



Geochemical and environmental investigation of sewage-irrigated soils and crops of Sabzevar, NE of Iran

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Abstract

The present study identifies the effects of sewage irrigation on the surface soils geochemistry and the concentration of heavy metals in plants of Sabzevar area, which were irrigated for a long time by wastewater. This study shows that the sewage irrigation has led to decreasing pH and increasing organic matter, and also it makes the accumulation of P_2O_5 , high-field-strength elements (Ga, Ta, Th, U and Y) and heavy metals (Cd, Co, Cu, Pb, Sn and Zn) in contaminated soils. Likewise, the concentration of rare-earth elements (REE) in contaminated soils is more than background samples with moderate enrichment of light REE compared with high REE in REE pattern diagram (mean $La_N/Lu_N = 5.77$). The calculated transfer factor and enrichment factor indexes in plants grown on the polluted soils are significantly higher than the control samples which show the heavy metal enrichment in the contaminated samples. Although the cultivated crops on this area (maize, beet, alfalfa, barely) are used only for animal feed, the heavy metal analysis indicated that the concentration of Cr, Cu, Ni and Pb in these plants, especially alfalfa and maize, is more than the maximum permitted levels defined in different standards.

Keywords Soil · Sewage irrigation · Geochemistry · Sabzevar · Iran

1 Introduction

The use of municipal and industrial sewage for agricultural irrigation in urban and suburban areas is a common practice, especially in the regions with limited freshwater sources. This method of irrigation can provide a rich source of organic matter and beneficial nutrients for plants [9, 46]. However, wastewater may contain many heavy metals and toxic elements such as As, Cd, Cr, Co, Ni, Hg, Pb and Zn. If sewage irrigation continues for a long time, excessive accumulation of toxic elements would lead to the contamination of soil and cultivated crops, which in turn has effects on the food chain quality and human health [17, 20, 43].

The sewage irrigation of agricultural soils has been increasingly used in Iran to compensate for the shortage of groundwater supply and partially solve the problem of wastewater disposal. In recent years, many studies were focused on the different aspects of sewage irrigation on the soil composition and crop yields (e.g., [16, 18, 44]). Much of these studies impress on the harmful results of wastewater irrigation which caused high elevation of heavy metal concentrations in soils and plants of various regions in Iran [14, 42]. Recently, in order to avoid environmental hazards, the Iranian Development of Environment prohibited the sewage irrigation of many vegetation, fruits and human feed crops, while the cultivation of animal feed and non-edible plants is still allowed. The farmland area to the south of Sabzevar (NE of Iran) has been

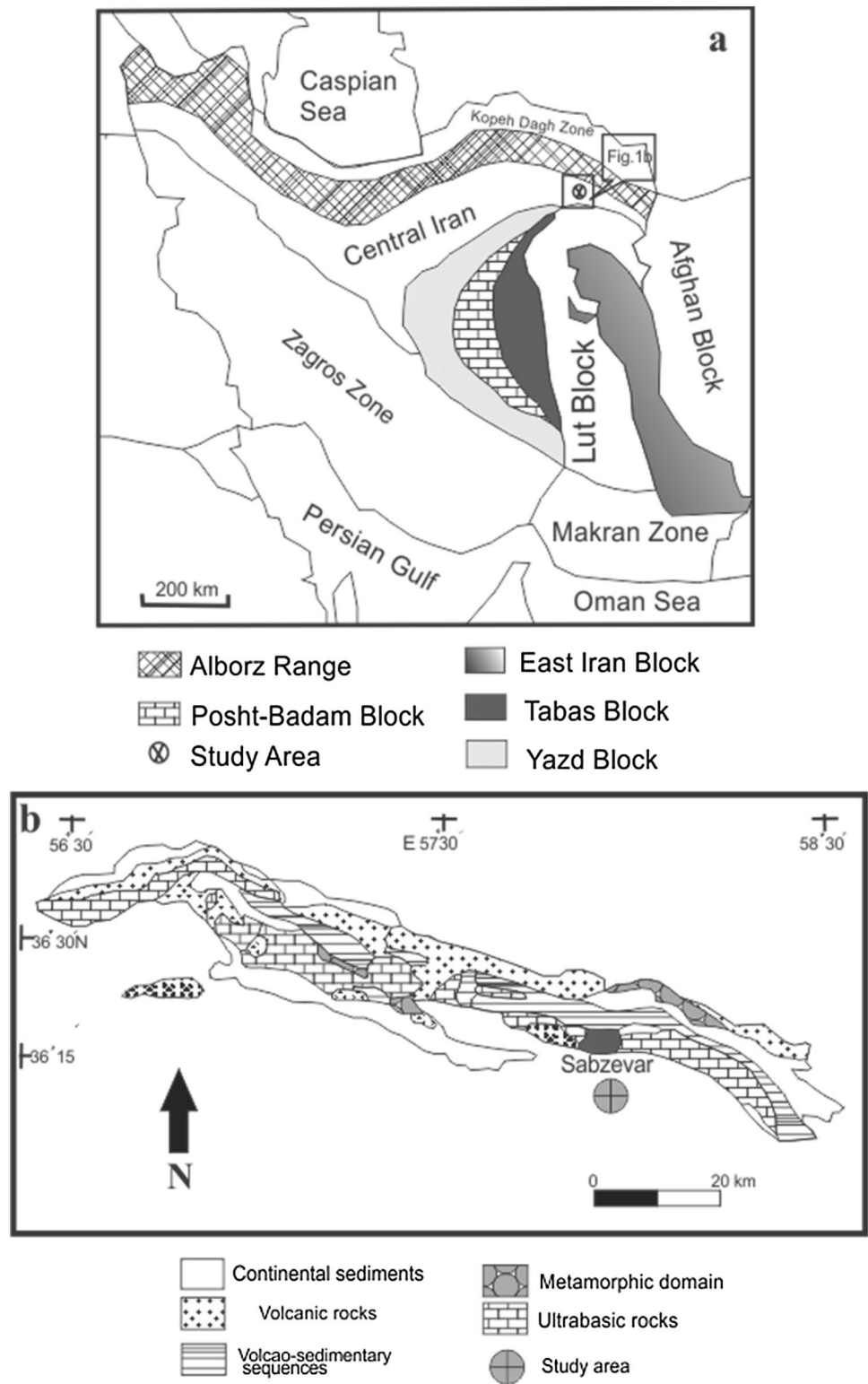
Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-019-1093-0>) contains supplementary material, which is available to authorized users.

