A GEOCHEMICAL INVESTIGATION OF PADDY (P) AND NON-PADDY (NP) SOILS ON A CATENA: A CASE STUDY OF GHAEMSHAHR IN MAZANDARAN PROVINCE, IRAN

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Abstract. Paddy soils are a main soil resource for food production and they cover a large area of the world's surface. A geochemistry study was performed on a catenary sequence of Paddy and Non-Paddy soils in the lowland and upland areas of Ghaemshahr City in Mazandaran Province, Iran. 10 soil profiles were investigated and then, a comparison was made between the Paddy and Non-Paddy soils based on their geochemical compositions and developments. Soil clay mineralogical analysis showed that the Non-Paddy soils had a large amount of vermiculite, whereas smectite was the dominant clay mineral of the Paddy soils. The cation exchange capacity, clay content, and bulk density are higher in the Paddy soils. Rice cultivation increases the amount of amorphous Fe and decreases the amount of free Fe-oxide. The results of free Fe-oxide and amorphous Fe assessments, revealed that the Non-Paddy and upland soils were more developed than the Paddy and lowland soils. The mean concentrations of the major elements did not show any significant differences between the two types of soils. The mean values of all the heavy metals, except for Mn and As, in the Paddy soils were lower than those of the Non-Paddy soils. The reason for the reduction of heavy metals in the P compared to NP soils was their probable relationships with Fe/Mn oxide minerals and subsequent leaching. Based on principal component analysis, the differences between the Paddy and Non-Paddy soils were related to Mn and Fe group elements. The results indicated that the concentrations of the elements and other properties of the Paddy soils were dependent on the soil parent materials, especially on the textures of the sedimentary layers.
Keywords: *geochemistry, heavy metal, principal component analysis, soil development, smectite*

Introduction

The chemical composition of soil in primary stage of pedogenesis, will be reflect the chemical composition of the parent material, whereas the chemical composition of adult soils highly controls by the factors of weathering environment (Thanachit et al., 2006). Rice is the main source of food for more than half of the world's population and is cultivated on almost 155 million hectares in 114 countries (Kögel-Knabner et al., 2010). Paddy soils are anthropogenic soils widely distributed in eastern Asia and some other parts of the world (Huang et al., 2015). The formation of P soil, which is hydromorphic, is severely influenced by anthropogenic factors (Gong, 1983). It is not a natural soil and can be strongly affected by such management techniques as leveling, tillage, puddling,

submerging (Wissing et al., 2013), and the use of fertilizers. Its formation is also enforced by a special management, which can lead to its characteristic redoximorphic features (Kölbl et al., 2014). Frequent flooding leads to anoxic situation in the soil and decrease rates of organic matter decomposition (Sahrawat, 2005), while it exacerbates mineral weathering (Nanzyo et al., 1999) and leaching process.

In paddy rice management, soils are held submerged for several months of the year and as a result, their geochemical, micromorphological, and mineralogical features undergo some changes triggered by periodic submergence and drainage. Moreover, P soils grow from various parent materials and may be extremely altered by their chemical compositions, mineralogies, and other properties, such as texture (Kyuma, 2004; Chandrajid, 2005; Prakongkep et al., 2008). Hasannezhad et al. (2008) and Sano et al. (2006) reported that clay mineralogy is further influenced by its parent material rather than by redoximorphic conditions. In contrast, Hasannezhad et al. (2008) found an enhanced formation of smectite that was caused by the hydromorphic conditions of the P soils developed on alluvial materials. Elements concentrations in P soils have been studied by Chandrajith et al. (2005), Prakongkep et al. (2008), and Halim et al. (2015). Prakongkep et al. (2008) discovered that the concentrations of the elements and other properties of Thai P soils frequently depended on their parent materials, especially on the textures of the alluvial layers.

Many P soils become contaminated with heavy metals (Wong et al., 2002; Kyuma, 2004), while some useful trace elements become deficient due to geochemical variations or crop harvest (Kon et al., 2001). The affluence of trace elements in tropical Asian P soils is significantly diverse. Trace elements in agronomical soils mainly depend on the geochemical compositions of their parent materials during the primary stage of tillage (De Temmerman et al., 2003). Mitchell (1974) reported that the total amounts of trace elements in soils basically depend on the types of their parent materials and on which pedogenic processes occur.

Halim et al. (2015) studied the heavy metals of P soils in Bangladesh and reported that the average amounts of Zn, As, Mn, Ni, Cu, Pb, and Cr found in the P soils and sub-soils were less than those causing the mean and moderate pollutions of the selected soils of the world. Domingo and Kyuma (1983), Wang et al. (2003), and Wong et al. (2002) investigated the concentrations of elements in the P soils of many tropical Asian countries and found significantly different abundances of trace elements in them. Each region was rich in some particular elements. Although the concentrations of trace elements in different soils and plants have been measured in numerous studies in several parts of the world (Kabata-pendias, 2011), little research has been conducted in this field in Iran.

