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Elemental Composition, Leachability Assessment and Spatial Variability Analysis of Surface Soils in the Mugan Plain in the Republic of Azerbaijan

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Abstract

The Republic of Azerbaijan has suffered from low agricultural productivity caused by soil salinization and erosion, and limited and insufficient soil data are available for economic and political reasons. In this study, soil elemental composition and heavy metal levels were assessed by comparing the results of XRF and ICP-OES analyses for the first time. Leachability assessment and spatial variability analysis were conducted to understand the soil salinization properties, and 632 surface soil samples categorized as agricultural (Ag) or salt-affected (SA) soils from the Mugan Plain were collected and analyzed. Based on our observations, the elemental concentrations of Ca, Fe, Cl and S were high among 20 elements compared with the median values for world soils. Apatite, calcite, gypsum, quartz, olivine, microcline and jarosite were proposed as possible mineral structures. The heavy metal guidelines suggested by the neighboring country of Georgia would be appropriate for assessing heavy metal contamination, and Ni and Pb were the most concerning elements. Leachability assessment confirmed that 99 % of the cationic ions were cationic salts and Na was the most problematic ion. Analysis of the electrical conductivity and sum of leachates showed that the exchange of interlayer cations, dissolution of minerals with low dissolution rates, transformation of metal (hydr)oxides and additional precipitation would be the reasons for this disparity. More leachable salts were accumulated in the lowland area, which is due to water movement and high evaporation. The spatial analysis results confirmed the reciprocal relationship between total Ca and total Fe and between total Fe and DW-leached Fe. This result indicates that less-stable iron complexes are prevalent in SA soils, while stable iron complexes are found in Ag soils. We believe that this approach can provide a foundation for the international study of Azerbaijani soil by sharing soil and salinization data with researchers worldwide and can help to diminish or solve agricultural problems in both Azerbaijan and neighboring countries suffering from soil salinization.

Keywords

Republic of Azerbaijan, soil salinization, elemental composition, heavy metal level, leachability test, spatial analysis

1 Introduction

The Republic of Azerbaijan (hereafter simply Azerbaijan) is a former member of Soviet Union, and the dissolution of Soviet Union led to the independence of Azerbaijan in 1991. The energy industry, including oil and natural gas, has accounted for over 80 % of Azerbaijan's exports in recent decades, and the recent oil price shock in 2014 dropped the gross domestic product (GDP) from 75.24 billion USD in 2014 to 37.87 billion USD in 2016, according to data from the World Bank. In addition, only 2 % of the labor force is employed in the energy industry, while over 40 % are in the agricultural sector, but the latter group only contributes less than 5 % of GDP. The reason for this low agricultural productivity is due to legacy from the Soviet time, various geological and environmental parameters, such as 1) high concentrations of salt in the soil caused by uplifted sediments; 2) low precipitation and water resources; 3) soil erosion from mountains and hillside fields, which represent 60 % of the total area; and 4) lack of knowledge and technology regarding soil characterization (Babaev et al., 2015; Feyziyev et al., 2016; Goverment of The Republic of Azerbaijan, 2014; Oglu, 2018). Despite these problems, agriculture in Azerbaijan still has high potential because of the various climate regions, 4.6 million ha of arable land, neighboring markets and newly installed irrigation systems (Goverment of The Republic of Azerbaijan, 2014; Oglu, 2018). However, to the best of our knowledge, there are only a few international studies reporting soil characteristics for a limited area in Azerbaijan; the data are limited because different soil analysis technologies, mainly from the Soviet Union, have been applied in Azerbaijan and modern analytical technology to characterize soil properties is lacking (Hommels et al., 2003). These reasons have blocked the development of modern agricultural and soil management systems in Azerbaijan. The Mugan Plain is located northwest of Iran in the southern part of Azerbaijan and is the most arable land in Azerbaijan. Many canals, called Kahriz in Azerbaijani, have been developed and are operated as underground water tunnels to supply water and prevent evaporation and contamination; however, the Mugan Plain still has severe salinity problems, and hot spots with high levels of salinity are easily observable. For this reason, understanding the fundamental soil properties in the Mugan Plain is essential to understanding Azerbaijani soils and to preparing further plans for agricultural productivity and desalinization (Babaev et al., 2015; Oglu, 2018).

Fundamentally, understanding soil characteristics and elemental concentrations is important to assess agricultural productivity and environmental soil quality, especially in developing countries (Towett et al., 2015). The soil elemental composition and distribution yield not only basic information to understand the reasons behind and progress of soil salinization problems but also the nutrient levels of soils for crop cultivation and the hazardous elements that may be transferred to humans through the crops (Frouz et al., 2011; Han et al., 2014). Only 16 % of 4.6 million ha has been cultivated as arable land because of soil erosion and salinization, and 44 % of the arable land suffers from soil salinization, which causes severe problems in agricultural productivity (Goverment of The Republic of Azerbaijan, 2014). In contrast to salinization data, soil pollution levels have not been previously reported. It is difficult to quantify heavy metal levels and establish guidelines to regulate contamination; thus, the toxic heavy metals and trace elements should be fully identified to enable the further development of agriculture in Azerbaijan.

Various techniques can be used to determine the elemental composition of soil; X-ray fluorescence (XRF) and inductively coupled plasma optical emission spectroscopy (ICP-OES) instruments were delivered to Azerbaijan and used for this study. XRF is a versatile tool to measure solid-phase samples, and no pretreatment is required, while ICP-OES has greater accuracy and can be used to detect trace levels in both the solid and water phase (Schneider et al., 2016). Comparing results from both techniques enables better interpretation of the elemental composition. Not only the elemental composition but also the mineral structure or binding mechanism is important to evaluate the availability of individual elements. X-ray diffraction (XRD) is the most suitable technique to analyze such information, but this method was not available for this study; thus, a leachability assessment was conducted to evaluate how various elements leach out to the water system and organisms (Janoš et al., 2010).

Spatial analysis is a type of geographical analysis used to mathematically and geometrically interpret spatially expressed patterns of natural conditions or human behavior (Emadi and Baghernejad, 2014; Towett et al., 2015). Recent developments in remote sensing and geographic information systems have enabled us to see results more clearly and easily with better spatial information (Daliakopoulos et al., 2016). The results of elemental composition and leachability assessment are essential to understand the fundamental properties of Azerbaijani soils, but the spatial distribution of such characteristics is also crucial to present the results to the government and public in a more easily understandable fashion.

Therefore, the objectives of this study were to 1) determine the elemental composition to achieve a fundamental understanding of Azerbaijani soils, 2) evaluate the results obtained using XRF and ICP-OES to collect accurate and correct data, 3) appraise the heavy metal levels using guidelines from other countries, 4) assess leachability to indirectly estimate the binding mechanism, and 5) interpret the spatial variability in elemental composition and leachability to evaluate the soil quality and improve agricultural productivity.

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2 Materials and Methods

2.1 Study area

All surface soil samples were collected from the Mugan Plain in Azerbaijan. The Mugan plain is geographically a part of the biggest lowland of the Caucasus region, Kur-Aras lowland. It is originally a large plain located in southern part of Azerbaijan and northern part of Iran (Fig. 1). Its main area is located within Azerbaijan (approximately 0.5 million ha). As its entire territory is at elevations (10-33 m) below sea level, accumulation processes have played an important role in formation of homogeneous topography, geology and soil continuum. Parent materials are mostly alluvial in the north, marine sediments in the south and east, lacustrine sediments in the central part, alluvial-proluvials in the south and south-west. Depending on the geomorphological structure and origin of the sediments, ground water level largely varies, from 0.5 m to a few meters. It has an arid climate with a mean annual precipitation and temperature of 24.5 mm and 14.9 °C, respectively (based on Shirvan City).

The grid sampling method was originally planned, but grid sampling was not completely applied due to access limitations to private land and insufficient time and resources. A total of 532 samples were collected with GPS locations for further analysis. The Mugan Plain has two distinctive sections: desert-like salt-affected soil in the middle and agricultural soil surrounding it (Fig. 1). Based on the presence of vegetation, the collected samples were categorized as agricultural soils (Ag soils) and salt-affected soils (SA soils) for further data interpretation. The two regions have been preliminarily addressed by Azerbaijani soil scientists, and the results are available in English in the National Atlas published by the government of the Azerbaijan Republic (2014). The Ag soils mainly consist of kaolinite with 0.25-0.5 % salt, while the SA soils have a majority of montmorillonite with over 1 % salt concentration. The soil texture has been identified as clay sandy loam for both soils, and the infiltration rate is 0.1-0.5 mm min^{-1}. The soils have 100-150 ton ha^{-1} organic matter, >9 % iron oxides, >57 % silicon oxide and good nutrient levels (no specific description). The average elemental concentrations of Zn, Co, Mn and Mo in the reference text were 62, 15.6, 1225 and 1.8 mg kg^{-1}, respectively (Goverment of The Republic of Azerbaijan, 2014).

