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Study of Reduction-Oxidation Potential and Chemical Charcteristics of a Paddy Field During Rice Growing Season

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Abstract: This study addressed the reduction-oxidation potential in paddy soil during rice-growing season and chemical properties of soil profiles in a semiarid area of Iran. Different stages of this research including field studies, laboratory analysis and interpretation of data had done by using of Excel and SPSS programs. Redox potential (Eh) and pH were measured at soil and water depths using a portable pH meter with Pt and glass electrode. The average of pH in surface horizons of all profiles before submerging was 7.57, but this average in the rice-growing season becomes 7.19. The average of cation exchange capacity of all profiles was 20.8 Cmol (+) kg^{-1} and the mean of calcium carbonate percent in control section depth of all soils were more than 40%. Measured values of Eh shows that Eh values in surface depths are more than subsurface layer (45 cm deep). The most Aerobic conditions in of 1-cm depth with Eh +440 mV and the most reduction conditions in 15 and 45 cm depths the Eh was +4.5 and -222 mV, respectively. The results of the date correlation analysis shows that there is a reciprocal significant relationship between times of submergence and the mean of Eh of all depths and the mean of pH in surface depths ($r = -0.600$, $p = 0.003$, $r = -0.747$, $p = 0.000$, respectively). Also there is a significant relationship directly between the mean Eh and the mean pH of surface depths($r = +0.897$, $p = 0.000$).

Key words: Reduction-oxidation potential, paddy fields, Ilam province, surface depths, surface horizons

INTRODUCTION

Paddy rice (*oryzae sativa*) is the major crops in the shirvan plain of Ilam province. Unfortunately, at this time, no research was done on the chemical characteristics of soils in this plain and this is the first study which done in the plain. Paddy soils are the most important natural resources in the world. In comparison with other non-paddy soils these soils have different physical and chemical properties. In comparison with other farm land, chemical characteristics of paddy soils are different, because the soil reaction (pH) normally and seasonal changed and solubility of some elements (particularly micronutrients) in soil solution are cause of poisoning and imbalance of elements in it that changes the texture, structure and nutrient status of plants. In conditions in which the soils are submerged, some significant changes in electro-chemical solution can accrue. Ponnamperuma (1972) believed that by reduction of soil or redox potential decreasing, the reaction (pH) in acid soils increased and pH in alkaline soils decreased. So it may affect on the absorption/desorption of nutrient elements. Reduction-oxidation potentials are indicators of nutrient availability and mobility of heavy metals and are also important in the development of pedogenic properties such as soil color, iron depletions and concentrations (Sigg, 2000). Redox potential measurements offer a semi quantitative assessment of the intensity of oxidation or reduction of a soil, which reflects many redox couples operating simultaneously in a dynamic system. The assessment of soil redox potential is particularly useful for characterizing the onset of reducing conditions in a soil caused by a lack of O_2 and for partly interpreting their associated biogeochemical processes such as denitrification or bacterial degradation processes (Crawford *et al*., 2000). The redox potential is related to the concentration of several redox pairs in the soil, oxygen is the first acceptor that plays an important role (Aldridge and Ganf, 2003). Soil microfauna capable of using terminal electron acceptors other than molecular oxygen are able to survive under these anaerobic conditions. Reduction of NO_3^- to N_2 generally occurs first, followed by Mn (III/IV)/Mn (II), Fe (III)/Fe (II), SO_4^{-2}/H_2S and organic matter/CH_4, however, considerable overlap between the different redox systems has been observed (Gao *et al*., 2002). Re-oxidation of these reduced chemical species may occur when the reduced form encounters dissolved oxygen has diffused into soil pore water from surface flood water,