Therefore, this paper aimed to firstly evaluate the concentrations of the major and trace elements in the studied P soils and secondly compare the P and NP soils under study based on geochemistry and soil development.

Material and methods

Study area and sampling

The study area was located in Ghaemshahr, Mazandaran Province in northern Iran (*Fig. 1*). Its average annual temperature and precipitation are 16.1°C and 734 mm, respectively. The soils were developed under xeric and thermic soil moisture and temperature regimes, respectively (Banaei, 1998). The parent materials in the studied

area were derived from alluviums altered from primary rocks content calcite, dolomite and loess moved to this flatland. 10 representative profiles were selected along a catena based on their topography for this research: 5 pedons for P and 5 others for NP soils. Soil colors were determined by Munsell color system (Munsell, 2014). The soils were defined and classified based on Soil Taxonomy (Soil Survey Staff, 2014; *Table 1*).
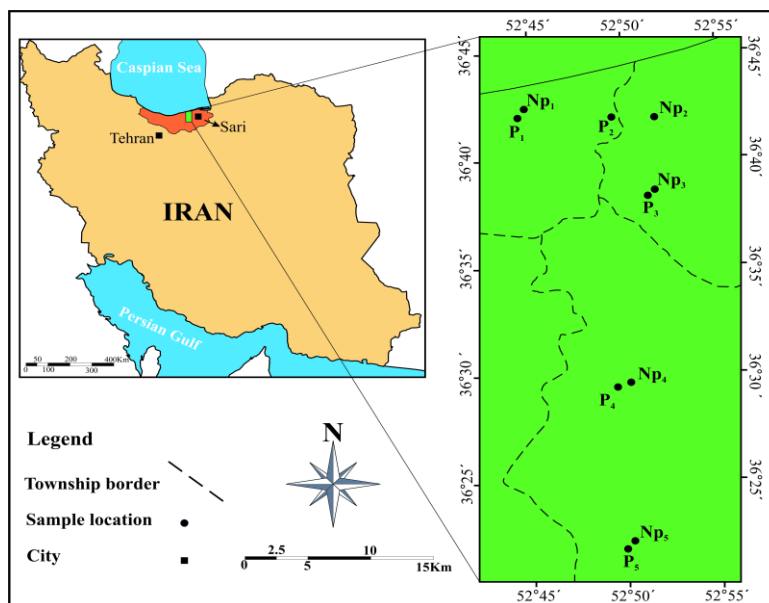
Figure 1. *Location of the study area and sampling sites along the 10 Pedons are indicated*

Physico-chemical analysis

Particle-size distribution was defined by the method of Bouyoucos hydrometer (Bouyoucos, 1962). The organic carbon contents of the soils were obtained through wet oxidation by using chromic acid and via return titration by using ferrous ammonium sulphate based on the method described by Nelson (1982). The pH of the soil samples was measured with a pH electrode in a suspension of 1:1 (soil: H_2O). Sodium acetate (NaOAc) was applied at pH 8.2 to evaluate CEC (Chapman, 1965). A titration method was employed to assess carbonate content (US Salinity Laboratory Staff, 1954). In addition, the method of Mehra and Jackson (1960) was used to evaluate dithionite-extractable Fe (Fe_d) for the bulk soil samples of < 2 mm. The taken samples were dried at 105°C for 24 h in an oven and weighted to determine Bulk Density (BD) through the method of paraffin sections (Blake and Hartge, 1986). Amorphous Fe (Fe_o) was extracted by using 0.3 M of ammonium oxalate solution (pH 3) in a dark place (McKeague and Day, 1966).

Mineralogical analysis

The method of Mehra and Jackson (1960) was utilized to eliminate the attaching chemical factors and dissociate the clay fractions (Kittrick and Hope, 1963). For clay discretion (< 2 μm), centrifugation of the iron-lacking soil samples at 750 rpm was done for 5.4 min (Kittrick and Hope, 1963). A D8 ADVANCE X-ray (Bruker) diffractometer was used to perform an X-ray analysis on the fine and coarse clay fractions (Jackson, 1975). To make a credible comparison between the Relative Peak Intensities (RPIs) of

the different samples, we made use of equal concentrations of the clay suspensions. 001 reflections were considered after Mg and K saturations and Ethylene Glycol (EG) salvation. Perusing of the K-saturated samples was followed after performing the drying and heating processes at 330 °C and 550 °C for 4 h. An overnight treatment of the samples with 1 N HCl solution at 80 °C was carried out for kaolinite identification in the presence of trioctahedral chlorite. A semi-quantitative assessment of the clay minerals was conducted based on the respective peak areas obtained from X-Ray Diffraction (XRD) in the glycol-treated samples (Johns and Grim, 1954).