2.2 Physicochemical characterization

The collected soils were air-dried, sieved to a particle diameter of <2 mm, and homogenized in preparation for further analysis. The soil pH and electrical conductivity (EC) were potentiometrically measured with a pH and EC meter (Orion 3 Star, Thermo, USA) in soil solution after agitating 5 g of soil sample with 25 ml of distilled water in a

50 mL polystyrene conical tube. For elemental composition, the soil samples were ball-milled, and a sample cup with polypropylene film was filled with the ground samples. Three different wavelengths of XRF (S1 Titan 600, Bruker, Germany) were emitted for 20 s each, for a total of 60 s per sample, and triplicate analysis was employed for all XRF measurements in the laboratory. The average and standard deviation of each sample were calculated using Instrument Tools software (Bruker, Germany). A total of 25-35 elements were detected in XRF analysis, and 20 elements were identified above the limit of detection (LOD). Oxide phase calculations were automatically applied by the XRF software; thus, Al_2O_3, K_2O, MgO and SiO_2 were identified as oxide minerals at the elemental concentrations measured. Fe, Mn, Ca, Cu, Na, P, S, Cl and Zn were identified as abundant elements, while As, Cr, Co, Ti, Ni, Se and V were determined as potential hazardous elements. The reproducibility of measurements was ensured by measuring reference materials provided by the manufacturer for every 30 measurements, and no significant changes were observed during measurement (C.V.<7.3 %). The XRF data were compared with the data obtained by ICP-OES with aqua regia digestion, as described below. Total 532 samples were collected, and different number of samples was employed for further analysis. The sample number was 532 for soil pH and EC, 346 for XRF, 93 for leachability assessment, and 116 for pseudo-total concentration by ICP-OES because of limitation in the resource and manpower for the experiment.

2.3 Leachability Assessment

Leachability assessment is used to evaluate the mobility of elements, and the method used here was modified from a previous study (Cappuyns and Swennen, 2008). Distilled water (DW) and aqua regia (AR) were employed; DW created leaching conditions simulating rainfall conditions, and AR was used to determine the pseudo-total concentration of elements. For the DW leaching test, the soil solutions from the pH and EC measurements were employed to save resources and time. After the pH and EC measurements were finished, the samples were equilibrated for 7 days; then, the soil solution from the pH and EC measurements was filtered with filter paper (5 μm pore size), and the filtrate was acidified with a drop of concentrated HNO_3 (62 %) and stored in the refrigerator for further ICP-OES analysis. For AR digestion, a modified version of ISO 11466:1995 was applied. One gram of ground soil sample and 10 mL of AR solution were placed in a 100 mL Teflon cup, capped with a Teflon cover and heated at 130 °C for 4 hr. After cooling, the digested sample was diluted with DW and transferred to a 50 mL volumetric flask for accurate dilution. The solution was filtered with filter paper (5 μm), and the solution was transferred to a conical tube and kept for further ICP-OES analysis. For ICP-OES analysis, multielement standard 5 (Cat. No. 54704, Sigma-Aldrich, USA) was used to quantify the concentrations of Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, V and Zn. The ICP-OES was purchased from Thermo (Icap-7200, USA) and had an automatic sampler (ASX-560, Teledynes, USA). The DW and AR samples were typically diluted 5-5000 times depending on the concentration, but concentrations below the LOD and guidance level were not remeasured. Triplicates were employed for all measurements. Leachability was calculated using the following equation:

$$Leachability\ (\%) = \left(C_{DW,i}/C_{AR,i}\right) \mathrm{X}\ 100 \qquad \text{(Eq. 1)}$$

where $C_{Dw,i}$ is the concentration of element i from the DW leaching test, while $C_{AR,i}$ is the concentration of element i from AR digestion.

2.4 Spatial analysis

All measured data were arranged in CSV format, and spatial analysis was conducted using the free and open source software QGIS 3.8.1. Inverse distance weighting (IDW) interpolation, a method to estimate a value from nearby locations by weighting distance, was employed. The equation for IDW interpolation is given as Eq. 2:

$$Z(x) = \sum_{i=1}^{n} d_i^{-u} Z_i / \sum_{i=1}^{n} d_i^{-u} \qquad \text{(Eq. 2)}$$

where Z(x) is an estimated value at the interpolated point, Z_i is the value at a measured point, n is the total number of measured points used in the interpolation, and d_i^{-u} is the distance between measured point i and the estimated point. For the illustration, the satellite map from Google Earth software was employed (Map data: Maxar technologies and CNES/Airbus).

3. Results and Discussion

3.1 Elemental concentration and composition

Table 1 summarizes the pH, EC, elemental concentration and composition of all Ag and SA soils obtained by XRF and reference data for world soils, crusts and sediments (Bowen, 1979). The elements were separated into major and minor elements based on their abundance; thus, different units (% and mg kg^{-1}) were applied. The average values of pH and EC were 7.93 and 1.53 mS cm^{-1} for all soils, 7.87 and 0.98 mS cm^{-1} for Ag soils, and 8.09 and 3.11 mS cm^{-1} for SA soils, respectively. The SA soils showed higher pH and EC values than the Ag soils, which implies that the presence of vegetation is highly correlated with salt concentration. The concentrations of the major elements in all soils were 5.17, 20.0, 7.81, 1.80, 1.85, 6.88, 0.13, 0.01, 0.52 and 0.81 % for Al, Si, Ca, K, Mg, Fe, Mn, Ti, Cl and S, while the concentrations of the minor elements were 19.1, 89.6, 164, 11.7 162, 8.6, 91.5, 85.5, 966.7 and 3.2 mg kg^{-1} for As, Co, Cr, Ga, Ni, V, Zn, Cu, P and Se, respectively. The concentrations of Al, Si, Mg and Ti were significantly lower than the median values in world soils, while the concentrations of Ca, Fe, Cl and S showed the opposite trend. The Cl and S concentrations were far greater than the range reported in the literature. For comparison, the ratio of the elemental concentration in SA soils to that in Ag soils is provided in Table 1. The ratios ranged from 0.81-1.12 except for Cl (2.26), S (1.95) and V (2.69), which implies that Cl and S could be the reason for the presence of vegetation coupled with cationic salts, such as Ca, K, Mg and Na; however, Na could not be detected by the XRF method employed, and thus, the Na concentration and distribution are discussed below with the ICP-OES results. In the case of V, there would be no significant effect on the vegetation because the average concentration was relatively low.

Before discussing the details of elemental composition, the two methods applied in this study should be compared and evaluated. Because XRF is versatile and easy to perform without extensive pretreatment, it is difficult to determine the abundance of trace elements, and particle size has a significant effect on measurements. In addition, salt is the major problem in Azerbaijani soils, but the Na concentration was not measurable using the current XRF system. In contrast, ICP-OES coupled with AR digestion has high accuracy and reproducibility and can measure ppb levels of contamination of over 60 elements, but it requires a phase transition from solid to liquid. During acid digestion, massive amounts of toxic acid are required, and it is extremely difficult to establish a satisfactory safety level in developing countries. Furthermore, AR digestion is used to determine the pseudototal concentration because it is difficult to break down phyllosilicate structures in soil; however, acid digestion using HF is not applicable in such an environment. For this reason, we analyzed 346 samples using XRF, while only 120 samples were measured by ICP-OES with AR digestion. The average concentrations of 11 elements by XRF and ICP-OES are plotted in Fig. S1 to evaluate the results obtained using the two methods.

The white circles indicate concentrations, and the gray dashed line indicates the 1:1 line where the concentrations measured by XRF and ICP-OES are equal. Points below the 1:1 line indicate that a higher concentration was obtained by XRF than by ICP-OES. All 11 elements were located below the 1:1 line, which indicates that XRF measured a higher concentration than ICP-OES. Previous studies have frequently reported similar disparities; Das and Ting (2017) reported an extraction efficiency of approximately 40-90 % for AR compared with

AR with HF digestion. Santoro et al. (2017) also found 10 % lower values from AR-only digestion than AR and HF digestion. Schneider et al. (2016) compared the results from portable XRF and ICP-OES using AR, and they found similar results to the current study. The previously reported average concentrations of Ca, Fe and Mn by XRF were 168, 111 and 96 % higher, respectively, than the results from ICP-OES, and the corresponding differences were 125, 227 and 106 % in this study. It is difficult to compare the values directly because the elemental composition and abundance of AR-resistant minerals in the soils determine the disparity between the two methods. In addition, Co showed the largest gap among the 11 elements, which was mainly caused by the differences between the LODs of the two methods.