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from roots of aquatic plants such as rice or from the atmosphere during the sampling (Doran *et al*., 2005). The rate of reduction of ferric iron in the presence of organic material is more than the case in which absence of organic matter because hemi substances of the organic matter play a role as a carrier and it decreases the content of direct contact of iron reducing microbes with insoluble oxide species (Rakshit *et al*., 2009). It had been demonstrated that Fe (II) in soil pore water was oxidized to ferric oxide and formed concentric layers around the root surfaces as the root aged, until the epidermis eventually become impregnated with iron oxide (Doran *et al*., 2006). Platinum-tipped redox probes that can be easily made and repaired are an asset to researchers who often require numerous probes for studied of soil redox potential. Now Platinum Electrodes (Pt) widely are used to measure soils Eh in the field and the laboratory. Soil Eh measurements in the field have usually been made at weekly intervals using a portable meter. Generally, in transitional system turning from oxidized to more reduced conditions (+350 to -100 mV). Redox potential (Eh) measurement is a reading of voltage difference a working electrode such as a Pt electrode and a reference electrode inserted in the soil. In most circumstances soil redox potential within the root-race in paddy soil is between +200 to -300 mV (Moormann and van-Breemen, 1978). The objective of this study is to study the chemical characteristics of soils under the rice cultivation and evaluating the changes of redox potential of paddy soils in Shirvan plain, Ilam province.

MATERIALS AND METHODS

This study addressed the redox potential in paddy soil during rice-growing season and chemical properties of soil profiles in a semiarid area of Iran.

Study area: This study was conducted on the Shirvan plain located in the northeast of Ilam province, from 46° 43' to 46° 51' E longitude and 33° 32' to 33° 35' N latitude (Fig. 1, 2). The average elevation of the area is about 800 m above sea level. The Saimerah and Shirvan rivers, which pass through the plain, have distinctive effects on transportation and sedimentation of materials. The study area is part of Zagros orogenic zone, which extends throughout the province. Two rock unites are recognized in the area. The Gachsaran formation (lower Miocene) composed of evaporitic sediments in the form of thick bedded alternating layers of anhydrite and marls (exposed in the gypsiferous Hills) and Asmari formation (Aligocene to Miocence) consists of grey marls with calcareous materials (exposed in the Charmin mountain).

Field sampling: Two transects were selected in Shirvan rivers terraces and 10 profiles were excavated totally(four profiles in the Lareny transect and six profiles in the Lomar transect). Each soil horizon was sampled for lab analysis. Profiles were georeferenced with a hand-held GPS (GPSmap 76 Cs, GARMIN).