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SN Applied Sciences (2019) 1:1065 | <https://doi.org/10.1007/s42452-019-1093-0>

Received: 10 May 2019 / Accepted: 13 August 2019 / Published online: 21 August 2019

Fig. 1 **a** The location of the studied area in the tectonic units of Iran (modified after Nabavi [34]). **b** A simple map illustrating lithological units of Sabzevar Range (modified from Rossetti et al. [39])



irrigated with wastewater for over 45 years. The cultivation of some plants such as beet, maize, alfalfa, barley, millet, sorghum (for animal feed) and cotton are permissible in the sewage-irrigated soils in this area. The regional soil composition and different relations between soil content

and physicochemical parameters have been defined by previous studies (e.g., [27, 30]). The primary goal of this study is to define the role of sewage irrigation to evoke geochemical variations in the surface soils. The next aim is the determination of heavy metal concentration in the

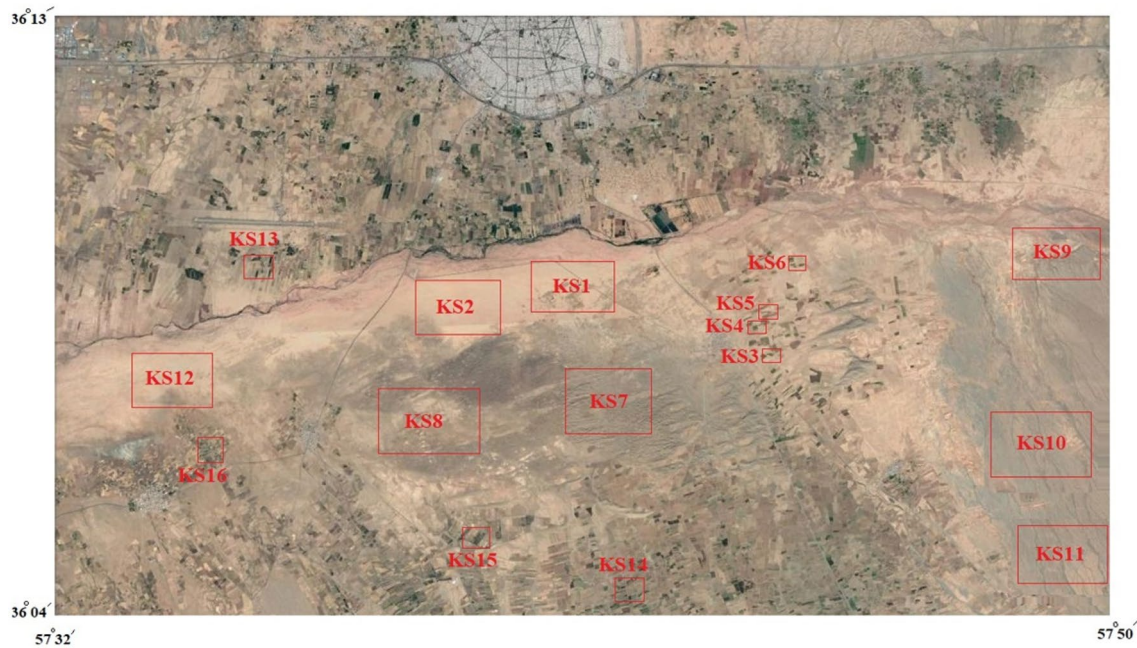


Fig. 2 The location of sampling sites in the studied area. KS1, KS2, KS7, KS8, KS9, KS10, KS11 and KS12 are the selected sites to determine background geochemistry of soils in this area. KS3 (maize farm), KS4 (alfalfa farm), KS5 (beet farm) and KS6 (barely farm) are

sewage-irrigated sites. KS13, KS14, KS15 and KS16 are maize, beet, alfalfa and barley farms which are the selected sites for well-irrigated soils

cultivated plants to monitor probable environmental hazards. The results of this study will be useful to constrain geochemical factors involving wastewater-polluted areas, and for local pollution control and management of wastewater consumption or treatment.

2 Materials and methods

2.1 Geological background and sample selection

The studied area is located to the south of Sabzevar town, NE of Iran. This area is a part of a geological unit titled Sabzevar Range (SR), which makes up the largest Iranian ophiolite mélangé. The SR is situated in the Central Iran Microcontinent (Fig. 1a) and exhibits complex geological characteristics that include folded relations [41], structural complications [6], distinct metamorphic rocks [39] and extensive tectono-magmatic evolution [22, 33]. The Sabzevar ophiolite mélangé is composed of all sections of ophiolitic sequences, but it is completely tectonized (Fig. 1b). This mélangé is formed in the Late Cretaceous extensional events resulted by back-arc rifting of Neo-Tethys [22, 39]. The ultramafic and serpentinitic rocks are the major occurrence of SR which are related to the ophiolite mélangé (Fig. 1b). In addition to the ophiolitic assemblage, there are a large number of post-ophiolitic rocks in

SR. These rocks appear as various plutonic, sub-volcanic and volcanic bodies, and many of them have adakitic properties [3, 19, 29, 40].

The studied area has even topography and is covered by alluvium deposits from northern ophiolitic mélangé (Fig. 1b). The soils of this area are mostly immature cambisols derived from weathering of those deposits. In this study, the surface soils (5–20 cm depth) were sampled with a stainless-steel hand trowel. The top-level soil (0–5 cm) was removed due to the presence of abundant waste and transported components. Sixteen sites were selected for sampling which includes four sewage-irrigated farms (as polluted soils), four well-irrigated farms (as non-polluted agricultural soils) and eight sites from not-irrigated soils of this region (as background samples). The two last groups are used as control samples to evaluate different geochemical and environmental changes induced by wastewater pollution. The location of sampling sites is shown in Fig. 2. At each sampling site, a mixed sample (near 3 kg) was collected by the integration of five subsamples. These subsamples were collected from four corners and the center of each sampling site regardless of the size area of the sampling site. The soil samples were air-dried and sieved to < 2 mm for further analyses.

The selected farms for background sites had the same agronomic practice including NPK (150 kg N, 30 kg P, 60 kg K) + manure fertilization (1 Mg dry weight solid cattle

Table 1 Physicochemical properties of studied soils

Sample no.	ID	pH	TOC	CEC	Sand	Silt	Clay
KS1	NN	7.73	0.537	13.53	54	36	10
KS2	NN	7.85	0.504	14.22	42	47	11
KS7	NN	7.79	0.435	13.83	45	43	12
KS8	NN	7.78	0.48	13.44	46	39	15
KS9	NN	7.75	0.51	13.23	47	39	14
KS10	NN	7.95	0.446	12.95	46	42	12
KS11	NN	7.69	0.559	13.7	48	40	12
KS12	NN	7.86	0.473	13.62	49	38	13
KS3	PA	7.16	1.763	15.1	35	40	25
KS4	PA	7.08	2.034	14.79	32	42	26
KS5	PA	7.11	1.985	15.37	34	41	25
KS6	PA	7.13	1.868	15.46	33	43	24
KS13	NA	7.52	0.98	14.58	34	41	25
KS14	NA	7.36	0.955	14.8	35	42	23
KS15	NA	7.48	1.025	14.65	36	41	23
KS16	NA	7.44	0.926	14.47	33	42	25
Mean	NN	7.80	0.49	13.57	47.13	40.50	12.38
SD	NN	0.08	0.04	0.38	3.48	3.42	1.60
Mean	PA	7.12	1.91	15.18	33.50	41.50	25.00
SD	PA	0.03	0.12	0.30	1.29	1.29	0.82
Mean	NA	7.45	0.97	14.63	34.50	41.50	24.00
SD	NA	0.07	0.04	0.14	1.29	0.58	1.15
<i>p</i> values		3E-09	2E-13	4E-06	1E-06	0.749	7E-10

NA non-polluted agricultural soils, NN background samples (non-agricultural non-polluted soils), PA sewage-irrigated soils (polluted soils)

manure ha⁻¹ year⁻¹). The sampling of all plants was done in September 2016. The plant samples were collected from the same area where the soil samples were gathered. In both polluted and non-polluted farms, eight plant samples were collected from edible portions of maize (grains), barely (grains), beet and alfalfa. For every plant, one sample was selected from sewage-irrigated soils (as polluted samples) and another sample was collected from well-irrigated soils (as control samples). The location and analyzed plant of each farm are described in the Fig. 2 caption. For clearing soil and other particles which adhere to the plant, we do the following steps. First, all samples were cleaned by tap water. Next, they were washed three times with deionized water. Then, the excess water was removed from samples with blotting paper, and then, samples were cut into small pieces. Finally, every sample was packed into a single bag and dried to 40 °C in an oven.