The correlation matrix of the two soil types is listed in Table S1 and was used to estimate the crystallized mineral composition based on the literature. XRD data would be better for analyzing the composition of mineral structures, but no XRD system was available in Azerbaijan, and it was impossible to export the soil samples to South Korea. Based on the correlation coefficients (r) among the XRF data, the general composition of elements was found. Al, Si, K, Fe, Mn and Ti in Ag soils showed a significant correlation (r>0.49), while significant correlations between Ca and S (r=0.49) and between Ca and P (r=0.55) were found. Fe also showed a significant correlation with Cu, Ni and Zn (r>0.64). SA soils also had significant correlations among Al, Si, K, Fe, Mn and Ti (r>0.49) and between Ca and S (r=0.7) and Ca and P (r=0.59). Cr, Cu, Ni and Zn showed significant correlations with 6 elements (Al, Si, K, Fe, Mn and Ti), and Fe had the highest correlation coefficient. Interestingly, Ca was not correlated with the 6 elements (r<0.18) in the Ag soils, except Fe (r=-0.41), while Ca in the SA soils showed a significant and negative correlation with the 6 elements.

Based on the correlation matrix among the 20 elements, it is reasonable to presume that 1) apatite ($Ca_{10}(PO_4)_6F_2$), which has low bioavailability, is the major phosphate mineral (Abedi and Talibudeen, 1974b; Paytan and McLaughlin, 2007); 2) calcite ($CaCO_3$) and gypsum ($CaSO_4•2H_2O$) are the major sulfate minerals, and calcite is dominant based on the molar ratio between Ca and S; 3) kaolinite and montmorillonite are abundant in the Ag soils and SA soils, but additional primary and secondary minerals are also present based on the relatively similar Al/Si molar ratio (0.264-0.269): quartz (SiO_2), olivine ($(Mg,Fe)_2SiO_4$), microcline ($KAlSi_3O_8$), and jarosite ($KFe_3(SO_4)_2(OH)_6$) (Abedi and Talibudeen, 1974a; Baldermann et al., 2019); and 4) the heavy metals present at the ppm level are mainly bound with iron-containing minerals, such as jarosite and iron (hydr)oxides. However, it was difficult to confirm the presence of iron (hydr)oxides because the soil color mainly ranged from light gray to dark gray despite the high concentration of iron and oxic conditions at the surface.

3.2 Abundance of heavy metals

Heavy metals are toxic elements, and they have harmful effects on the ecosystem and human health, but most countries have different criteria for heavy metal concentrations depending on their natural abundance in native soils. In addition, most developing countries do not have such criteria to regulate soil pollution; thus, it is difficult to evaluate the soil pollution level. Employing criteria from neighboring countries or developed countries is an alternative approach, but the soils of Azerbaijan are unique because the soil is uplifted from sea sediment. Neighboring Russia has its own guidelines for heavy metal contamination, and Georgia has no standard guidelines, but Bakradze et al. (2018) suggested guideline values depending on the ecological state of soils. It was difficult to find guidelines for Iran and Armenia; thus, the soil criteria for England are listed as an example of a developed country in Table 2.

Table 2 summarizes the statistical values for 8 heavy metals and soil guideline values from the three countries mentioned above. The average concentrations of As, Se, Cd, Cr, Cu, Ni, Pb and Zn were 19.1, 3.25, 0.26, 60.6, 50.3, and 86.6 mg kg^{-1}, and the maximum values were 39.0, 10.5, 0.49, 102, 90.2, 146, 83.4 and 130 mg kg^{-1}, respectively.

The concentration of metalloid As in all samples by XRF did not exceed 50 mg kg^{-1}, which is the guideline value in England, while 39 % of the samples had metalloid Se contents (determined by XRF) above the guideline level (3 mg kg^{-1}). The LOD for Se was calculated to be 0.1 mg kg^{-1}; thus, the average value only represented 305 instead of 346 samples. Cd is considered a highly dangerous heavy metal, but only 54 out of 116 samples had concentrations above the LOD (10 µg kg^{-1}), and the maximum concentration was below the minimum guideline value for Georgia, indicating that no significant level of Cd is present in the Mugan Plain. Most countries regulate chromate, which has an oxidation state of +6, but impose fewer regulations on the total chromium applied. The concentration of total Cr was also below the guideline values. In the case of Cu, Ni, Pb and Zn, some samples exceeded the minimum guideline values, but only Ni was above the maximum guideline value for England. The percent of samples exceeding the minimum guideline values for Russia was 39, 91 and 22 % for Cu, Ni and Zn, respectively. In addition, 66 and 13 % of the samples had concentrations over the guideline values of Georgia and England, respectively. The concentrations of Cr, Cu, Ni and Zn by XRF showed higher levels, as illustrated in Fig. 2. As mentioned above,

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this disparity may be caused by the presence of crystal-structured minerals, which are vulnerable to AR digestion, and most countries employ the acid digestion method instead of XRF; thus, the ICP-OES results are mainly discussed here. However, heavy metals sequestered in crystal-structured minerals will not easily dissolve, leach to the water system and be taken up by organisms.

It is difficult to define the contamination levels of Azerbaijani soils because there are no guideline values from the Azerbaijani government and no background studies have properly addressed this issue. However, the guidelines from Russia would be strict for Azerbaijan, while the guidelines from England are flexible. Studies from Georgia would be appropriate to evaluate the heavy metal levels in Azerbaijan (Bakradze et al., 2018). We believe that the results of this study will be useful for evaluating heavy metal levels and can be employed in further approaches to define guideline levels for Azerbaijan.

3.3 Leachability assessment

Based on the results of pH, EC and elemental composition, salt ions, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-}, were identified as the reasons for the low vegetation in the SA soils. It is crucial to evaluate the binding mechanisms of these ions in soils to assess the salinity effect on vegetation. For example, Na in highly soluble precipitates, such as halite (NaCl), thenardite (Na_2SO_4) and glauberite ($Na_2Ca(SO_4)_2$), is easily dissolved and transported to the water system and plants, while primary and secondary minerals, such as albite ($NaAlSi_3O_8$) and Na-intercalated montmorillonite ($Na(Al,Mg)_2Si_4O_{10}$), are resistant to environmental weathering and have no significant salinity effect on the water system and plants. Sequential extraction procedures (SEPs) are usually employed to characterize binding mechanisms (Tessier et al., 1979), but it was not feasible to conduct SEPs in Azerbaijan; thus, DW extraction was conducted to simulate precipitation conditions. XRF confirmed the relatively high abundance of Cl- and S-containing minerals, but the measurement of such elements using ICP-OES is difficult; thus, the leachability of essential elements and heavy metals was calculated.

Table 3 lists the results of DW extraction and AR digestion for 15 elements, categorized as all, Ag and SA soils. The concentrations of major elements from DW extraction were 1.89, 763, 1863, 90.0, 258, 0.81 and 0.14 mg kg^{-1} for Al, Ca, Na, K, Mg, Fe and Mn, while the concentrations of minor elements were 0.17, 0.15, 8.56, 0.04, 0.08, 0.11, 0.54 and 0.12 mg kg^{-1} for Li, Mo, Sr, Cd, Cr, Ni, Cu and Zn, respectively. The DW-extracted concentrations in SA soils differed significantly from those in Ag soils, especially for Ca, Na, K and Mg, which are the reason for salinity. The sum of the average concentrations in the DW extracts of Ag soils was 2040 mg kg^{-1}, while the sum was 5307 mg kg^{-1} in the SA soils. It was difficult to describe a relationship using concentrations obtained from two extraction and digestion approaches for 15 elements; thus, leachability was selected to easily describe this effect.

The leachability of major elements in the Ag soils was 0.01, 0.89, 47,8, 1.50, 1.28, 0.003, and 0.02 % for Al, Ca, Na, K, Mg, Fe and Mn, respectively, while the corresponding values in the SA soils were 0.00, 2.50, 65.3, 3.18, 2.06, 0.001 and 0.02 %. Except for Al and Fe, the leachability of other elements was significantly increased. Based on the concentration data, higher levels of abundance were found in the SA soils, but the leachability results indicate that in addition to exhibiting higher concentrations, the major elements in the SA soils were more easily mobilized by water extraction. In addition, monovalent ions such as Na and K showed high leachability, and Na was clearly distinguished from the other elements because the fraction of Na (Na/sum of 15 elements) in the DW extract was 0.508 and 0.639 for Ag and SA soils, respectively. The cationic salt fraction ((Ca+Na+K+Mg)/sum of 15 elements) in the DW extract was 0.993 and 0.996 for Ag and SA soils, respectively, which indicates that the mobility of these salts governs soil productivity by affecting plants.