Geochemical analysis

The geochemical analyses of the soil samples were done via X-Ray Fluorescence (XRF) spectroscopy of the compacted powder/pellets (Nisbet et al., 1979) and aqua regia digestion with a blend of $HClO_4$, HNO_3, HCl, and HF at 200 °C followed by ICP/OES and ICP/MS for the major and trace elements, respectively. Also, many trace elements were analyzed through Instrumental Neutron Activation Analysis (INAA) (Hoffman, 1992). The geochemical analyses were performed at the Actlabs laboratory (Ontario, Canada).

Statistical analysis

The concentration of elements and physicochemical properties including texture and CEC of P and NP soils were statistically analyzed using Principle Component Analysis (PCA) with the SPSS (version 21). Also Independent Samples T-test was applied to compare the concentration of elements in P and NP soils and if there were significant differences between two land uses based on the concentration of elements by the SPSS (version 21).

Results and discussion

Physico-chemical properties

The major physicochemical and morphological properties of the studied soils are presented in *Table 1*. As depicted in this table, the soils have Munsell colors ranging from 2.5Y to 10YR. The P soils were poorly drained since displaying a 2.5Y hue resulted from the annual redoximorphic conditions over many years. The evidence showed that endosaturation was responsible for the redoximorphic properties of the soils. A considerable diversity was observed between the textures of the P and NP soils, from clay to silty clay loam. A higher amount of clay was found in the lowland area (*Table 1*). This could be explained by the depositions of the clay-size particles originated from the upland area (Khormali et al., 2009). Wilding et al. (1982) reported that soil texture in a lowland area is finer than in any other locations. According to *Table 1,* Profile NP_5 has a coarser texture compared with the other profiles (SiCL). The other soils have a relatively heavy texture (silty clay to clay). $CaCO_3$ percentage ranges from 2% in the C horizon of NP_4 to 27% in the A horizon of P_4. BD showed considerable differences in the 2 selected land uses. BD was higher in the P than in the NP soils. P_2 and NP_2 had the highest and lowest contents of BD, respectively. Soil compaction caused by tillage processes had increased BD in the P soils. According to Dang et al. (2002), tillage practices decrease soil Organic Matter (OM) and result in a higher BD and lower total porosity.

Table 1. *Morphological and physicochemical properties of the studied soils*

Horizon	Depth (cm)	Color (moist)	pH	CECᵃ (cmol(+)kg⁻¹)	Sand (%)	Silt (%)	Clay (%)	Textural classᵇ	CCEᶜ (%)	OCᵈ (%)	BDᵉ
				NP₁, Haplaquolls							
A	0-20	10YR3/2	7.76	32	4	44	52	SiC	15	1.26	1.78
AB	20-40	2.5Y3/2	7.80	34.1	8	44	50	SiC	16	1.19	1.81
B_g	40-60	2.5Y5/3	8.02	34.1	6	48	46	SiC	14	0.86	1.84
BC_g	60-100	2.5Y4.5/3	8.22	34.5	6	44	50	SiC	18	2.15	1.80
				P₁, Haplaquepts							
A_p	0-15	2.5Y4.5/4	7.79	41.8	10	32	58	C	19	1.02	1.89
AB_g	15-40	2.5Y4.5/4	7.89	38	8	33	59	C	18	1.06	1.96
B_g	40-70	2.5Y4.5/3	7.82	37	7	37	56	C	23	0.16	1.95
BC_g	70-100	2.5Y4/2	7.93	32	8	42	50	SiC	20	0.62	1.94
				NP₂, Calciaquepts							
A	0-10	10YR4/4	6.04	38.3	14	40	46	SiC	4	3.06	1.83
AB	10-35	2.5Y3/2	7.65	35.8	10	41	49	SiC	7	1.17	1.82
B_kg1	35-70	2.5Y4/2	7.57	30.0	14	42	44	SiC	18	0.66	1.80
B_kg2	70-100	2.5Y4/1.5	7.50	34.9	13	42	45	SiC	14	0.64	1.81
C_g	100-130	2.5Y4/1.5	7.47	21.6	12	40	48	SiC	12	0.46	1.78
				P₂, Haplaquepts							
A	0-20	10YR4/3	8.04	45	10	36	54	C	13	2.03	1.99
B_wg1	20-50	2.5Y3/4	7.83	35	12	38	58	C	5	0.47	1.99
B_wg2	50-70	2.5Y3/4	7.78	28.3	14	40	56	C	5	1.40	1.91
C_g	70-90	2.5Y3/5	7.70	31	8	42	50	SiC	10	1.63	1.89
				NP₃, Calciaquolls							
A	0-25	10YR3/2	7.24	38	9	42	49	SiC	11	3.54	1.78
B_g	25-55	2.5Y3.5/2	7.80	33	11	41	48	SiC	13	0.78	1.72
C_kg	55-80	10YR4/2	7.99	32	14	34	52	C	18	0.51	1.70
				P₃, Calciaquepts							
A_pg	0-20	2.5Y4/1	7.75	41	12	36	52	C	13	1.62	1.90
B_g	20-45	2.5Y4/1	7.70	42	12	34	54	C	12	1.24	1.92
B_kg	45-65	2.5Y4/2	7.81	44.1	10	34	56	C	13	0.62	1.91
C_g	65-90	2.5Y4/2	8.01	40	18	32	50	C	9	0.64	1.89
				NP₄, Haploxerolls							
A	0-19	10YR3/2	7.67	30	17	41	42	SiC	9	1.48	1.70
B_w1	19-45	10YR3/3	7.78	28.7	17	43	40	SiC	10	0.78	1.68
B_w2	45-65	10YR3/4	7.84	27.9	19	42	39	SiCL	5	0.55	1.72
C	65-100	10YR3/3.5	7.69	31.2	23	35	42	C	2	0.4	1.71
				P₄, Endoaquepts							
A_g	0-18	2.5Y4/1	7.65	40	20	29	51	C	27	1.87	1.97
CB_g	18-45	2.5Y4/4	7.85	32	17	30	53	C	24	0.66	1.95
C_g	45-90	10YR4/6	7.77	30	26	34	40	C	25	0.35	1.92
				NP₅, Calcixerolls							
A	0-27	10YR3/2	7.75	32.4	16	44	40	SiCL	9	1.37	1.67
AB	27-44	10YR3/3	7.81	29.9	18	43	39	SiCL	3	0.73	1.65
B_K	44-66	10YR3/4	7.77	32	20	41	39	SiCL	12	0.8	1.68
CB	66-90	10YR3/3.5	7.65	22.8	21	37	42	C	13	1.0	1.63