2.2 Analyses

The soil pH was measured in a 1:2.5 ratio of soil/solution (a solution of water and 1 M KCl) with a glass electrode pH meter. For measuring the total organic carbon content

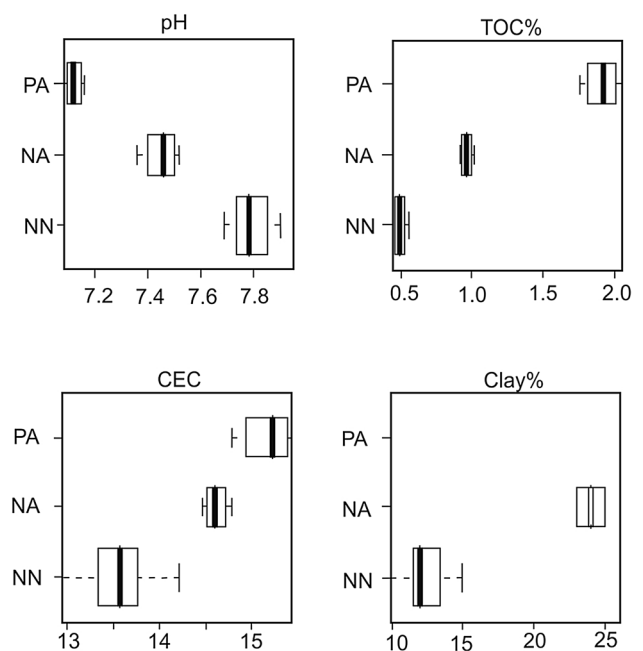


Fig. 3 The physicochemical differences (mean values) among various soils in the study area. NN=background samples, PA=sewage-irrigated soils, NA=non-polluted agricultural samples

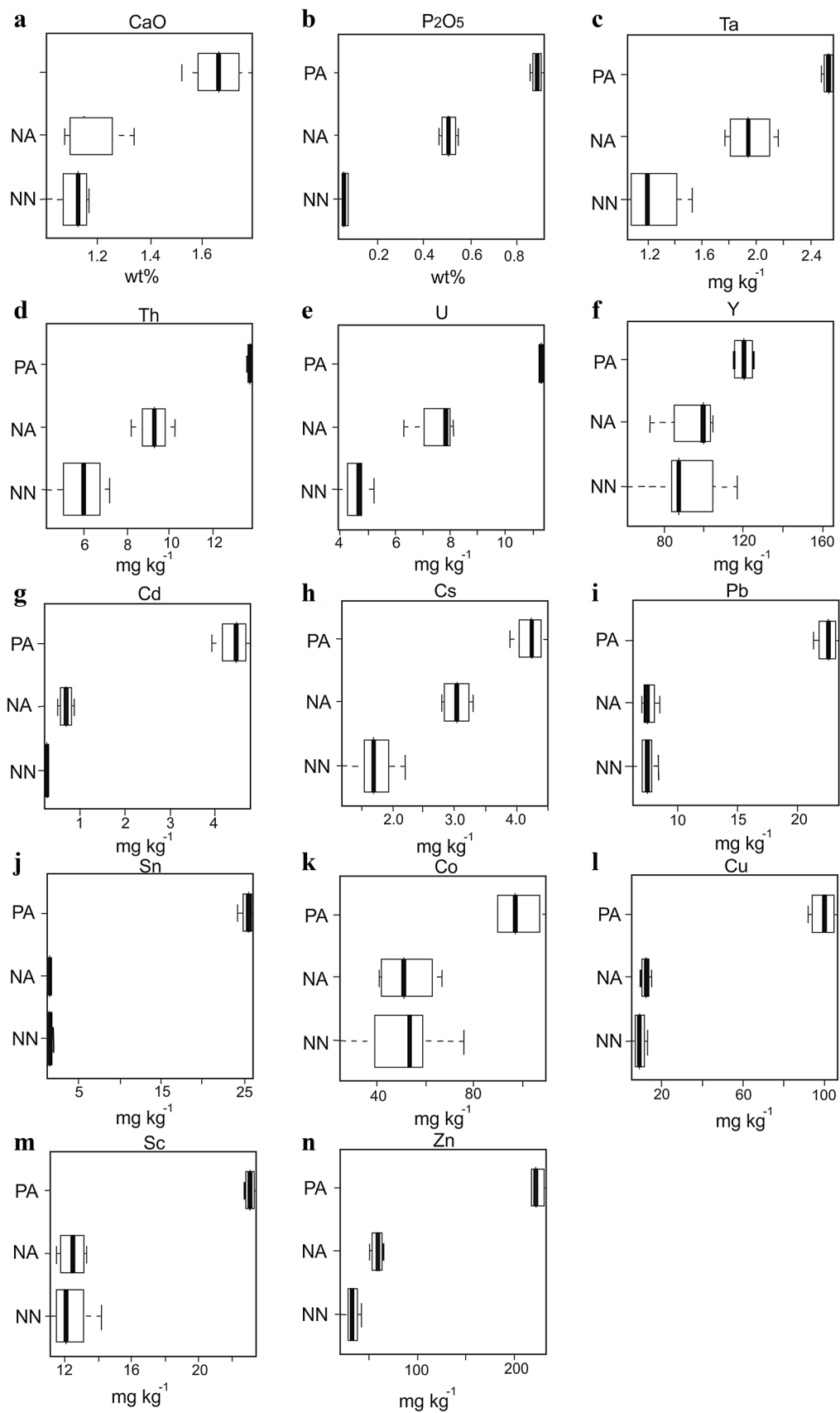


Fig. 4 Major oxides (wt%) and trace element (mg kg⁻¹) concentrations (mean values) of different soil samples. Abbreviations are given in Fig. 3