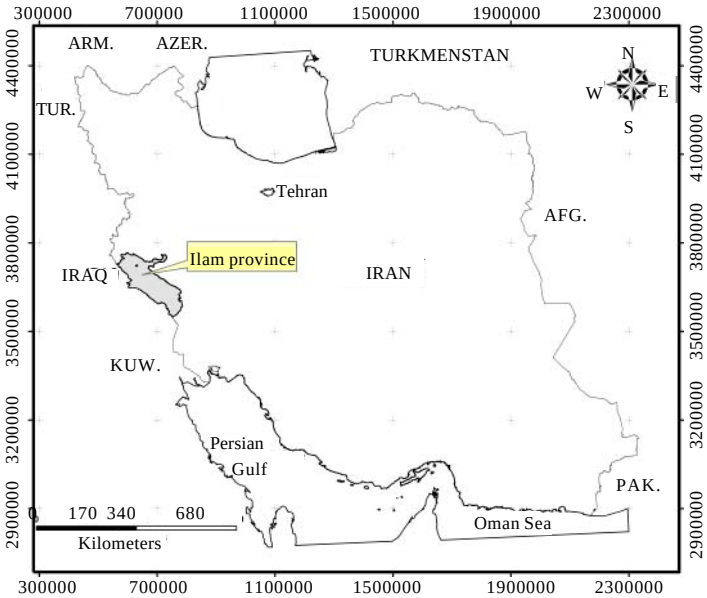

Fig. 1: Location of Ilam Province, southwestern Iran

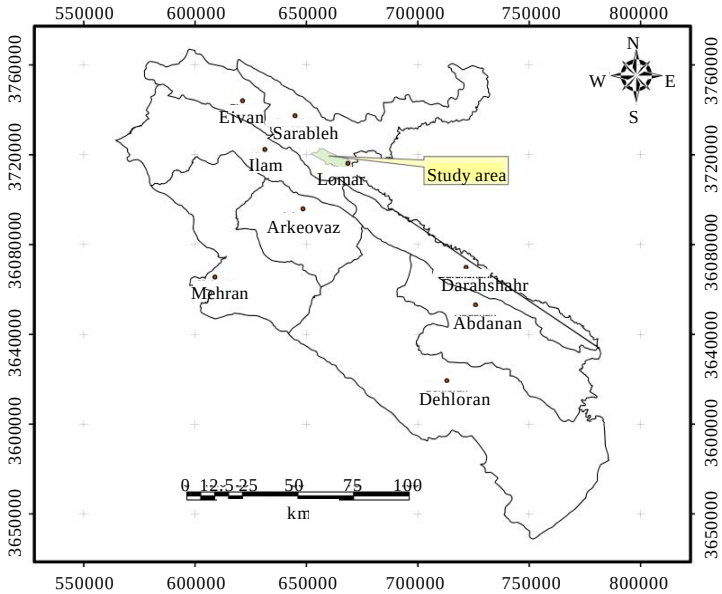

Fig. 2: Location of the study area in Ilam province

Methods: It should be noted that due to close similarities between 10 profiles, six soil samples of them were chosen for chemical analysis. All analyses were conducted on air-dried soil passed through a 2 mm sieve (Soil Survey Laboratory Staff, 1996). Soil pH was determined using an electrode pH-meter for a saturated soil paste using deionised water (McLean, 1982). The electrical conductivity (EC) was also measured in the saturated paste (Rhoades, 1982). Organic carbon was determined using the Walkley-Black method (Nelson and Sommers, 1982). Total N in the A horizons was measured using the Kjeldahl method (Bremmer and Mulvaney, 1982). To determine the exchangeable potassium, the neutral 1 N ammonium acetate extraction method was used (Knudsen *et al*., 1982). The Olsen method was used to determine extractable phosphate using a molybdate reaction for colorimetric detection (Olsen and Sommers, 1982). Calcium carbonate was determined for all soil samples using method described by Nelson (1982). Cation exchange capacity and exchangeable bases were determined with the ammonium acetate technique (pH 7.0) (Thomas, 1982). Free Fe (Fe_d), Si (Si_d) and Al (Al_d) were extracted via Dithionite-Citrate-Bicarbonate (DCB) method (Mehra and Jackson, 1960). The concentrations of metal were determined with an inductively coupled argon plasma analyzer (ICP; Jobimyvon. Co., Model JY138, Ultrace).

Redox potential measurement: This study addressed the redox potential in paddy soil during rice-growing season and chemical properties of soil profiles in a semiarid area of Iran. Using the combination platinum electrode Package, ERPt-13 model did reduction-oxidation potential (Eh) Measurement. In this electrode, half-cell reference and electrolyte reference includes Ag/AgCl and 3 M KCl+ AgCl, respectively. According to the Eh reading based on the measured temperature at the same time, half-cell reference potential was added, so according to the Table 1, final Eh may be calculated based on the following equation:

Table 1: Potential of the reference half cell Ag/AgCl, 3M KCl in different temperatures

Potential (mV)	Temperature (°C)
224	0
221	5
217	10
214	15
211	20
205	25
203	30
200	35
196	40
192	45
188	50

$$Eh_{(final)} = Eh_{(was\ read)} + Eh_{(half\text{-}cell\ reference)}$$

Using the portable pH meter (CPC 401 model) and platinum electrodes (ERPt-13 model), the Eh and pH reading at 1, 5, 10, 15, 45 cm depths in during rice-growing season was done daily from the 2nd day of rice planting to the 8th day and it was done every other day

to 22nd and weekly up to the rice harvesting time. Also temperature in soil depths and Eh, pH and Electrical Conductivity (EC) were measured in the surface water. These measurements were operated in Lareny land and in the location of number one profile. In this study, installation of permanent platinum electrode was performed in similar to Torabi's method (Torabi, 2001). Meanwhile, Pe was calculated by using the following equation:

$$Pe = (Eh/59.2)$$

Interpretation and analysis of data was performed by using of Excel and SPSS programs.

