concentration of S (2.85 times), As (29.63 times), Cr (1.12 times), and Ni 3.46 times were higher than the World healthy soil requirements (Cicek and Koparal [9]; Alloway [4]). Thus, As element had the highest toxic range among the other studied elements in the Zagros region soil samples, this is the area where the most detrimental TEs contamination for soil and plants occurred, depending on the season of the year. Furthermore, in line with our results that sulfur concentration in soils and leaves were found more elevated than that of the regulated limits, in the work of Cicek and Koparal ([9]), sulfur in soils and oak trees (Quercus infectoria L.) living adjacent to an SO<sub>2</sub> pollution source in Turkey showed higher concentrations than that of the regular range for soils and plants.

According to Kabata-Pendias and Pendias ([14]); Padmavathiamma and Li ([31]), the concentrations of Cu, Zn, and Pb in plants are in the ranges of 2-20,10-150 mg kg<sup>-1</sup>, and less than 10 mg kg<sup>-1</sup> are normal. In our results, these elements were below the regulated limits in Baneh trees. Safari et al. ([38]) showed that the concentration of Pb element contrary to Ni had the toxic range in the leaf and bark of deciduous tree species at different distances from the gas refinery. However, in our research, Pb and Ni elements did not exceed the limits in barks and leaves.

The mean  $I_{geo}$  of As and S were in moderately to strongly polluted ranges, and Pb, Mn, and Ni were in moderately polluted ranges. Cr, Cu, and Zn Mn were unpolluted to moderately polluted ranges. Although sulfur and As had a high PI, Cr, Zn, and Cu had relatively low PI indices. The PLIs in all soil samples were in a very highly polluted range. The IGR's operations contaminated soil samples from various seasons and distances. All of the investigated TEs were enriched in the leaves and barks of Baneh trees (with EF > 2). Also, the leaves showed higher EF than the barks of trees. This elemental enrichment might come from the soil or the atmosphere.

The BCF demonstrated the capacity of various organs of trees to accumulate TEs from the soil. To all of the elements tested, tree leaves had a BCF < 1. However, tree barks had BCF>1 for As and Pb elements, showing that Baneh trees could absorb these from soil readily. The concentration of As element was high in the bark. According to our findings, it was deposited from the atmospheric section and absorbed from the soil. Besides, this is the result of several years' deposition. These factors caused As to have a high and toxic range in the Baneh trees. In addition, most metal ions exhibited the lowest mobility in soils with a high pH (>7). However, the mobility rate of ions in soils can be enhanced with a change in pH (>5) conditions (Kabata-Pendias [15]; Serbula et al. [39]).

In line with our results, the pH of the soils was more than 7, indicating that the TEs had poor mobility in the soils, which Baneh roots slowly absorbed. Serbula et al. ([39]) found that Pb, Cu, and Zn have BCF < 1 in the leaves of Robinia pseudoacacia L. from various locations. Found they were poorly absorbed by the soil, resulting in soils with a pH greater than 7. The elements of Pb and As in barks of Baneh trees, on the other hand, were highly absorbed from soils and had a higher BCF. Bing et al. ([7]) showed that in air pollution conditions, As, Cr, Mn, Ni, and S with low BCF had a lower ability to be absorbed from the soil portions than other elements. In our case, elements were efficiently accumulated in the foliar organs of Baneh trees because of the slow absorption capacity.

Trace elements are available in two forms: soluble and crystallized. Besides, their accumulation in trees is related to different tree organs and types of elements (Alatou and Sahli [3]). The greatest metal accumulation sub-indexes were for sulfur in leaves and copper in barks. As compared to barks, leaves had higher MAI, which showed that the leaves were more enriched with studied elements from the air than barks. Accordingly, these trees are suitable for accumulating atmospheric elements emitted from the IGR. Tree barks with their structure to retain atmospheric pollutants and metals can give a valuable monitoring basis for long-term air pollution surveys (Berlizov et al. [6]). With their unique structures and characteristics, tree barks and leaves have varying capabilities for accumulating metallic contamination from the soil or air. Deposition in the outer surface of barks and translocation through the xylem from roots are the essential factors for TEs accumulation in tree barks (Alatou and Sahli [3]). According to Krämer ([18]), metal transportation system efficiency, antioxidant defense responses, and overall physiological status are significant indicator factors of element amounts transferred to the aboveground parts of trees.