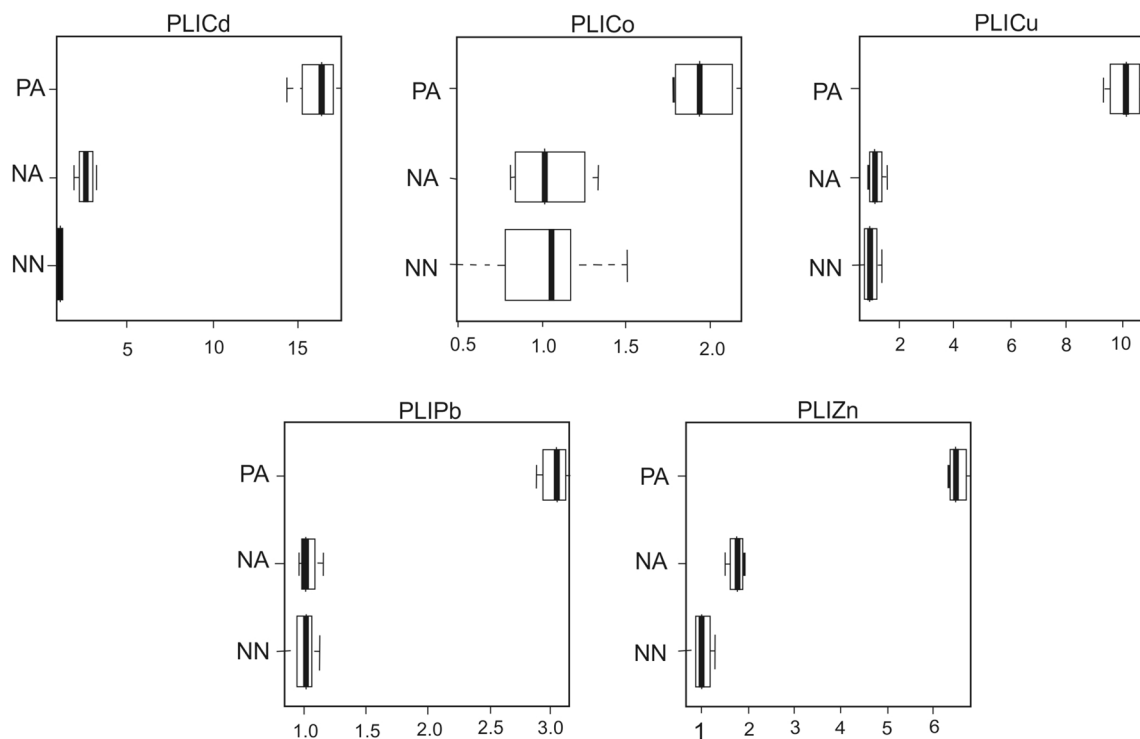


Fig. 5 The calculated average of pollution load index (PLI) in various soil samples. Abbreviations are given in Fig. 3

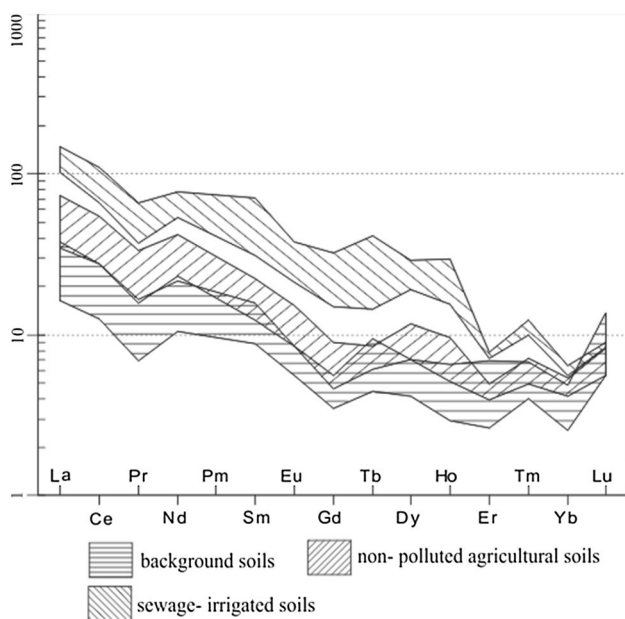


Fig. 6 Chondrite-normalized REE plot of soil samples (normalization values from Sun and McDonough [45])

(TOC) and the cation exchange capacity (CEC), the modified wet oxidation method (Walkley–Black) and Bower and Hatcher procedure [7] were used, respectively. In order to obtain the size distribution of soil samples, granulometric

analysis was carried out by sieving (sand) and sedimentation and extraction with a Robinson pipette (clay and silt), and the size fractions were classified as clay (< 0.002 mm), silt (0.002–0.05) and sand (0.05–2 mm).

To perform chemical analyses, soil samples were ground to a fine powder (< 200 nm). Major oxides were determined by XRF after fusion with lithium tetraborate. Typical precision was better than $\pm 1.5\%$ for an analyte concentration of 10 wt%. The powdered soils were digested by a strong multi-acid method: 0.25 gm of each sample was heated by a mixture of $\text{HNO}_3\text{-HClO}_4\text{-HF}$ acids, and the residual fraction was dissolved in HCl to represent the total concentration of elements. Then, the trace element concentrations were analyzed by ICP-MS. The XRF and ICP-MS analyses were performed in Actlabs laboratory, Canada, by Dolan et al.'s [13] methodology. Detection of limits of these analyzes is presented in the last rows of supplementary Table 1. Since the detection limit was not applicable for some heavy metals in ICP-MS results (Table 1, supplementary), the concentrations of Cd, Co, Cr, Cu, Ni, Pb and Zn were analyzed by flame atomic absorption spectrometer (Varian AA240) in Abram Institute, Iran.

The bioavailable content of heavy metals in surface soils was determined by DTPA (diethylene triamine pentaacetic acid) extraction using the method of Lindsay and Norwell [26]. In this method, a buffered solution of 20 mL of a 0.005-M DTPA, 0.01 M CaCl_2 and 0.1 M triethanolamine

Table 2 The heavy metal concentration (mg kg^{-1}) of soil samples resulted from DTPA extraction

Sample no.	ID	Cd	Co	Cr	Cu	Ni	Pb	Zn
KS1	NN	0.04	10.3	6.25	2.03	65.53	1.25	8.85
KS2	NN	0.04	6.57	4.49	1.29	62.51	1.58	8.13
KS7	NN	0.05	4.92	3.02	2.35	66.24	1.39	9.72
KS8	NN	0.03	10.45	4.01	1.2	66.15	1.6	6.35
KS9	NN	0.04	14.81	5.83	1.66	73.7	1.42	12.08
KS10	NN	0.04	9.16	4.47	2.29	62.38	1.48	11.85
KS11	NN	0.05	10.78	4.2	2.73	74.2	1.63	10.19
KS12	NN	0.04	12.84	4.13	1.86	65.59	1.5	9.04
KS3	PA	2.48	34.29	23.44	34.18	203.19	13.47	111.23
KS4	PA	2.26	27.92	23.61	39.87	205.56	12.58	114.8
KS5	PA	2.55	35.16	24.26	38.6	201.69	13.1	119.29
KS6	PA	2.47	27.96	23.7	35.72	206.3	13.57	108.12
KS13	NA	0.13	13.51	8.49	3.97	61.13	2.15	18.51
KS14	NA	0.22	8.73	7.25	3.18	75.05	1.81	22.67
KS15	NA	0.18	8.14	5.16	2.32	6.37	1.88	23.72
KS16	NA	0.2	11.65	6.33	2.49	73.86	1.92	21.66
Mean	NN	0.04	9.98	4.55	1.93	67.04	1.48	9.53
SD	NN	0.01	3.17	1.03	0.53	4.53	0.13	1.89
Mean	PA	2.44	31.33	23.75	37.09	204.19	13.18	113.36
SD	PA	0.13	3.93	0.36	2.60	2.13	0.45	4.80
Mean	NA	0.18	10.51	6.81	2.99	54.10	1.94	21.64
SD	NA	0.04	2.52	1.41	0.75	32.44	0.15	2.25
<i>p</i> values		5E-17	2E-07	6E-13	6E-15	4E-09	2E-18	1E-16

was used to dissolve 10 g of soil sample for 2 h. Then, the contents were filtrated and analyzed for Cd, Co, Cr, Cu, Ni, Pb and Zn by flame atomic absorption spectrometer. The analysis of BCR-100 standard showed that the precision of resulted data was $\pm 5\%$. The dried plant samples were ground in a stainless-steel mill and digested in a mixture of distilled HNO_3 and HClO_4 (in the ratio of 3:1); and the heavy metal concentrations were analyzed by atomic absorption spectrometer.