P5, Haplaquepts											
A_{pg}	0-21	2.5Y3.5/2	7.28	37	18	32	50	C	16	1.84	1.92
B_{g1}	21-47	2.5Y3/3	7.82	32	15	35	50	C	18	1.18	1.93
B_{g2}	47-65	2.5YR4/1	7.81	30	19	34	47	C	17	1.08	1.90
C_g	65-95	2.5YR3/1	7.92	30	20	35	45	C	10	0.62	1.91

[a]CEC: cation exchange capacity
[b]C: clay, si: silty, L: loam, S: sandy
[c]CCE: cation exchange capacity
[d]OC: organic carbon
[e]BD: bulk density

Bar graphs of mean values of Fe_d and Fe_o for surface horizon of soil profiles are shown in *Figure 2*. In most soils, based on morphological properties, pedogenic Fe and clay content, soil age is estimated (Costantini and Damiani, 2004). Dethier et al. (2012), reported that, the Dominant forms of Fe in soils, are Fe_t, Fe_d, Fe_o. Therefore, (Fe_d-Fe_o) indicates crystalline form of Fe, Fe_o/Fe_d represents the degree of crystallinity of Fe oxides, and finally (Fe_d-Fe_o)/Fe_t indicates the ratio of crystalline to total Fe (Schaetzl, 2005). Rezapoor et al. (2009) studied different forms of Fe oxides and their distribution in calcareous soils in Northwest of Iran, and reported that, with increasing weathering, Fe_d increases and Fe_o/Fe_d decreases. In hydromorphic condition and deficiency of oxygen, Fe is converted to Fe (II), and in this condition, the possibility of forming a crystalline Fe oxides is lower, resulting in a higher Fe_o/Fe_d ratio. In this study, paddy soils have a higher amount of Fe_o compared to non-paddy soils, whereas, non-paddy have a higher content of Fe_d. B_k horizon of NP_5 has a higher content of Fe_d and lower content of Fe_o, whereas, C_g horizon of P_1 has a lower content of Fe_d and a higher content of Fe_o. The studied paddy soil samples have higher contents of Fe_o results in higher ratios of Feo/Fed compared to non-paddy soils. Along the catena, from lowland to upland, this ratio always decreases, which is probably an indication of higher weathering in upland soils compared to the lowland soils.
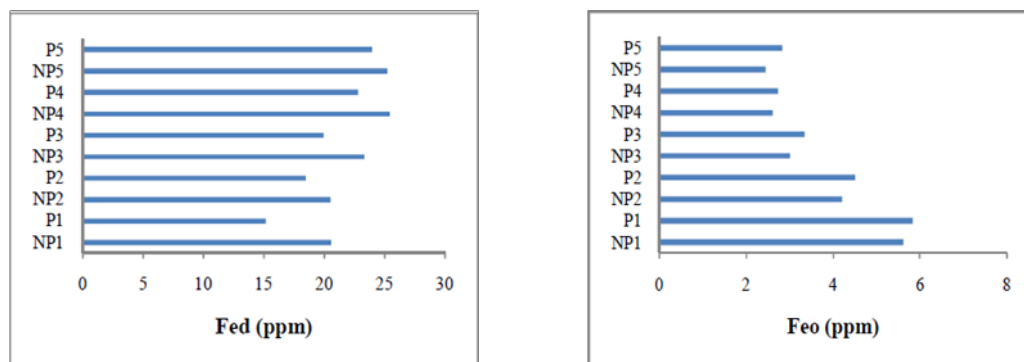