Not only does the leachability of major cations cause salt stress in the soil, but the leachability of heavy metals is also important because such compounds can easily accumulate in organisms through the food chain, eventually affecting human health. The leachability of heavy metals such as Cd, Cr, Cu, Ni and Zn with respect to guideline values was evaluated and discussed, and the values for Li, Mo and Sr, detected during ICP-OES measurements, are listed for further study. In the case of Pb, the concentration of most samples was below the LOD (0.015 mg kg^{-1}); thus, Pb was excluded. The concentrations of Cd, Cr, Cu, Ni and Zn in the DW extracts were 0.04, 0.08, 0.54, 0.11 and 0.12 mg kg^{-1}, respectively, and the concentrations showed no significant difference with respect to soil type. The concentrations of Cd and Cr were close to the LOD (0.02 for Cd and 0.03 mg kg^{-1} for Cr) in the ICP-OES measurements. The leachability of Cd, Cr, Cu, Ni and Zn in all soils was 13.0, 0.13, 1.09, 0.12 and 0.19 %, respectively. The higher leachability values for Cd were caused by the low concentration close to the LOD for both the DW extraction and AR digestion method. Except for Cd and Cu, the leachability of other heavy metals was less than 0.19 %; considering that Cu acts as an essential element at low concentration and the abundance was relatively low, Cu would not cause severe hazardous effects to water bodies and the ecosystem (Alloway, 1995).

3.4 Leachability and spatial analysis

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Understanding soil properties starts with observing and analyzing the characteristics of the soil itself and the surrounding environment; however, it is almost impossible to acquire the data required to interpret soil properties in developing countries because of insufficient instruments and expertise. For this reason, the pH, EC and elevation were measured, and the correlations were evaluated and are illustrated in Fig. 2. The spatial analysis results using the IDW interpolation method are illustrated in Fig. 3 for 3 environmental parameters: Al/Si molar ratio, Ca and Fe concentration by XRF, and Fe and Na concentration by DW leaching test.

The coefficient of determination between the pH and cationic salt elements (Ca, K, Mg and Na) showed no significant correlation (r^2<0.08) in either Ag or SA soils, except for the correlation with Mg in SA soils. The Mg leachability decreased with increased pH (r^2=0.15), which is typical of cation dynamics in soils. Based on the spatial analysis results, the pH was higher in the SA soils than the Ag soils, but the difference was not critical because on the difference between the average values listed in Table 1 was 0.22. An interesting result was observed in the correlation between cationic salt elements and EC: a significant correlation was observed in the Ag soils (0.25<r^2<0.78), while a much smaller correlation was observed in the SA soils (0.00<r^2<0.47). The slope was also higher in the Ag soils. Based on the DW extraction results, the percent of cationic salt elements among the 15 elements was 99.4-99.6 %; thus, a significant correlation was expected. The difference in response time between EC and DW extract analysis could be the reason for the difference. In addition, the dissolution of minerals with a low dissolution rate, partial reduction of metal (hydr)oxides or additional precipitation with microbial carbonate during incubation could explain the difference. Na showed a poor correlation, even though it was the most abundant element (over 60.6 %) among the 15 elements and monovalent Na is the most stable ion in solution during precipitation because of its low reactivity. Intercalation between the 2:1 layered sheets of montmorillonite is the key mechanism for the interlayer distance and leachability of ions, and the exchange of intercalated Na with divalent cations has been previously reported (Han et al., 2016; Li et al., 2012); thus, Na ions from the interlayers may alter the correlation between Na leachability and EC. Based on the spatial analysis, EC values from eastern SA soils were higher than those in soils from other regions. The western SA soils showed a gradual decrease in EC, while the pH was similar to that in eastern SA soils. Based on the local information and satellite image, the western SA soils are subjected to irrigation treatment to remove salts, while the eastern part is still abandoned, which would cause the low level of EC. In the case of elevation, the opposite patterns were observed; the coefficient of determination was higher in SA soils (0.05<r^2<0.22) than in Ag soils (0.00<r^2<0.10), and the slope of the reciprocal correlation was lower in SA soils. Based on this information, the soils in the lowland have more leachability, which indicates that dissolution caused by precipitation and soil water runoff leads to the accumulation of salt ions in the lowland. However, spatial analysis of elevation data showed that the northwest is the highest region and the elevation gradually decreases toward the southeast regions. Such elevation properties could suggest that the high leachability in the lowland area is a result of bias, but the Na concentrations obtained from DW leaching tests also showed similar levels in SA soils from the western and eastern regions; thus, bias can be excluded.

The spatial distribution of the Al/Si molar ratio was calculated to estimate the indirect abundance of kaolinite and montmorillonite; the ideal molar ratios of kaolinite and montmorillonite are 1:1 and 1:2, respectively. The abundance of montmorillonite is an important factor because of the swelling properties and water holding capacity of montmorillonite (Li et al., 2012). The swelling caused by the intercalation of water molecules in the interlayers of montmorillonite increases the volume and decreases the infiltration rate. This property disturbs vertical water movement; thus, surface water will run off, causing soil erosion or ponding and evaporation with salt accumulation. The Al/Si ratio was 0.270 and 0.264 for Ag and SA soils, showing no significant difference, but the spatial distribution indicated a low Al/Si ratio in the eastern SA soils and a similar distribution to that of EC. This variation could be due to the difference in montmorillonite abundance, as suggested in the previous literature mentioned above (Goverment of The Republic of Azerbaijan, 2014). The Ca and Fe concentrations measured by XRF showed an opposite concentration trend to that observed in spatial analysis; the Ag soils showed lower concentrations of Ca than the SA soils, while the opposite was observed for Fe. IDW interpolation did not show the distribution of Ca properly because several hot spot points were observed, mainly located in Ag soils with no crops. Iron (hydr)oxides are the major minerals for Fe, and they also retain nutrients due to their large surface area; thus, the correlation between vegetation and Fe concentration but not Ca was reasonable. However, the total Fe concentration showed a different distribution from the Fe concentration determined by DW extraction, which showed the opposite pattern. Comparison of the total Fe and leached concentrations indicates that the SA soils have less-stable iron compounds. Based on our observations, it was difficult to define the major mineral structure of iron because the collected soils had a high Fe concentration, but the soil was not yellow or red; such colors are mainly derived from ferric (hydr)oxides, such as goethite, hematite, lepidocrocite, ferrihydrite and maghemite (Claudio et al., 2017). Siderite, pyrite and magnetite are mainly abundant under reducing conditions, but the surface soils were presumed to be under oxic conditions; thus, such minerals were not considered. Jarosite would be present but not prevalent,

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considering the sulfur concentration. Calcium ferrite or calcium aluminoferrite are possible minerals because a significant correlation with cationic metals was reported (Table 1), and they present with Al, Fe, Ca, Mg, Ti and Zn. However, there is no concrete evidence of an Fe mineral structure; thus, further study should be performed to examine the cycle of iron in this region. The Na concentrations determined by the leaching test were similar to the pH distribution and also showed a concentration gap between the eastern and western regions. Based on the total concentration data, fewer salts were present in the middle of the SA soils; satellite images obtained in Dec. 1987 showed that a water pond was located in that region, and a recent satellite image showed the presence of vegetation. For this reason, the pond caused downward water movement with salt ions; thus, the middle region showed results distinct from those in the eastern and western regions.

4. Conclusion

In this study, the elemental composition of the Mugan Plain in Azerbaijan was measured using two methods, XRF and ICP-OES. The two methods were compared and evaluated in terms of soil element analysis and salinity characterization, and the heavy metal level and leachability were assessed. The spatial variability in elemental composition and leaching concentration was also determined to understand the potential risks of heavy metals and salinization and to find a way to improve the agricultural productivity of Azerbaijan.

Based on our observations, the elemental concentrations of Ca, Fe, Cl and S were relatively high among 20 elements, and apatite, calcite, gypsum, quartz, olivine, microcline and jarosite compose the mineral structure of Azerbaijani soils. The XRF results showed higher levels of concentration and were significantly correlated with the ICP-OES results obtained with AR digestion. The heavy metal guidelines suggested by neighboring Georgia would be appropriate for heavy metal contamination, and Ni and Pb are the most concerning elements in Azerbaijani soils. Leachability tests confirmed that 99 % of the cationic ions were cationic salts, and Na was the most problematic ion (50.1-63.9 %). Exchanging interlayer cations, the dissolution of minerals with low dissolution rates, the transformation of metal (hydr)oxides and additional precipitation are the reasons for the disparity between the EC and leaching test results, and more leachable salts were accumulated in the lowland. The spatial analysis results confirmed the reciprocal relationship between total Ca and total Fe and between total Fe and DW-leached Fe. This relationship indicates that less-stable iron complexes are prevalent in SA soils, while stable iron complexes are found in Ag soils; however, it was impossible to determine the crystal structure of these iron complexes from previous studies and current results.