All the statistics were performed by means of the SPSS version 17.0 software for Windows. Data from the different chemical measurements were subjected to one-way analysis of variance (ANOVA). The statistically significant difference was set at 5%. Mean values obtained for the variables studied in the different groups were compared by one-way ANOVA (Duncan's multiple ranges) assuming that there were significant differences among them when the statistical comparison gave $p < 0.05$.

2.3 Evaluation of pollution and quality indexes

A modified pollution load index (PLI) was calculated as the following equation to evaluate heavy soil contamination by sewage irrigation [48].

$$\text{PLI} = C_{\text{soil}}/C_{\text{reference}}$$

C_{soil} and $C_{\text{reference}}$ are the concentrations of heavy metal in the contaminated and background samples, respectively. The mean values of non-polluted non-agricultural samples (NN samples of supplementary Table 1) were used as the background concentration for each element.

The transfer factor (TF) was calculated by dividing the concentration of an element in a plant by the total element concentration in the soil [48].

Further to investigate the role of sewage irrigation on the plant composition, enrichment factor (EF) was calculated using the following equation [8]:

$$\text{EF} = [\text{concentration of metal in a plant grown on the polluted soil}/\text{concentration of metal in polluted soil}]/[\text{concentration of metal in a plant grown on control soil}/\text{concentration of metal in control soil}].$$

3 Results and discussion

3.1 Physicochemical parameters

The physicochemical properties of soil samples show systematic variations between polluted, non-polluted agricultural and background soils (Table 1). The polluted samples have the highest values of TOC (1.7–2.03%,

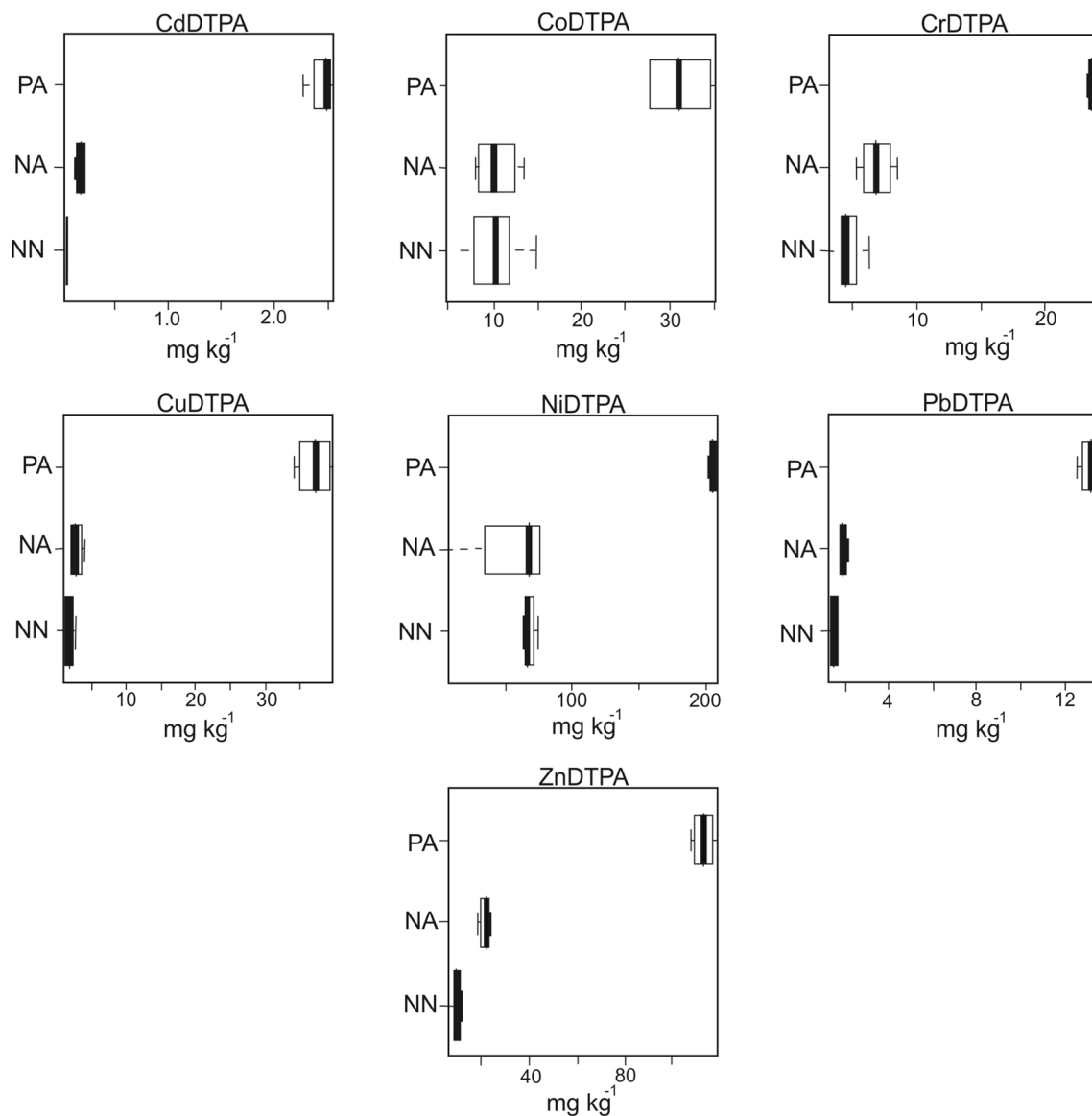


Fig. 7 The mean values of DTPA extraction of heavy metals in the studied soils. Abbreviations are given in Fig. 3

mean 1.91 ± 0.12), CEC (14.79–15.48, mean 15.18 ± 0.30 cmol(+)/kg) and clay content (24–26%, mean $25\% \pm 1$) while pH measurements in these soils (7.08–7.16, mean 7.12 ± 0.03) are lower than other samples. In other side, background samples are distinguished by high pH (7.69–7.95, mean 7.80 ± 0.08) and low TOC (0.43–0.56%, mean $0.49\% \pm 0.04$), CEC (12.95–14.72, mean 13.57 ± 0.38 cmol(+)/kg) and clay content (10–15%, mean $12\% \pm 2$); non-polluted agricultural soils have intermediate quantities of these parameters (Table 1 and Fig. 3).

The pH is a key parameter in controlling the metal mobility and availability (e.g., [32]), and most of the metals tend to be available at lower acidity [37]. The organic content of the soil is another important factor that positively relates to the heavy metal quantities [24]. Many

studies indicate that wastewater irrigation results in addition to TOC in soil (e.g., [10, 23]). In the studied area, long-time sewage irrigation decreased soil pH (7.1 vs. 7.8) and increased dissolved organic carbon (1.9 vs 0.5%) compared to background soils, which could enhance the phyto-availability of heavy metals. Other chemical data approved this assumption which will be discussed in the next sections. Agricultural activity has increased clay content of the studied soils that is a common characteristic of the agricultural soils in the Sabzevar area [29, 30].