As is the persistent carcinogen and global metalloid that had high bioaccumulation in the environment. It has harmful effects on the metabolism and bioenergetics of tissues in plants, animals, and humans. Different ills related to poisons of this metalloid are in the air, soil, and water (Kaur et al. [16]). The trees' anatomical characteristics, such as the structure of different tissues, pore cells, and leaf area, are the most important determining factors of absorption and accumulation of air pollutants and toxic elements by trees (Safari et al. [38]). Almost all the studied elements in this work accumulated in the leaf organs. Among TEs, the most dangerous was detecting a high concentration of As in leaves and barks of analyzed trees. Arsenic was found at significant concentrations in both the atmosphere and the soil. Furthermore, it was found in dangerous concentrations in soil samples from the Zagros area, which might cause severe physiological and structural disorders.

#### Conclusions

Sulfur and TEs concentrations in contamination seasons (summer and autumn) and distances (up to 2500 m) in soils and Baneh tree components differed from the spring and control distance. The concentrations of S, As, Ni, and Cr were higher than Iranian and international soil standards. Soil features, including low EC, alkaline conditions, and abundant clay particles, were the major causes of soil element contamination. Because of the poor mobility and availability of the soil's trace elements (e.g., weaker extractions), trees slightly absorbed and accumulated elements from soil sections. As opposed to the barks, the leaves have the largest elemental accumulation capacity due to the different anatomical structures and sensitivities of the organs to atmospheric elements. The PCA findings revealed that the IGR's air pollution directly impacted the concentrations of all components in soils, barks, and leaves. Food systems may be disrupted by potentially harmful materials in soils and trees, putting the health and lives of wildlife in jeopardy. As a result, it is advised that the risk level to the food web in the Zagros habitats surrounding the gas refinery be assessed regularly.

Acknowledgements The authors are grateful for the ecology lab of Tarbiat Modares University for soil properties analysis.

Author contributions HD conceived the idea and acquired funding, carried out field and experimental studies, analyzed and curated the data, structured, wrote, and improved the manuscript. NP contributed to the final version of the manuscript with software, data interpretation, and review-editing.

**Data availability** The data used to support the findings of this study are available from the corresponding author upon reasonable request.

Code availability Not applicable.

#### Declarations

**Competing interest** The authors declare no competing interests.

Ethics approval Not applicable.

**Plant involving research** Handling plants was carried out under the relevant institutional, national, and international guidelines and legislation. The permissions or licenses were obtained to collect Baneh (*Pistacia atlantica* Desf.) trees in Zagros Forests.

Consent to participate Not applicable.

Consent to publish Not applicable.

#### References

 Aghdash HD, Zare-Maivan H, Heydari M, Sharifi M, Lucas-Borja ME, Dey DC (2021) Acorn germination and oak (Quercus brantii Lindl.) seedling development dramatically affected by spatial position of maternal trees from Ilam gas refinery, Iran. Ecol Eng 170:106329