This study only provides fragmented information on the spatially resolved elemental concentration and leachability of surface soils in Mugan, and several assumptions and estimations were applied due to insufficient analytical resources and expertise. However, we believe that this approach will be a foundation for international studies of Azerbaijani soil by enabling the sharing of soil and salinization data with researchers worldwide and that these results will help to diminish or solve agricultural problems in not only Azerbaijan but also similar countries suffering from soil salinization.

Data availability.

The data set of fundamental soil characteristics (pH and EC) and the elemental concentration by XRF and ICP-OES are available upon a request to the corresponding author (Hee-Myong Ro, hmro@snu.ac.kr).

Author contribution.

Junho Han conducted the experiment design, analyst training, quality control of data and manuscript writing, and Hee-Myong Ro and supervised the experiment and manuscript writing. Zaman Mammadov and Elton Mammadov performed the soil sampling and experimental measurement using pH and EC meter, XRF and ICP-OES, and Seoyeon Lee and Jisuk Park were responsible for data interpretation and validation. Garib Mammadov and Guliyev Elovsat provided the laboratory, resource and background information for the study.

Competing interests.

The authors declare that they have no conflict of interest.

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References

Abedi, M. J. and Talibudeen, O.: The calcareous soils of Azerbaijan. I. Catena development related to the distribution and surface properties of soil carbonate., J. Soil Sci., 25(3), 357–372, doi:10.1111/j.1365-2389.1974.tb01132.x, 1974a.

Abedi, M. J. and Talibudeen, O.: The calcareous soils of azerbaijan ii. phosphate status, J. Soil Sci., 25(3), 357–372, doi:10.1111/j.1365-2389.1974.tb01132.x, 1974b.

Alloway, B.: Heavy Metals in Soils Trace Metals and Metalloids in Soils and Their Bioavailability., 1995.

Babaev, M. P., Gurbanov, E. A. and Ramazanova, F. M.: Main types of soil degradation in the Kura-Aras Lowland of Azerbaijan, Eurasian Soil Sci., 48(4), 445–456, doi:10.1134/s106422931504002x, 2015.

Bakradze, E., Vodyanitskii, Y., Urushadze, T., Chankseliani, Z. and Arabidze, M.: About rationing of the heavy metals in soils of Georgia, Ann. Agrar. Sci., 16(1), 1–6, doi:10.1016/j.aasci.2017.09.002, 2018.

Baldermann, A., Abdullayev, E., Taghiyeva, Y., Alasgarov, A. and Javad-Zada, Z.: Sediment petrography, mineralogy and geochemistry of the Miocene Islam Dağ Section (Eastern Azerbaijan): Implications for the evolution of sediment provenance, palaeo-environment and (post-)depositional alteration patterns, Sedimentology, doi:10.1111/sed.12638, 2019.

Bowen, H. J. M.: Environmental chemistry of the elements., Environ. Chem. Elem. [online] Available from: https://www.cabdirect.org/cabdirect/abstract/19800700395 (Accessed 5 August 2019), 1979.

Cappuyns, V. and Swennen, R.: The use of leaching tests to study the potential mobilization of heavy metals from soils and sediments: A comparison, Water. Air. Soil Pollut., 191(1–4), 95–111, doi:10.1007/s11270-007-9609-4, 2008.

Claudio, C., Di Iorio, E., Liu, Q., Jiang, Z. and Barrón, V.: Iron oxide nanoparticles in soils: Environmental and agronomic importance, J. Nanosci. Nanotechnol., 17(7), 4449–4460, doi:10.1166/jnn.2017.14197, 2017.

Daliakopoulos, I. N., Tsanis, I. K., Koutroulis, A., Kourgialas, N. N., Varouchakis, A. E., Karatzas, G. P. and Ritsema, C. J.: The threat of soil salinity: A European scale review, Sci. Total Environ., 573, 727–739, doi:10.1016/j.scitotenv.2016.08.177, 2016.

Das, S. and Ting, Y.-P.: Evaluation of Wet Digestion Methods for Quantification of Metal Content in Electronic Scrap Material, Resources, 6(4), 64, doi:10.3390/resources6040064, 2017.

Emadi, M. and Baghernejad, M.: Comparison of spatial interpolation techniques for mapping soil pH and salinity in agricultural coastal areas, northern Iran, Arch. Agron. Soil Sci., 60(9), 1315–1327, doi:10.1080/03650340.2014.880837, 2014.

Feyziyev, F., Babayev, M., Priori, S. and L'Abate, G.: Using Visible-Near Infrared Spectroscopy to Predict Soil Properties of Mugan Plain, Azerbaijan, Open J. Soil Sci., 06(03), 52–58, doi:10.4236/ojss.2016.63006, 2016.

Frouz, J., Hrčková, K., Lána, J. and Krištůfek, V.: Can laboratory toxicity tests explain the pattern of field communities of algae, plants, and invertebrates along a toxicity gradient of post-mining sites?, Appl. Soil …, 51(1), 114–121, doi:10.1016/j.apsoil.2011.09.007, 2011.

Goverment of The Republic of Azerbaijan: National Atlas of the Republic of Azerbaijan., 2014.

Han, J., Kim, J., Kim, M., Moon, D. H., Sung, J.-S. and Hyun, S.: Chemical extractability of As and Pb from soils across long-term abandoned metallic mine sites in Korea and their phytoavailability assessed by Brassica juncea., Environ. Sci. Pollut. Res. Int., 22(2), 1270–8, doi:10.1007/s11356-014-3441-3, 2014.

Han, J., Ro, H.-M., Cho, K. H. and Kim, K.-W.: Fluxes of nutrients and trace metals across the sediment-water interface controlled by sediment-capping agents: bentonite and sand, Environ. Monit. Assess., 188(10), 566, doi:10.1007/s10661-016-5583-x, 2016.

Hommels, a., Scholte, K. H., Munoz-Sabater, J., Hanssen, R. F., Van der Meer, F. D., Kroonenberg, S. B., Aliyeva, E., Huseynov, D. and Guliev, I.: Preliminary ASTER and INSAR imagery combination for mud volcano dynamics, Azerbaijan, IGARSS 2003. 2003 IEEE Int. Geosci. Remote Sens. Symp. Proc. (IEEE Cat. No.03CH37477), 3(May), 1573–1575, doi:10.1109/IGARSS.2003.1294179, 2003.

Janoš, P., Vávrová, J., Herzogová, L. and Pilařová, V.: Effects of inorganic and organic amendments on the mobility (leachability) of heavy metals in contaminated soil: a sequential extraction study, Geoderma, 159(3–4), 335–341, doi:10.1016/j.geoderma.2010.08.009, 2010.

Li, Y., Wang, X. and Wang, J.: Cation exchange, interlayer spacing, and thermal analysis of Na/Ca-montmorillonite modified with alkaline and alkaline earth metal ions, J. Therm. Anal. Calorim., 110(3), 1199–1206, doi:10.1007/s10973-011-2109-1, 2012.

Oglu, A. Z. H.: Agriculture in Azerbaijan and its Development Prospects, Int. J. Med. Biomed. Stud., 2(4), 79–91, doi:10.32553/ijmbs.v2i4.37, 2018.

Paytan, A. and McLaughlin, K.: The oceanic phosphorus cycle, Chem. Rev., 107(2), 563–576, doi:10.1021/cr0503613, 2007.

Santoro, A., Held, A., Linsinger, T. P. J., Perez, A. and Ricci, M.: Comparison of total and aqua regia extractability of heavy metals in sewage sludge: The case study of a certified reference material, TrAC - Trends Anal. Chem., 89, 34–40, doi:10.1016/j.trac.2017.01.010, 2017.

Schneider, A. R., Cancès, B., Breton, C., Ponthieu, M., Morvan, X., Conreux, A. and Marin, B.: Comparison of field portable XRF and aqua regia/ICPAES soil analysis and evaluation of soil moisture influence on FPXRF results, J. Soils Sediments, 16(2), 438–448, doi:10.1007/s11368-015-1252-x, 2016.

Tessier, A., Campbell, P. and Bisson, M.: Sequential extraction procedure for the speciation of particulate trace metals, Anal. Chem., 51(7), 844–851 [online] Available from: http://pubs.acs.org/doi/abs/10.1021/ac50043a017 (Accessed 16 June 2014), 1979.