3.2 Soils geochemical composition

The geochemical compositions of the studied soils are presented in supplementary Table 1. All samples show similar

Table 3 The calculated bioavailability (%) of heavy metals in the studied soil samples

Sample no.	ID	Cd	Co	Cr	Cu	Ni	Pb	Zn
KS1	NN	16.00	19.01	0.50	20.14	9.02	20.13	28.06
KS2	NN	14.29	20.81	0.50	18.70	9.69	20.82	28.10
KS7	NN	16.13	19.74	0.37	19.29	10.03	19.39	27.39
KS8	NN	13.64	20.05	0.51	20.30	9.40	19.16	28.22
KS9	NN	13.79	19.53	0.52	19.26	9.81	20.76	27.61
KS10	NN	14.29	19.62	0.46	18.42	10.06	19.84	28.03
KS11	NN	16.67	19.93	0.60	19.93	10.42	20.12	27.84
KS12	NN	15.38	20.30	0.51	20.35	9.98	19.95	28.38
KS3	PA	54.39	32.86	2.51	37.07	25.01	58.95	50.92
KS4	PA	57.36	31.08	2.49	37.35	25.10	58.98	50.95
KS5	PA	52.90	31.81	2.51	37.42	25.06	58.82	51.15
KS6	PA	55.76	31.01	2.58	36.91	24.97	57.99	49.88
KS13	NA	25.49	20.16	0.82	25.40	10.03	25.21	36.03
KS14	NA	25.29	20.17	0.72	25.75	9.96	25.56	36.25
KS15	NA	27.69	19.90	0.62	17.60	0.92	25.34	36.10
KS16	NA	27.03	19.69	0.69	24.83	10.20	25.40	36.74
Mean	NN	15.02	19.87	0.50	19.55	9.80	20.02	27.95
SD	NN	1.17	0.54	0.06	0.74	0.43	0.58	0.33
Mean	PA	55.10	31.69	2.52	37.19	25.03	58.69	50.73
SD	PA	1.90	0.86	0.04	0.24	0.06	0.47	0.57
Mean	NA	26.37	19.98	0.71	23.39	7.78	25.38	36.28
SD	NA	1.17	0.23	0.08	3.88	4.58	0.15	0.32
<i>p</i> values		3E–15	1E–13	7E–16	7E–09	6E–08	5E–21	4E–19

content in major oxides of SiO_2 , TiO_2 , Al_2O_3 , FeO_t , MgO , K_2O and Na_2O . The concentration of CaO in polluted soils is slightly higher than that in the other samples; but P_2O_5 concentration in background samples (0.04–0.08 wt%) is much less than that in non-polluted agricultural (0.47–0.53 wt%) and polluted (0.86–0.92 wt%) soils (Fig. 4a, b).

The three different groups of selected soils display distinct trace element contents. In comparison with other samples, the polluted surface soils show a generally higher concentration of many high-field-strength elements (HFSE) such as Ga, Ta, Th, U and Y (supplementary Table 1; Fig. 4c–f). In particular, these soils are enriched in heavy metals of Cd, Co, Cu, Pb, Sn and Zn (Fig. 4g–n).

The PLI values emphasize on the high enrichment of Cd, Cu, Zn, Pb and Co in the contaminated soils (Fig. 5). The enrichment of these metals in soils could result in different fertilizers or wastewater irrigation [1, 38]. As it is shown in supplementary Table 1 and Fig. 5, the non-polluted agricultural soils of SR have slightly higher heavy metal concentration than background which could be ascribed to phosphatic fertilizer, but severe metal enrichment of polluted samples (Fig. 5) is originated from sewage irrigation.

All samples have a high concentration of Ni (620–826 mg kg^{-1}) and Cr (695–1035 mg kg^{-1}), and there is no the obvious difference between polluted and other soils content (supplementary Table 1). However, the total

concentration of Ni and Cr could not be indicator of sewage-irrigation pollution in SR soils because not only the existence of high total concentration of Cr and Ni is an evident geochemical characteristic of serpentinitic and ultramafic-derived soils [4] but also SR soils normally have high concentration of these elements [30].

The use of rare-earth elements (REE) in soil investigations has been increasingly developed in recent years. The REE could be an appropriate indicator to define pedogenetic processes, weathering condition and source identification of soils [12, 25]. The REE composition of SR surface soils is significantly dependent on parent materials [28, 31]. So, the investigation of sewage irrigation on REE content could be helpful to determine soil geochemical variations in this area. In the studied area, background samples have relatively low REE concentrations (mean $\Sigma\text{REE} = 40.73 \text{ mg kg}^{-1}$) with moderate enrichment of light REE (LREE) compared with heavy REE (HREE) in REE pattern diagram (mean $\text{La}_N/\text{Lu}_N = 5.77$; Fig. 6). The REE concentration increases in non-polluted agricultural soils (mean $\Sigma\text{REE} = 90.13 \text{ mg kg}^{-1}$; mean $\text{La}_N/\text{Lu}_N = 12.45$); and polluted samples show the highest REE quantities (mean $\Sigma\text{REE} = 180.44 \text{ mg kg}^{-1}$) with intense enrichment of LREE/HREE (mean $\text{La}_N/\text{Lu}_N = 20.31$; Fig. 6). These results suggest that increasing REE concentration and enhancing LREE/