- Alahabadi A, Ehrampoush MH, Miri M, Aval HE, Yousefzadeh S, Ghaffari HR, Ahmadi E, Talebi P, Fathabadi ZA, Babai F (2017) A comparative study on capability of different tree species in accumulating heavy metals from soil and ambient air. Chemosphere 172:459–467
- Alatou H, Sahli L (2019) Using tree leaves and barks collected from contaminated and uncontaminated areas as indicators of air metallic pollution. Int J Phytorem 21:985–997
- Alloway BJ (2012) "Heavy metals in soils: trace metals and metalloids in soils and their bioavailability," Springer Science & Business Media (vol. 22)
- 5. Baker AJ (1981) Accumulators and excluders-strategies in the response of plants to heavy metals. J Plant Nutr 3(1-4):643-654
- Berlizov A, Blum O, Filby R, Malyuk I, Tryshyn V (2007) Testing applicability of black poplar (*Populus nigra* L.) bark to heavy metal air pollution monitoring in urban and industrial regions. Sci Total Environ 372:693–706
- Bing H, Wu Y, Zhou J, Sun H (2016) Biomonitoring trace metal contamination by seven sympatric alpine species in Eastern Tibetan Plateau. Chemosphere 165:388–398
- Cao L, Lin C, Gao Y, Sun C, Xu L, Zheng L, Zhang Z (2020) Health risk assessment of trace elements exposure through the soil-plant (maize)-human contamination pathway near a petrochemical industry complex Northeast China. Environ Pollut 263:114414
- Cicek A, Koparal A (2004) Accumulation of sulfur and heavy metals in soil and tree leaves sampled from the surroundings of Tuncbilek Thermal Power Plant. Chemosphere 57:1031–1036
- Da Silva YJAB, do Nascimento CWA, Cantalice JRB, da Silva YJAB, Cruz CMCA (2015) Watershed-scale assessment of background concentrations and guidance values for heavy metals in soils from a semi-arid and coastal zone of Brazil. Environ Monit Assess 187, 1-10.
- De Nicola F, Baldantoni D, Sessa L, Monaci F, Bargagli R, Alfani A (2015) Distribution of heavy metals and polycyclic aromatic hydrocarbons in holm oak plant–soil system evaluated along urbanization gradients. Chemosphere 134:91–97
- Estefan G, Sommer R, Ryan J (2013) Methods of soil, plant, and water analysis: a manual for the West Asia and North Africa Region, 3rd edn. ICARDA, West Asia
- Hu Y, Wang D, Wei L, Zhang X, Song B (2014) Bioaccumulation of heavy metals in plant leaves from Yan' an city of the Loess Plateau, China. Ecotoxicol Environ Saf 110:82–88
- Kabata-Pendias A, Pendias H (2001) Trace elements in soils and plants-CRC Press. Boca Raton
- 15. Kabata-Pendias A (2010) "Trace elements in soils and plants," CRC Press
- Kaur S, Kamli MR, Ali A (2011) Role of arsenic and its resistance in nature. Can J Microbiol 57(10):769–774
- Keshavarzi B, Najmeddin A, Moore F, Moghaddam PA (2019) Risk-based assessment of soil pollution by potentially toxic elements in the industrialized urban and periurban areas of Ahvaz metropolis, southwest of Iran. Ecotoxicol Environ Saf 167:365–375