Towett, E. K., Shepherd, K. D., Tondoh, J. E., Winowiecki, L. A., Lulseged, T., Nyambura, M., Sila, A., Vågen, T. G. and Cadisch, G.: Total elemental composition of soils in Sub-Saharan Africa and relationship with soil forming factors, Geoderma Reg., 5, 157–168, doi:10.1016/j.geodrs.2015.06.002, 2015.

Table 1 Summary of statistics for the average (Avg.), standard deviation (Std.), coefficient of variance (C.V.), median (Med.), minimum (Min.), and maximum (Max.) element concentrations determined using XRF, categorized into all, agricultural and salt-affected soils from the Mugan Plain. The reported values for world soils, crust and sediments are from Bowen (1979). Total 532 and 346 samples were employed for pH and EC measurement and elemental composition, respectively.

Parameters		All soils						Agricultural soils						Salt-affected soils						Ratio	World soils		Crusts	Sediments
		Avg.	Std.	C.V.	Med.	Min.	Max.	Avg.	Std.	C.V.	Med.	Min.	Max.	Avg.	Std.	C.V.	Med.	Min.	Max.	(B/A)	Med.	Range	Avg.	Avg.
pH		7.93	0.40	5.04	7.86	7.10	9.44	7.87	0.39	4.91	7.80	7.10	9.44	8.09	0.39	4.87	8.07	7.21	9.34	1.03	-	-	-	-
EC (mS cm^{-1})		1.53	2.18	0.14	0.50	0.12	23.0	0.98	1.50	0.15	0.41	0.12	10.8	3.11	2.94	0.10	2.33	0.24	23.0	3.17	-	-	-	-
Major elements (%)	Al	5.17	0.69	13.40	5.22	2.62	7.09	5.22	0.65	12.46	5.25	3.10	7.09	4.82	0.86	17.95	4.97	2.62	6.83	0.92	7.1	1-30	8.2	7.2
	Si	20.02	2.45	12.23	20.32	10.91	26.74	20.16	2.29	11.34	20.41	13.14	26.74	19.01	3.23	16.98	19.62	10.91	25.70	0.94	33	25-41	27.7	24.5
	Ca	7.81	2.08	26.62	7.75	2.56	16.88	7.70	1.88	24.39	7.73	2.56	16.88	8.60	3.06	35.64	8.09	3.56	16.87	1.12	1.5	0.07-50	4.1	6.6
	K	1.80	0.27	14.87	1.81	0.84	2.58	1.81	0.25	13.64	1.82	1.02	2.56	1.74	0.38	21.97	1.77	0.84	2.58	0.96	1.4	0.08-3.7	2.1	2
	Mg	1.85	0.40	21.88	1.84	0.39	3.10	1.85	0.40	21.35	1.86	0.47	2.88	1.79	0.46	25.44	1.74	0.39	3.10	0.97	0.5	0.04-0.90	2.3	1.4
	Fe	6.88	0.73	10.62	6.91	3.77	8.88	6.94	0.67	9.63	6.95	3.94	8.88	6.45	0.98	15.15	6.66	3.77	8.06	0.93	4	0.2-55	4.1	4.1
	Mn	0.13	0.02	13.49	0.14	0.06	0.26	0.13	0.02	13.02	0.14	0.07	0.26	0.13	0.02	16.18	0.13	0.06	0.17	0.96	0.1	0.002-1.0	0.095	0.077
	Ti	0.01	0.00	15.42	0.01	0.00	0.01	0.01	0.00	14.76	0.01	0.00	0.01	0.01	0.00	16.57	0.01	0.00	0.01	0.89	0.5	0.0015-2.5	0.56	0.38
	Cl	0.52	0.46	87.20	0.38	0.14	3.65	0.45	0.32	71.57	0.36	0.14	2.64	1.02	0.82	79.58	0.74	0.16	3.65	2.26	0.001	0.0008-0.18	0.013	0.019
	S	0.81	1.87	2.32	0.19	0.01	15.74	0.70	1.60	2.29	0.18	0.02	15.61	1.58	3.10	1.96	0.26	0.01	15.74	1.95	0.007	0.0003-0.16	0.026	0.22
Minor elements (mg kg^{-1})	As	19.1	5.7	29.7	19.5	4.5	39.0	19.4	5.7	29.2	19.5	4.5	39.0	16.9	5.2	31.1	16.5	6.0	27.0	0.87	6	0.1-40	1.5	7.7
	Co	89.6	43.0	48.0	88.5	0.0	232.5	91.7	42.6	46.5	91.5	0.0	232.5	74.7	43.1	57.7	78.0	0.0	190.5	0.81	8	0.05-65	20	14
	Cr	164.8	63.9	38.8	159.0	16.5	492.0	164.7	63.9	38.8	160.5	16.5	492.0	165.4	64.4	38.9	154.5	31.5	321.0	1.00	70	5-1,500	100	72
	Ga	11.7	4.6	39.6	12.0	0.0	25.5	11.9	4.6	38.7	12.0	0.0	25.5	10.2	4.6	45.0	10.5	0.0	21.0	0.85	20	2-100	18	18
	Ni	161.7	36.7	22.7	162.0	15.0	334.5	164.0	36.7	22.4	165.0	15.0	334.5	145.0	32.7	22.5	141.0	69.0	234.0	0.88	50	2-750	80	52
	V	8.6	22.1	257.9	0.0	0.0	150.0	7.1	19.7	276.6	0.0	0.0	147.0	19.1	33.4	174.2	0.0	0.0	150.0	2.69	90	3-500	160	105
	Zn	91.5	11.5	12.5	93.0	36.0	151.5	92.3	10.8	11.7	93.0	36.0	151.5	85.9	14.0	16.3	85.5	48.0	114.0	0.93	90	1-900	75	95
	Cu	85.5	13.2	15.4	85.5	34.5	138.0	86.7	12.8	14.8	87.0	34.5	138.0	76.9	12.7	16.6	76.5	42.0	109.5	0.89	30	2-250	50	33
	P	966.7	280.7	29.0	949.5	361.5	2860.5	959.9	281.3	29.3	936.8	361.5	2860.5	1015.4	272.5	26.8	999.0	417.0	1705.5	1.06	800	35-5300	1000	670
	Se	3.2	2.1	64.0	3.0	0.0	10.5	3.3	2.1	63.6	3.0	0.0	10.5	3.1	2.1	66.8	3.0	0.0	9.0	0.95	0.40	-	0.05	0.42

Table 2 Summary of the methods, number of samples, average (Avg.), standard deviation (Std.), coefficient of variance (C.V.), minimum (Min.), and maximum (Max.) values for 8 heavy metals, as well as soil guideline values from the neighboring countries of Russia and Georgia and the developed country of England. The percent of samples above the minimum and maximum soil guideline values are listed to show the heavy metal levels.

		Parameters (mg kg^{-1})						Guideline values (mg kg^{-1})			% of samples above the guideline value	
Element	Method[a]	# of samples[b]	Avg.	Std.	C.V.	Max.	Min.	Russia[c]	Georgia[c]	England[d]	Minimum	Maximum
As	XRF	346	19.1	5.69	29.73	39.0	4.50	-	-	50	0	-
Se	XRF	305	3.25	2.08	64.0	10.5	0.10	-	-	3	39	-
Cd	ICP-OES	54	0.26	0.12	45.5	0.49	0.01	-	1	3	0	0
Cr	ICP-OES	116	60.6	16.1	26.6	102	27.2	-	-	400	0	-
Cu	ICP-OES	116	50.3	16.0	31.8	90.2	22.3	55	100	200	39	0
Ni	ICP-OES	116	86.6	23.8	27.4	146	37.7	85	75	110	66	13
Pb	ICP-OES	116	52.9	14.4	27.2	83.4	25.9	30	159	300	91	0
Zn	ICP-OES	116	64.3	16.5	25.7	130	29.7	100	300	450	22	0

[a] The results from ICP-OES are listed because the XRF results are provided in Table 1.
[b] Different numbers of samples were used because values below the limit of detection were not employed for the calculation.
[c] Maximum permissible concentration reported by Bakradze et al. (2018).
[d] Specific limits for heavy metals in soils for agricultural purposes and after sewage sludge application (EC directive 86/278/EEC).

Table 3 Comparison and leachability assessment of distilled water extracts and aqua regia digestates using ICP-OES, categorized into all, agricultural and salt-affected soils.