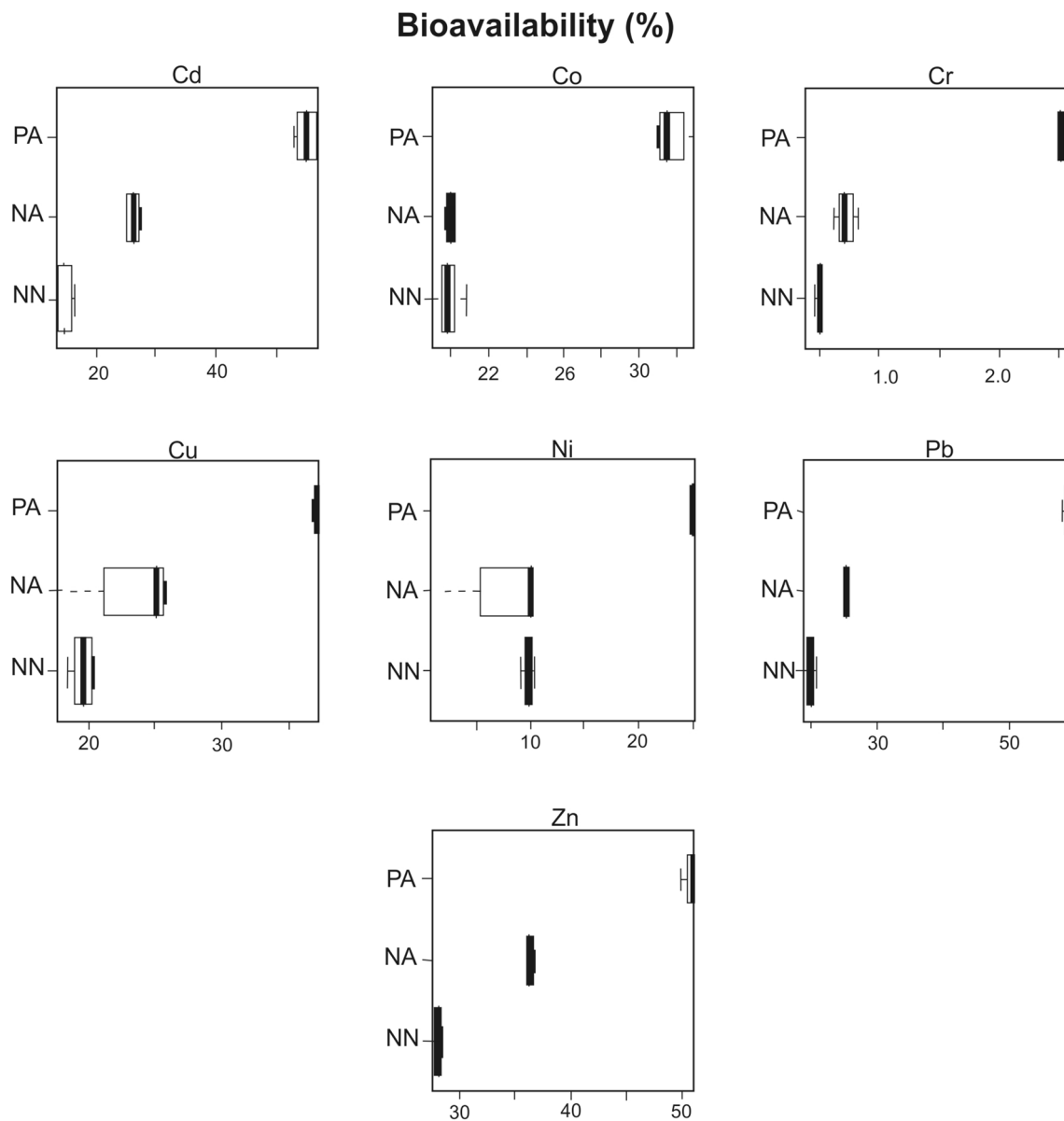


Fig. 8 The bioavailability (%) comparison of different soil samples. Abbreviations are given in Fig. 3

HREE are the consequences of agricultural activities and wastewater irrigation in the surface soils of SR.

3.3 Soil bioavailability

The DTPA extraction method provides a suitable proxy for evaluating heavy metal bioavailability of plants in soils and soil solutions, especially in serpentine and ultramafic-derived soils [21, 35]. The results of DTPA extraction for soil samples are shown in Table 2. The polluted soils have the highest concentration of heavy metals in DTPA extraction (Fig. 7). In this regard, Ni and Zn demonstrate higher values, while Cd and Pb release lower concentrations

(Table 2). However, the order of extractable content is not the same in all samples, so that some background soils (KS1, KS8, KS9 and KS11 samples) have higher extractable Co than Zn (Table 2).

In the environmental investigation of soil chemistry, the detecting bioavailable capabilities of soil samples are a crucial issue. Here, the bioavailability is defined as DTPA-extractable percent value divided by total concentration. The bioavailability values order in the studied soils is completely different from DTPA extraction, and there are various trends among polluted, background and non-polluted agricultural samples (Table 3). Cr and Ni show the lowest bioavailability in all soils. Chromium should be considered

Table 4 The heavy metals concentration (mg kg^{-1}) of plants

Sample no.	ID	Plant	Cd	Co	Cr	Cu	Ni	Pb	Zn
KS3	CS	Maize	0.12	2.86	10.35	39.83	112.79	5.69	78.46
KS5	CS	Beet	0.19	2.16	8.56	31.42	96.22	1.14	72.5
KS4	CS	Alfalfa	0.35	2.23	23.74	103.24	178.2	7.65	93.38
KS6	CS	Barely	0.28	0.18	4.57	14.39	12.34	0.47	131.6
KS13	NS	Maize	< 0.01	0.23	2.82	5.31	4.37	0.08	9.18
KS14	NS	Beet	0.02	0.28	2.06	3.9	3.95	0.11	8.7
KS15	NS	Alfalfa	0.02	0.47	4.19	13.86	10.45	0.19	15.22
KS16	NS	Barely	< 0.01	0.05	0.23	4.13	0.52	0.02	17.23
FAO/WHO			0.1	50	2.3	73	67	0.3	100

CS contaminated samples (grown on sewage-irrigated soils), NS non-contaminated samples (well-irrigated soils)

The last row is the maximum permissible limit of crops defined by the FAO/WHO [15]

Table 5 The calculated transfer factor (TF) of heavy metals for different plants of the studied area

Sample no.	ID	Plant	Cd	Co	Cr	Cu	Ni	Pb	Zn
KS3	CS	Maize	0.03	0.03	0.01	0.43	0.14	0.25	0.36
KS5	CS	Beet	0.04	0.02	0.01	0.30	0.12	0.05	0.31
KS4	CS	Alfalfa	0.09	0.02	0.03	0.97	0.22	0.36	0.41
KS6	CS	Barely	0.06	0.00	0.00	0.15	0.01	0.02	0.61
KS13	NS	Maize	–	0.00	0.00	0.34	0.01	0.01	0.18
KS14	NS	Beet	0.02	0.01	0.00	0.32	0.01	0.02	0.14
KS15	NS	Alfalfa	0.03	0.01	0.01	1.05	0.02	0.03	0.23
KS16	NS	Barely	–	0.00	0.00	0.41	0.00	0.00	0.29

unavailable because its bioavailability is less than 1% in unpolluted samples and does not exceed 2% in the polluted soils (Fig. 8). As a whole, background samples have low heavy metal bioavailability with maximum values of Zn (mean 28%) followed by Pb, Cu and Cd. The bioavailable content of heavy metals in non-polluted agricultural soils is the same or slightly higher than that in background samples, while the bioavailable values of heavy metals become extremely high in the polluted soils, so that Pb, Cd and Zn show > 50% bioavailability (Fig. 8). This means that agricultural activities alone have no effect on the amount of bioavailability, but irrigation with sewage has been an effective factor in increasing bioavailability.

3.4 Heavy metal concentration of plants

The heavy metal concentration of analyzed plants is shown in Table 4. The heavy metal contents of edible parts change dramatically among various plants and different elements. All plants cultivated in sewage-irrigated soils accumulate higher heavy metals in comparison with control samples. The Cd concentrations of the control samples are very low ($\leq 0.02 \text{ mg kg}^{-1}$), while polluted plants have Cd concentrations higher than 0.12 mg kg^{-1} Cd (Table 4). In the plants of polluted soils, although the amount of Co concentration

in maize, beet and alfalfa is similar ($2.16\text{--}2.86 \text{ mg kg}^{-1}$), barely has a significantly lower Co concentration. The highest content of Cr is accumulated in alfalfa, and the lowest value is obtained from barley (Table 4). The control plants have low Cu and Ni concentrations (less than 14 mg kg^{-1} and 11 mg kg^{-1} , respectively), while polluted samples contain elevated values of these metals over 100 mg kg^{-1} alfalfa for Cu and maize and alfalfa for Ni (Table 4). The Pb concentration in polluted plants exceeds 5 mg kg^{-1} in alfalfa and maize samples which are cultivated in sewage-irrigated soils. The concentration of Zn in barely, unlike the other heavy metals, shows the highest values, so that polluted sample releases 131.6 mg kg^{-1} Zn (Table 4). The concentrations of Cd, Cr, Ni and Pb in all plants cultivated on the polluted soils exceed the maximum permissible limit of crops [15, 36] (Table 4). The Co concentrations are below the permissible limit, and alfalfa and barely have a higher concentration of Cu and Zn than the permissible limit, respectively. However, as mentioned before, the plants cultivated in the studied area would not be consumed by humans. The permissible limit legislations are not comprehensive for animal feeds and do not include all heavy metals. The maximum standard concentrations have been determined as 0.5, 10, 35 and 5 mg kg^{-1} for Cd, Cr, Cu and Pb, respectively, for animal feed in China