Figure 2. Bar graphs of mean values of Fe_d and Fe_o for surface horizon of soil profiles

Mineralogical characteristics

Figure 3 demonstrates the results of X-ray diffractograms recorded in the selected P and NP soils. Two cases of peaks were shown for almost identical results. As can be observed, illite, chlorite, kaolinite, smectite, and vermiculite exist in the clay fraction.

The main mineral found in the P soils was smectite whereas in NP soils was illite. Illite and chlorite as clay minerals are mostly seen in areas with a limited process of soil formation (Wilson, 1999). Their existence in parent materials mostly determines their abundance in soils. The P soils in this study displayed a higher amount of smectite due to their several months of poor drainage and saturation each year (*Fig. 3b*). In these conditions, smectite neo-formation had occurred due to the reduction of some iron in the presence of some soluble ions like Al, Mg, and Si coming from the adjacent uplands (Borchardt, 1989). Small amounts of kaolinite were also found in all the studied soil profiles. In the NP soils, vermiculite was present in large amounts (*Fig. 3a*). Vermiculite occurrence in these soils was mainly caused by high leaching conditions and K removal from mica (Douglas, 1989).
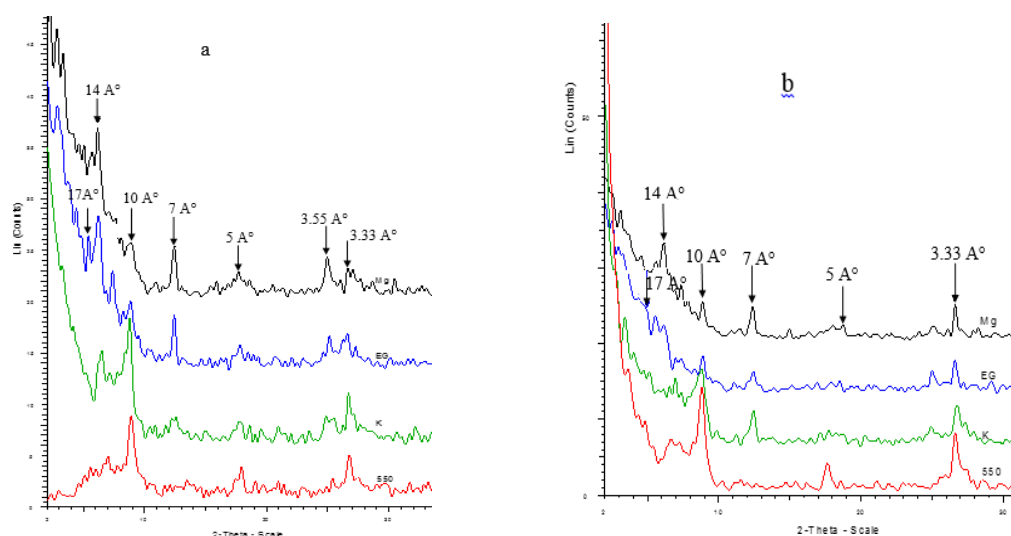
Figure 3. *X-Ray diffraction patterns of clay fraction for the representative soil profiles. (a) Bkg₁ horizon of NP₂ and (b) Bwg horizon of P₂*

Geochemical analysis

The full geochemical analyses of the soils are not demonstrated because of the large data set obtained, but the mean concentrations of the P and NP soils are exhibited in *Table 2*. Si, Al, Ca, Fe, Mg, and K were the most elements found in both P and NP soils. None of the major element concentrations showed any significant differences between the P and NP soils. The contents of Ba, Cs, S, and Zr in the P soils were higher, but Br and Rb amounts were lower than those of the NP soils. The mean values of all the heavy metals in the P soils, except for Mn and As, were lower than those of the NP soils.