Categories		Parameters	Al	Ca	Na	K	Mg	Fe	Mn	Li	Mo	Sr	Cd	Cr	Ni	Cu	Zn	Sum
Distilled water extraction (N=93)	All soils (N=93)	Avg.	1.89	763	1863	90.0	258	0.81	0.14	0.17	0.15	8.56	0.04	0.08	0.11	0.54	0.12	2988
		Std.	6.53	1265	3117	105	471	3.12	0.17	0.11	0.15	15.5	0.01	0.03	0.03	0.20	0.10	4673
		C.V.	345	166	167	117	182	386	124	61.8	99.7	181.3	33.2	36.6	30.7	37.1	84.0	156
		Min.	0.00	7.32	5.5	1.1	0.7	0.04	0.01	0.01	0.01	0.02	0.02	0.04	0.04	0.17	0.03	17
		Max.	60.01	5698	19167	623	3181	29.0	0.82	0.58	0.73	69.4	0.11	0.16	0.21	1.26	0.86	26053
	Agricultural Soils (N=66)	Avg.	2.38	511	1236	64.5	216	1.05	0.13	0.15	0.10	5.18	0.03	0.08	0.11	0.53	0.11	2040
		Std.	7.70	1007	2929	81.5	499	3.68	0.18	0.10	0.08	11.4	0.01	0.03	0.03	0.17	0.07	4372
		C.V.	323	197	236	126	230	352	140	66.2	81.6	220	22.6	37.8	28.2	32.9	65.6	214
		Min.	0.00	7.32	5.5	1.1	0.7	0.04	0.01	0.01	0.01	0.02	0.02	0.04	0.04	0.17	0.03	17
		Max.	60.01	5698	19167	623	3181	29.0	0.82	0.58	0.73	69.4	0.11	0.16	0.21	1.26	0.86	26053
	Salt-affected Soils (N=27)	Avg.	0.68	1379	3393	152	361	0.22	0.16	0.24	0.28	16.8	0.04	0.07	0.11	0.57	0.14	5307
		Std.	0.69	1603	3081	131	386	0.19	0.14	0.10	0.20	20.6	0.02	0.02	0.04	0.25	0.14	4648
		C.V.	100	116	90.8	86.6	106	86.0	91.3	43.9	72.0	122	48.9	32.8	35.2	44.9	105	88
		Min.	0.00	111	184	17.7	34.1	0.04	0.03	0.07	0.01	0.87	0.02	0.04	0.05	0.34	0.05	532
		Max.	2.44	5351	13422	431	1522	0.68	0.58	0.50	0.72	69.4	0.11	0.137	0.21	1.26	0.86	20712
Aqua regia digestion (N=93)	All soils (N=93)	Avg.	23461	56517	3342	4440	17130	29465	769	22.1	0.44	227	0.27	60.7	86.6	50.2	64.6	135708
		Std.	8573	32868	2797	1530	4167	6444	240.4	5.95	0.51	90.2	0.11	15.1	21.9	15.9	16.3	42896
		C.V.	36.5	58.2	83.7	34.5	24.3	21.9	31.2	26.8	115	39.7	40.7	24.8	25.3	31.8	25.2	32
		Min.	9810	15626	529.1	1748	9190	19440	399	9.39	0.59	103.9	0.03	28.2	40.3	22.2	30.3	76019
		Max.	44056	159806	18031	989	26401	43895	1298	39.7	3.38	545	0.49	101	145	90.1	130	247573
	Agricultural Soils (N=66)	Avg.	23384	57075	2583	4296	16948	30048	787	22.2	0.48	203	0.26	62.9	90.0	51.8	65.5	135690
		Std.	8266	33059	1732	1365	4028	6286	230	6.07	0.53	59.0	0.11	15.3	22.1	15.7	14.8	43627
		C.V.	35.4	57.9	67.0	31.8	23.8	20.9	29.3	27.3	109	28.9	42.0	24.3	24.5	30.4	22.6	32
		Min.	9810	15626	529.1	1748	9190	19440	399	9.39	0.73	103.9	0.03	28.2	40.3	22.2	30.3	76019
		Max.	44056	159806	18031	9894	26401	43895	1298	39.7	3.38	545.5	0.49	101	145.9	90.1	130	247573
	Salt-affected Soils (N=27)	Avg.	23649	55151	5197	4792	17575	28038	727	21.8	0.33	284	0.29	55.2	78.4	46.3	62.2	135752
		Std.	9443	32981	3892	1854	4539	6720	261	5.73	0.44	123	0.11	13.2	19.7	16.1	19.5	41865
		C.V.	39.9	59.8	74.9	38.7	25.8	24.0	36.0	26.2	134	43.4	38.6	23.9	25.1	34.8	31.4	31
		Min.	9810	24142	1065	2245	11093	19440	401	13.3	0.59	114	0.15	29.0	41.3	22.2	34.4	85557
		Max.	42593	157429	18031	9593	25284	38802	1244	33.6	1.06	545	0.46	81.3	104	72.3	130	246990
Leachability (%)	All soils		0.01	1.35	55.73	2.03	1.51	0.003	0.02	0.78	35.20	3.77	13.05	0.13	0.12	1.09	0.19	2.20
	Agricultural soils		0.01	0.89	47.87	1.50	1.28	0.003	0.02	0.66	20.96	2.54	13.09	0.13	0.12	1.03	0.17	1.50
	Salt-affected soils		0.00	2.50	65.28	3.18	2.06	0.001	0.02	1.08	85.96	5.91	12.97	0.14	0.15	1.24	0.23	3.91

Figure Captions

Fig. 1 Google satellite map of the study area and location of sampling points. The blue circles and red triangles indicate agricultural and salt-affected soils, respectively. The light green line and white diamond indicate the border and capital, respectively, of the administrative division. A total of 532 samples were collected and plotted. The satellite map was from Google Earth software (Map data: Maxar technologies and CNES/Airbus).

Fig. 2 Scatter plots and regression results between environmental parameters (pH, EC and elevation) and the leachability data (Ca, K, Mg and Na) for agricultural soils (blue circles) and salt-affected soils (red triangles). r^2 indicates the coefficient of determination.

Fig. 3 Spatial analysis results using IDW interpolation for pH (a), EC (b), elevation (c), AS/Si ratio by XRF (d), satellite image with sampling positions (e), Ca content (f), Fe content by XRF (g), Fe concentration by DW leaching (h), and Na concentration by DW leaching (i). Darker colors indicate higher concentrations. The satellite map in the center was from © Google Earth software (Map data: Maxar technologies and CNES/Airbus).

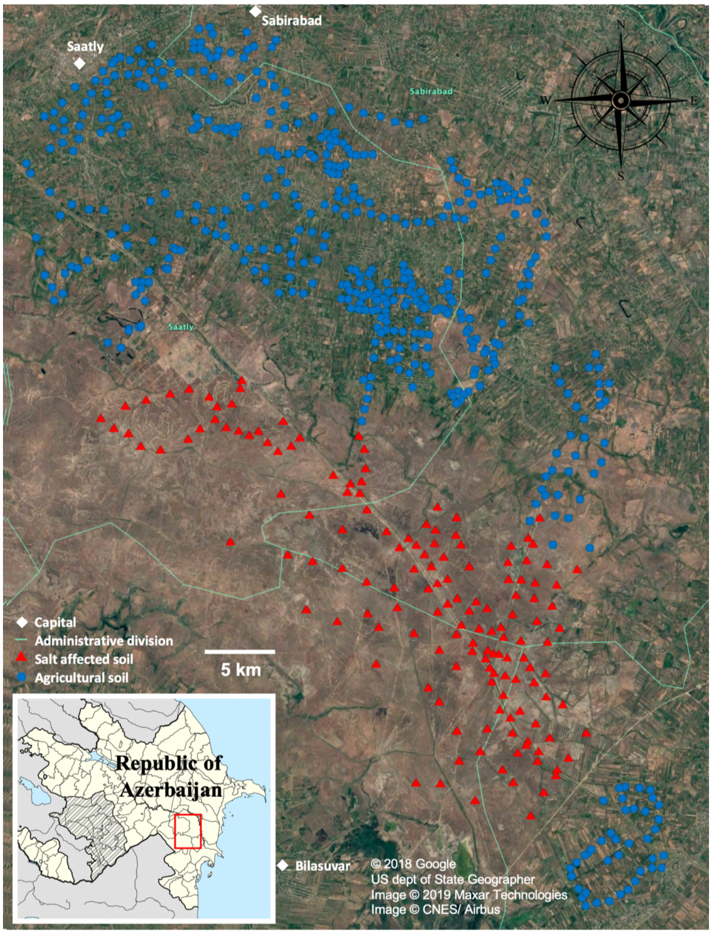
Sabirabad
Saatly
Sabirabad
Saatly
N
W
E
S
◆ Capital
Administrative division
▲ Salt affected soil
● Agricultural soil
5 km
Republic of Azerbaijan
Bilasuvar
© 2018 Google
US dept of State Geographer
Image © 2019 Maxar Technologies
Image © CNES/ Airbus