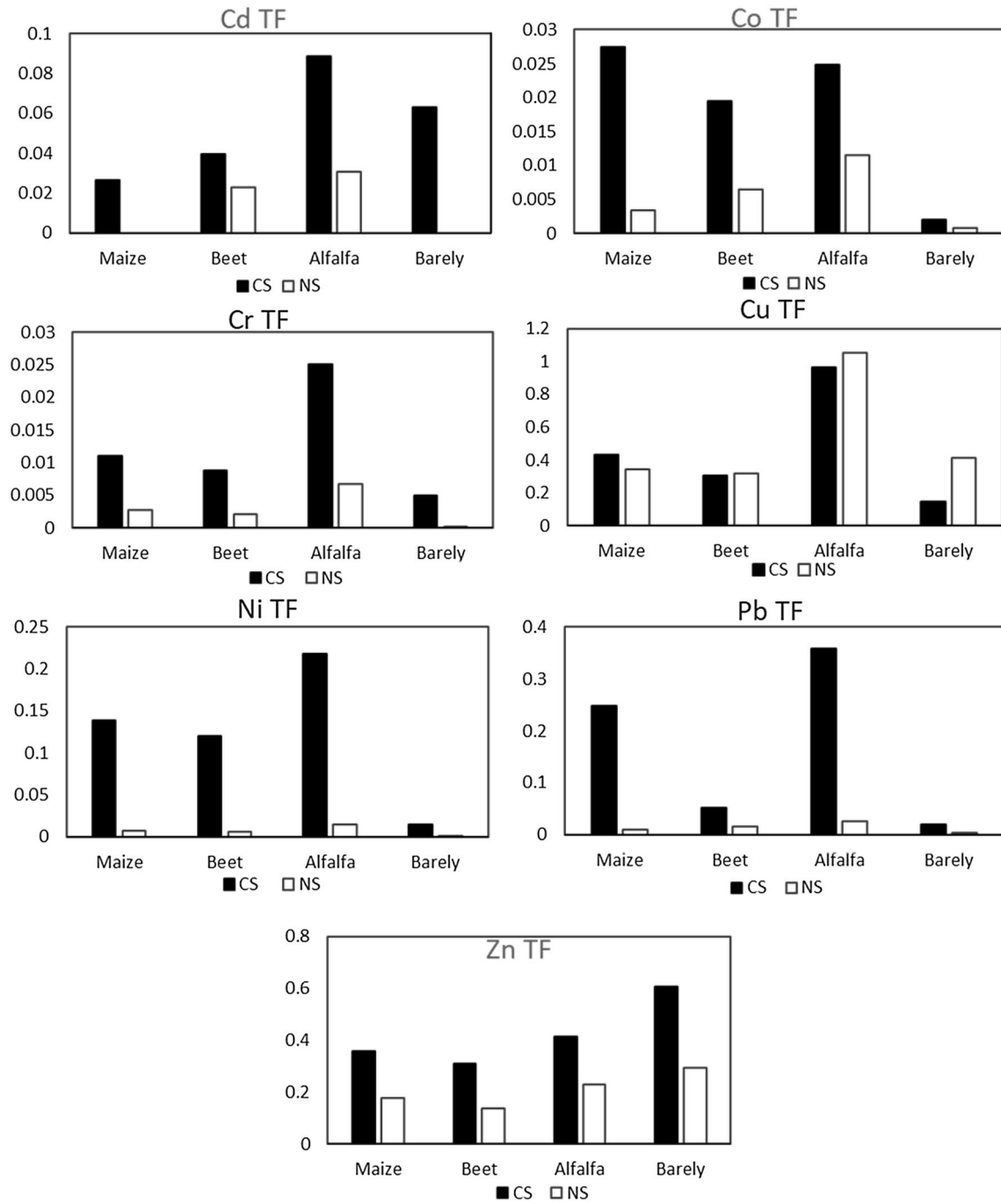


Fig. 9 Different transfer factor (TF) values of heavy metals for plants grown on the polluted (CS) and un-contaminated (NS) soils

Table 6 The calculated enrichment factor (EF) of heavy metals in plants cultivated on the sewage-irrigated soils

Plant	Cd	Co	Cr	Cu	Ni	Pb	Zn
Maize	–	7.99	4.06	1.27	19.36	26.55	2.01
Beet	1.71	3.02	4.32	0.96	22.81	3.29	2.23
Alfalfa	2.89	2.16	3.76	0.92	14.48	14.01	1.79
Barely	–	2.36	19.73	0.36	20.80	7.59	2.08

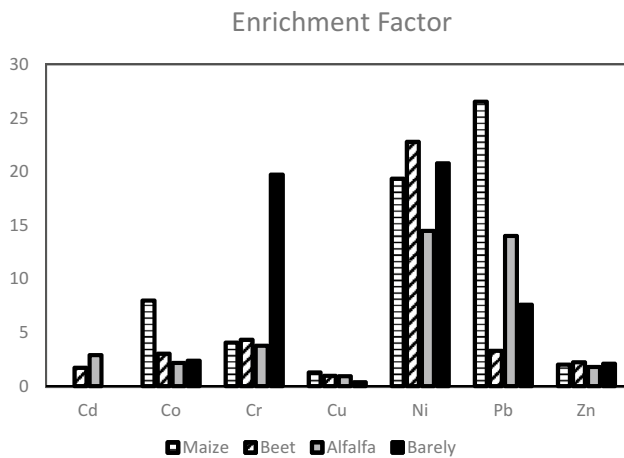


Fig. 10 The calculated enrichment factor (EF) of heavy metals in sewage-irrigated plants of SR

[47]. In comparison with this standard, polluted alfalfa and maize have a higher concentration of Cr, Cu and Pb than permissible limits.

3.5 Transfer factor (TF) and enrichment factors (EF) of heavy metals

The resulted TF values are presented in Table 5. The main reasons for variations in transfer factors among different plants are various concentrations of elements in soils and differences in element uptake by every plant [2, 11]. The TF is a principal factor in controlling environmental risks to consumers (animals or humans) for any specific plant or metal [20, 46]. Generally, the contaminated plants have higher TF than the control samples (Fig. 9). High TF values indicate relatively poor retention in soils or reflect better efficiency of plants to absorb the element, and in turn, low TFs represent the intense sorption of the element to the soil colloids [5]. Similar to SR, high content of heavy metal in soils and elevated TF values of plants were reported in other sewage-irrigated areas (e.g., [8, 17, 46, 48]).

From Table 6, it is understood that all heavy metals except Cu show high enrichment in the plants grown on the sewage-irrigated soils. For example, the EF is very high for Ni and Pb in maize and alfalfa, for Ni in beet, and for Ni and Cr in barely (Fig. 10).

4 Conclusion

Long-term sewage irrigation induced distinctive geochemical changes in the soils to the south of Sabzevar, NE of Iran. These soils have been intensely enriched in many heavy metals, HFSE and REE compared to background

samples. The wastewater irrigation has led to a decrease in pH and increase in TOC in soils, which in turn enhanced heavy metal bioavailability. The concentration of heavy metals in plants that were cultivated on the sewage-irrigated soils is significantly higher than control samples. The calculated TF and EF indexes indicate that heavy metal adsorption in plants that grow in polluted soils is considerably higher than that in other samples. Although animal feed plants are allowed to cultivate in sewage-irrigated areas, the concentration of heavy metals such as Cr, Cu and Pb in some plants such as alfalfa and maize is higher than all standard levels determined for crops or animal feed. Therefore, it is necessary to keep regular monitoring of toxic elements in the sewage-irrigated soils and plants and reconsider environmental rules that permit animal feed crops in the intensely polluted areas such as the studied area.

Acknowledgements Some analytical cost of this Project was funded by Payame Noor University (Grant No. 518407). Authors would like to thank two anonymous referees who provided valuable suggestions for improving the quality of the paper.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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