Strong associations were found between Fe/Mn oxides and other heavy metals in the P soils. In paddy rice management, soils are commonly submerged and thus, excessive soil water may elevate leaching and migration of soluble heavy metals. Talyor and Mckenzie (1966) discovered that Co content was dependent on Mn oxide minerals. Therefore, the lower heavy metal contents in the P compared to the NP soils could be ascribed to Fe/Mn oxide minerals.

The mean concentrations of Si, Mn, Mg, As, Co, Cr, Cs, Cu, Ni, and Rb in the studied soils were higher than the amounts reported for normal surface soils worldwide

(Essington, 2004; Kabata-Pendias, 2011), whereas the mean values of Mn, Ti, As, Co, Cr, Cu, Ni and Zn were higher than the amounts reported for the other contaminated P soils (Wong et al., 2002; Wang et al., 2003; Chandrajith et al., 2005). Only Pb concentration was lower than those of the global and other unpolluted P soils. The amounts of other elements in the studied P soils were comparable to the values obtained for the normal surface soils and P soils in the world. Pb concentration is lower than both worldwide and other unpolluted paddy soils. In comparison to the critical soil concentration values established, only Cr values were higher (Alloway, 1995).

Table 2. *The mean values of some oxides and elements in studied P and NP soil samples, mean values for uncontaminated P soils, mean values of normal surface soils worldwide and critical soil concentration for contaminated soils*

Element	Mean values for non-paddy soils	Mean values for paddy soils	Mean values for uncontaminated paddy soils[a]	Mean values for normal surface soils worldwide[b]	Critical soil concentration[c]
(g kg^{-1})					
SiO2	509.6	507.75		250-410	
Al2O3	148.7	137.48		10-300	
Fe2O3	62.9	60.32		2-550	
MnO	1.08	1.21	0.39	0.27-0.53	1.5-3
MgO	23.4	23.46		0.4-9	
CaO	66.7	78.9		0.7-500	
Na2O	8.7	9.4		0.15-25	
K2O	24.9	23.31		0.08-37	
TiO2	8.3	8.3	5.4	2.3-26	
P2O5	1.9	2.13		0.035-5.3	
(mg kg^{-1})					
As	12.55	13.33	1.7	4.4-9.3	
Ba	403.33	416.11		175-520	
Be	2.11	2.11		0.35-3.52	
Br	14.11	11.11		1-110	
Co	21.66	21.33	10.2	4.5-12	25-50
Cr	112.44	108.33	64	12-83	75-100
Cs	9.22	9.55		5.06	
Cu	45.88	40.88	20.7	13-24	60-125
Ni	61.77	57.44	25.5	13-34	100
Pb	20.11	17.88	23.3	22-44	100-400
Rb	160	158.88		30-120	70-400
S	340	400		30-1600	
Sr	209	254.11		87-210	
Zn	101.11	93.55	61	45-100	
Zr	152.8	170.11		60-2000	

[a]Data from Wong et al. (2002); Wang et al. (2003); Chandrajith et al. (2005)
[b]Data from Essington (2004); Kabata-Pendias (2011)
[c]Data from Alloway (1995)

Independent Samples T-test

An Independent Samples T-test was applied to compare the concentration of elements in P and NP soils and if there were significant differences between two land uses based on the concentration of elements. Levene's test was conducted to evaluate homogeneity of variance. Results are presented in *Table 3*. As seen in *Table 3,* Result of Levene and T-test of all elements were not statistically significant ($p > 0.05$). The results indicated that there was no significant difference between the mean (M) and standard deviation (SD) of concentration of elements in P and NP soils.

Table 3. *Independent Samples T-test of some oxides and elements between studied P and NP soil samples*

Element	P soils		NP soils		df	t	p
	M^a	SD^b	M	SD			
SiO2	507.75	41.40	509.60	57.20	16	0.080	0.937
Al2O3	137.48	14.80	148.70	10.80	16	-1.840	0.084
Fe2O3	60.32	4.70	62.90	6.00	16	-1.010	0.326
MnO	1.21	0.23	1.08	0.20	16	1.160	0.263
MgO	23.46	3.40	23.40	2.20	16	0.490	0.961
CaO	78.90	20.00	66.70	23.60	16	1.170	0.256
Na2O	9.40	1.90	8.70	3.00	16	0.615	0.547
K2O	23.31	2.90	24.90	2.60	16	-1.240	0.233
TiO2	8.30	0.49	8.30	0.52	16	-0.138	0.892
P2O5	2.13	0.35	1.90	0.25	16	1.150	0.265
As	13.33	2.23	12.55	3.04	16	0.618	0.546
Ba	416.11	53.14	403.33	43.28	16	0.559	0.584
Be	2.11	0.33	2.11	0.33	16	0.000	1.000
Br	11.11	4.70	14.11	4.25	16	-1.41	0.175
Co	21.33	2.59	21.66	2.17	16	0.295	0.772
Cr	108.33	6.51	112.44	6.26	16	-1.364	0.191
Cs	9.55	1.50	9.22	2.04	16	0.393	0.699
Cu	40.88	5.62	45.88	9.95	16	-1.312	0.208
Ni	57.44	5.29	61.77	6.18	16	-1.690	0.130
Pb	17.88	3.01	20.11	2.52	16	0.080	0.109
Rb	158.88	24.72	160.00	46.36	16	0.063	0.950
S	400.00	16.00	340.00	15.00	16	0.919	0.372
Sr	254.11	51.20	209.00	40.15	16	2.080	0.054
Zn	93.55	10.00	101.11	13.05	16	-1.370	0.187
Zr	170.11	41.78	152.80	21.46	16	1.107	0.285