Fig. 1

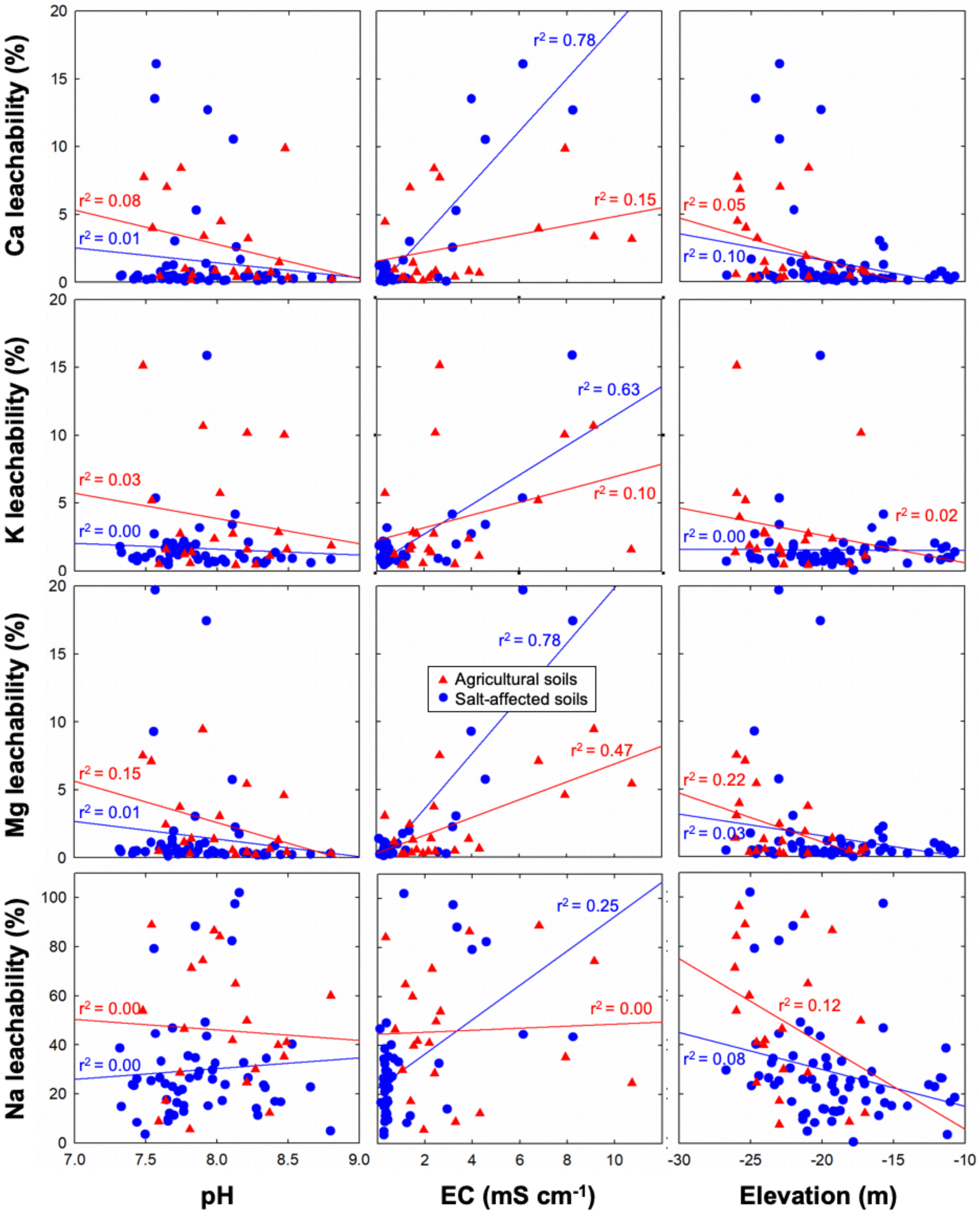
Ca leachability (%)
K leachability (%)
Mg leachability (%)
Na leachability (%)
pH
EC (mS cm-1)
Elevation (m)
Agricultural soils
Salt-affected soils
r2 = 0.08
r2 = 0.01
r2 = 0.78
r2 = 0.15
r2 = 0.05
r2 = 0.10
r2 = 0.03
r2 = 0.00
r2 = 0.63
r2 = 0.10
r2 = 0.02
r2 = 0.00
r2 = 0.15
r2 = 0.01
r2 = 0.78
r2 = 0.47
r2 = 0.22
r2 = 0.03
r2 = 0.00
r2 = 0.00
r2 = 0.25
r2 = 0.00
r2 = 0.12
r2 = 0.08
0
5
10
15
20
20
40
60
80
100
7.0
7.5
8.0
8.5
9.0
2
4
6
8
10
-30
-25
-20
-15
-10

Fig. 2

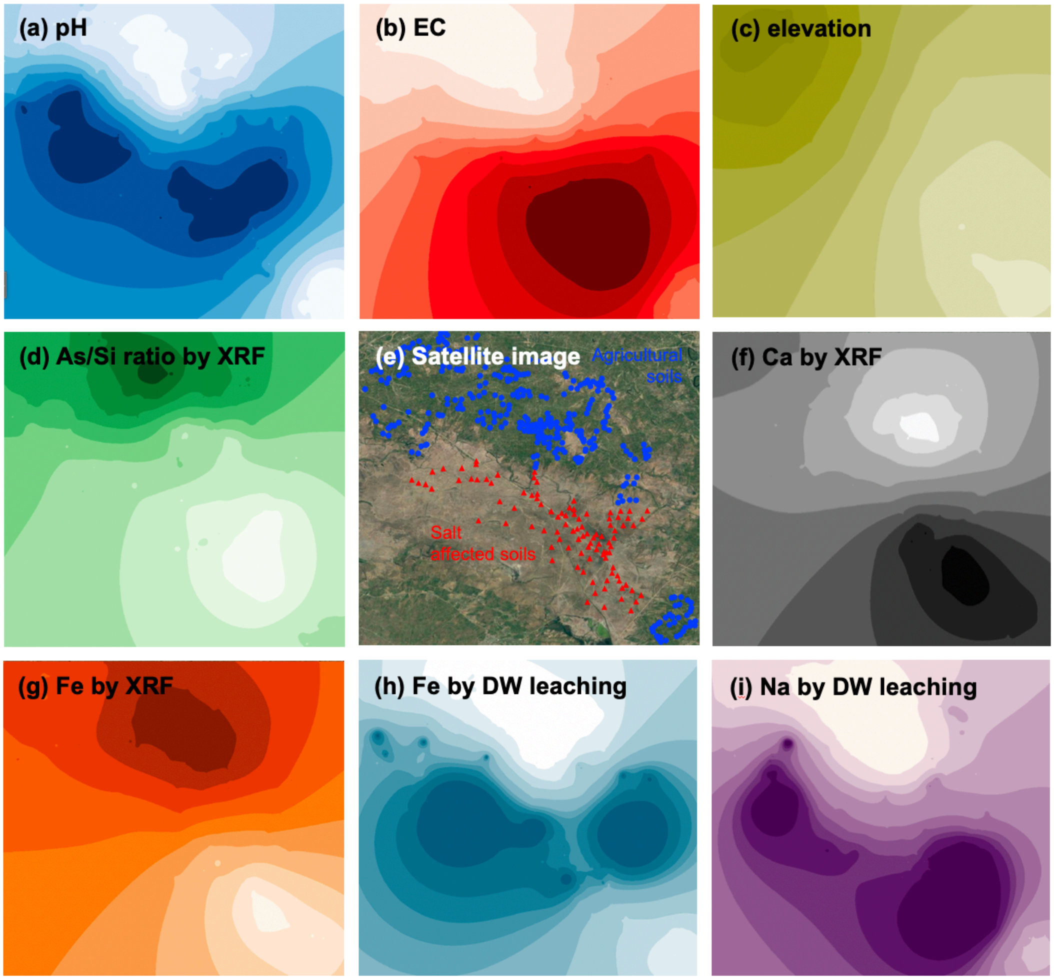
(a) pH
(b) EC
(c) elevation
(d) As/Si ratio by XRF
(e) Satellite image
Agricultural soils
Salt affected soils
(f) Ca by XRF
(g) Fe by XRF
(h) Fe by DW leaching
(i) Na by DW leaching

Fig. 3