- Krämer U (2010) Metal hyperaccumulation in plants. Annu Rev Plant Biol 61:517–534
- Kravitz B, Robock A, Oman L, Stenchikov G, Marquardt AB (2009) Sulfuric acid deposition from stratospheric geoengineering with sulfate aerosols. J Geophys Res Atmos 114.
- Lee K, Do Hur S, Hou S, Burn-Nunes LJ, Hong S, Barbante C, Boutron CF, Rosman KJ (2011) Isotopic signatures for natural versus anthropogenic Pb in high-altitude Mt. Everest ice cores during the past 800 years. Sci Total Environ 412:194–202
- Leitgeb E, Ghosh S, Dobbs M, Englisch M, Michel K (2019) Distribution of nutrients and trace elements in forest soils of Singapore. Chemosphere 222:62–70
- 22. Leustek T, Saito K (1999) Sulfate transport and assimilation in plants. Plant Physiol 120:637–644
- Li L, Wu J, Lu J, Min X, Xu J, Yang L (2018) Distribution, pollution, bioaccumulation, and ecological risks of trace elements in soils of the northeastern Qinghai-Tibet Plateau. Ecotoxicol Environ Saf 166:345–353
- Liang J, Fang H, Zhang T, Wang X, Liu Y (2017) Heavy metal in leaves of twelve plant species from seven different areas in Shanghai, China. Urban For Urban Green 27:390–398
- Liu Y-J, Zhu Y-G, Ding H (2007) Lead and cadmium in leaves of deciduous trees in Beijing, China: development of a metal accumulation index (MAI). Environ Pollut 145:387–390
- 26. Liu J-J, Ni Z-X, Diao Z-H, Hu Y-X, Xu X-R (2018) Contamination level, chemical fraction and ecological risk of heavy metals in sediments from Daya Bay, South China Sea. Mar Pollut Bull 128:132–139
- Loring DH, Rantala RT (1992) Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth Sci Rev 32:235–283
- Milicevic T, Relic D, Skrivanj S, Tesic Z, Popovic A (2017) Assessment of major and trace element bioavailability in vineyard soil applying different single extraction procedures and pseudo-total digestion. Chemosphere 171:284–293
- Mingorance M, Valdes B, Oliva SR (2007) Strategies of heavy metal uptake by plants growing under industrial emissions. Environ Int 33:514–520
- Mutia TM, Fridriksson T, Jónsdóttir IS (2016) Concentrations of sulphur and trace elements in semi-arid soils and plants in relation to geothermal power plants at Olkaria, Kenya. Geothermics 61:149–159
- Padmavathiamma PK, Li LY (2007) Phytoremediation technology: hyper-accumulation metals in plants. Water Air Soil Pollut 184:105–126
- Palmer RG, Troeh FR (1977) Introductory soil science laboratory manual. Introductory soil science laboratory manual
- Pen-Mouratov S, Shukurov N, Steinberger Y (2008) Influence of industrial heavy metal pollution on soil free-living nematode population. Environ Pollut 152:172–183
- Qing X, Yutong Z, Shenggao L (2015) Assessment of heavy metal pollution and human health risk in urban soils of steel industrial city (Anshan), Liaoning, Northeast China. Ecotoxicol Environ Saf 120:377–385

- Ramachandra T, Sudarshan P, Mahesh M, Vinay S (2018) Spatial patterns of heavy metal accumulation in sediments and macrophytes of Bellandur wetland, Bangalore. J Environ Manage 206:1204–1210
- Richardson AD, Keenan TF, Migliavacca M, Ryu Y, Sonnentag O, Toomey M (2013) Climate change, phenology, and phenological control of vegetation feedbacks to the climate system. Agric for Meteorol 169:156–173
- Rodriguez JA, Nanos N, Grau JM, Gil L, Lopez-Arias M (2008) Multiscale analysis of heavy metal contents in Spanish agricultural topsoils. Chemosphere 70:1085–1096
- Safari M, Ramavandi B, Sanati AM, Sorial GA, Hashemi S, Tahmasebi S (2018) Potential of trees leaf/bark to control atmospheric metals in a gas and petrochemical zone. J Environ Manage 222:12–20
- Serbula SM, Miljkovic DD, Kovacevic RM, Ilic AA (2012) Assessment of airborne heavy metal pollution using plant parts and topsoil. Ecotoxicol Environ Saf 76:209–214
- 40. Sheikh-Hassani M, Torkzaban B, Ataei S, Zeinanloo A, Ghahremaninejad F, Hosseini-Mazinani M (2010) Morphological evaluation of ancient olive genotypes across the Zagros mountains of Iran. In XXVIII International

Horticultural Congress on Science and Horticulture for People (IHC2010): Olive Trends Symposium-From the 924, 327–333.

- Solgi E, Esmaili-Sari A, Riyahi-Bakhtiari A, Hadipour M (2012) Soil contamination of metals in the three industrial estates, Arak, Iran. Bull Environ Contam Toxicol 88:634–638
- Solgi E, Keramaty M, Solgi M (2020) Biomonitoring of airborne Cu, Pb, and Zn in an urban area employing a broad leaved and a conifer tree species. J Geochem Explor 208:106400
- 43. Turtscher S, Berger P, Lindebner L, Berger TW (2017) Declining atmospheric deposition of heavy metals over the last three decades is reflected in soil and foliage of 97 beech (*Fagus sylvatica*) stands in the Vienna Woods. Environ Pollut 230:561–573

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