[a]Mean
[b]Standard deviation

Parent material uniformity

The relationship between the total amounts of Ti and Zr was applied as an index of uniformity for soil parent materials (Alonso et al., 1991). As shown in *Figure 4,* P$_1$ and NP$_1$ have the Ti/Zr ratios of about 56-58 and 59-60 through their profiles in the lowland

area, respectively. In P_3 and NP_3, Ti/Zr ratios are relatively constant around 52-53 and 56-59, respectively. Finally, in the upland region, Ti/Zr ratios in P_5 and NP_5 are nearly 47-54 and 48-51, respectively. Few differences were observed in Ti/Zr ratios in the C compared to the other horizons, which demonstrated uniformity of the parent materials. Nable et al. (1999) and Marques et al. (2004) reported that the slight variations of 5 and 16 units respectively in Ti/Zr ratios in the profiles indicate the uniformity of parent materials. Therefore, the studied soil parent materials were uniform.
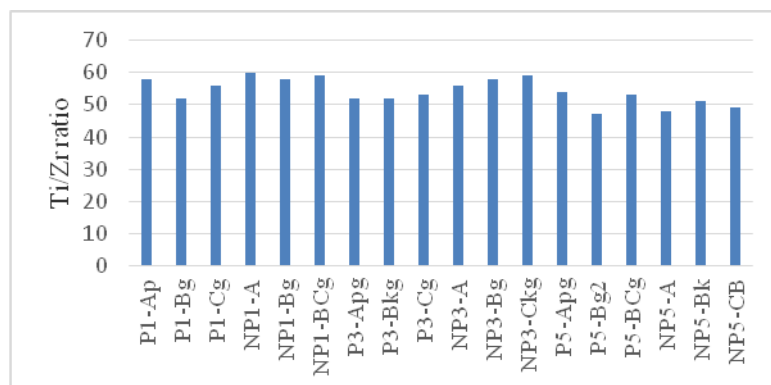

Figure 4. *Bar gragh of Ti/Zr ratio of studied paddy and non-paddy soils*

Principal component analysis

Principal component analysis (PCA) was applied to assess the elements under similar geochemical treatments and group the soil samples according to their geochemical associations (Weber and Davis, 1990; Bellehumeur et al., 1994). PCA of the concentrations of the introduced elements and physicochemical properties, including texture and CEC, were applied for all the P and NP soils. The PCA results of the concentrations of the elements and physicochemical properties of the NP soils are displayed in *Figure 5b*. 2 factors illustrated only 72% of variation in the data. Finally, 4 affinity groups were identified. The first group was composed of Si, Zr, and Na relevant to the textures of the soils. Quartz (SiO_2) was the basic mineral in the sand fraction. Zr was a residual element in the soils, the main (Stiles et al., 2003; Kabata-Pendias, 2011) and abundant (Lukashev and Pietukhova, 1974) mineral of which is zircon ($ZrSiO_4$) in sandy soils. The second group contained Ca, Co, and Fe. The reasons for the presence of Ca in this group were unknown. The third group included CEC, Zn, Cs, and Br and the last group was comprised of clay, Al, K, Ni, Mg, Cr, Sr, and Ba. This group was associated with clay content since the mentioned elements were parts of oxides and clay minerals (Kabata-Pendias, 2011; Sterckeman et al., 2006).

The PCA results of the concentrations of the elements and physicochemical properties of the P soils are exhibited in *Figure 5b*. 68% of variation in the data for these soils was illustrated by 2 factors. 3 groups of properties were distinguished. The first group contained sand, Na, Zr, and Si, which were linked to the textures of the soils. The second group consisted of CEC, clay, Al, Fe, K, Ni, As, Cs, Co, Pb, Zn, Rb, Ba, Mn, and Mg. Al, K, Rb, and Cs were related to feldspar and clay contents (Sterckeman et al., 2006; Kabata-Pendias, 2011). Being parts of the group of subordinate oxides, Mn, Pb, Zn, Ni, Zn, Ni, Co, As, and Cu were linked with Fe since they can be exchanged with Fe in the oxide structure (Kabata-Pendias, 2011). Manganese is responsible for the

great degree of assembly of Mn concretion with some trace elements, especially with Pb, Cr, and As. Moreover, the oxidation of these metals by Mn oxides probably controls their redox behaviors in soils (Bartlett, 1986). The third group included Ca, Sr, Br, and S. Strontium belongs to the alkaline earth metals and has the same behavior as Ca. Its physical properties, particularly the size of its ionic radius, are partly similar to those of Ca, indicating their possibility of being replaced with each other (Kabata-Pendias, 2011).
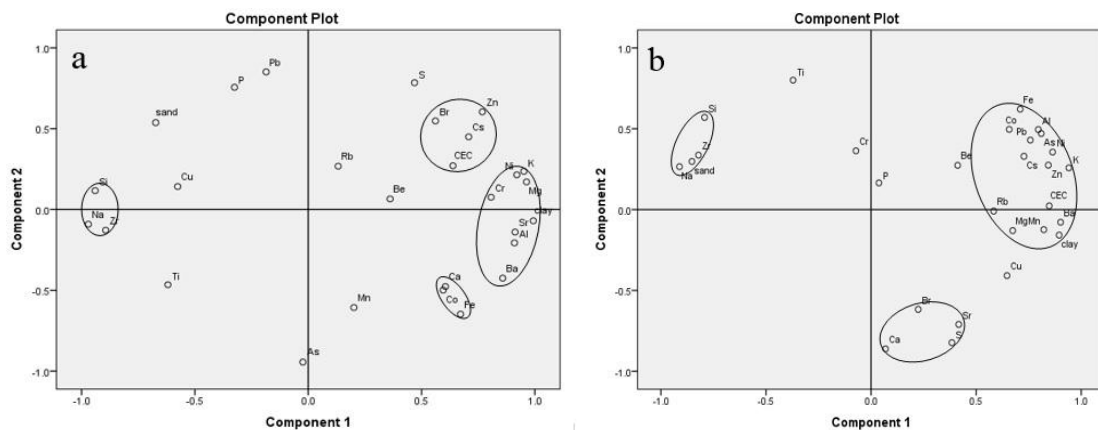
Figure 5. PCA results for the chemical composition and physicochemical properties of studied soils: (a) distribution of elements and soil properties of non-paddy soils (b) distribution of elements and soil properties of paddy soils

Based on PCA, the difference between the P and NP soils was related to the group elements of Mn and Fe. In the P soils, most of the heavy metals were gathered in one group and linked with Fe and Mn, while they were diffused in the NP soils. Mn and Fe are the most frequent metals in the lithosphere and thus, their oxides and hydroxides cause the solubility or alluviation of heavy metals in soils (Jounes and Jacobson, 2009). These oxides and hydroxides also play a main role in As, Pb, Cu, Zn, Cr, and Ni preservations in soils (Aydinalp and Marinova, 2003).

Conclusions

This research revealed that the concentrations of the elements and other properties of P soils depend on soil parent materials, especially the textures of sedimentary layers. Ti/Zr ratio confirmed uniformity of the parent materials along the catena and within the profiles. Profiles P_5 and NP_5 with a deep water table were the most weathered soils based on Fe_d and Fe_o values. The studied profiles had higher Si amounts and lower Ca, Mg, and K contents compared with the other pedons of the catena; however, Al and Fe amounts were uniform. Profiles P_1 and NP_1 were less weathered because they had the lowest positions in the landscape with shallower water tables. In the collation between the P and NP soils, the Ca, S, Sr, Ba, and Zr contents of the former soils were found to be higher than those of the latter soils. Contrarily, the amounts of Cr, V, and some heavy metals, including Pb, Ni, Cu, and Zn were higher in the latter soils compared to those of the former soils. The reason for the reduction of heavy metals in the P compared to NP soils was their probable relationships with Fe/Mn oxide minerals and

subsequent leaching. Clay mineralogy revealed that Smectite amount was higher in the P soils because of its poor annual drainage and saturation for a long period of time. Vermiculite was the dominant clay mineral under well-drained conditions. There were two reasons for finding no significant differences between the P and NP soils under study based on geochemical properties: 1) short period of rice cultivation; and 2) lack of any significant differences between them in terms of drainage.

We suggested that complementary studies, including microprobe analysis, be performed on thin sections of the studied soils in order to determine if the smectite in clay fraction of soils is formed from other minerals deformation or in situ formation.

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