RESULTS AND DISCUSSION

Chemical characteristics of soils: The results of some physical and chemical characteristics of soils are obtained. Range of changes studied in all saturated soil paste pH has fluctuated between 7.24 and 8.08. The mean of surface pH in all soil horizons is 7.58. High soil pH affected from parent calcareous materials and the time of samples harvest was about 3 months after the rice growing that in this time the soil were not submerged. If we compare the values of pH with its values it shows the pH during the rice growing, we can find that pH of soil decreases after submerged the soil. The main effect of submerged is to increase pH of acid soils and decreased pH in alkaline and calcareous soils (Fig. 3). As can be see in Fig. 3, pH in surface horizons that are affected under submerged conditions in rice growing season are less than subsurface horizons. The value of pH in submerged calcareous and alkaline soils compared to aerobic conditions is lower and it is due to more CO_2 that is accumulated in submerged soil. Many researchers have shown that the pH of alkaline soils is very sensitive toward partial pressure changes of CO_2. The existence of PH more than 7 in the wet soil is depending on the climate or parent materials or both of them. The effect of parent materials can be seen in the best uniformity form in Bangladesh climate, so that all soils with high pH are covered with materials alluvial and they have free $CaCO_3$. The percent of organic matter in all soils is variable between 1.17 (profile No. 2) to 2.33 (profile No. 1) (Fig. 3).

The lowest amount of organic matter in surface horizons was belong to profiles 2 and 3, because they are young and the history of rice cultivation is short and also terracing and land leveling. Soils with organic mater in moderate to large amounts, can correct soil pH to neutral amount (6.5-7.5). This range is very useful for rice growth, because most nutrients absorbed by rice in this area is suitable. Surface horizons of all profiles have a Cation

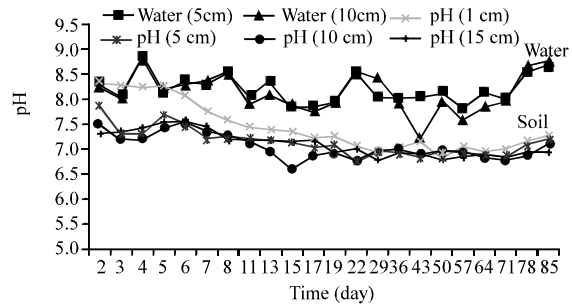

Fig. 3: Changes of redox potential at soil and water depths during rice-growing season

Exchange Capacity (CEC) changes range between 18 (profile No. 2) to 24 (profile No. 1) Cmol (+) kg^{-1} soil, average 20.8 Cmol(+)/kg soil and the lowest amount in the 2C horizon of profile 2 is (10 Cmol (+) kg^{-1} soil). The average of CEC in 410 samples of paddy soils in Asia tropical countries was 18.6 Cmol (+)kg^{-1}. Paddy soils (Fig. 3) in Java, Indonesia and the Philippines are rich with good quality and medium clays with high CEC are. The weight mean percent of calcium carbonate in control section depth of all profiles (except profile No. 4) were between 40% (profile No. 1) and 61.9% (profile No. 2). This is the main factor that controls pH in these soils. All profiles of the region do not show a regular and logical trend with calcium carbonate increasing in depth from the surface or vice versa that demonstrates the parent material is alluvial.

Fe_d in profiles No. 1 and 2 generally increases with depth, so that its content in 3Btkb horizon in profile No. 1 was twice compared to surface horizon (Table 2), which indicates more evolution in this layer. Nunez and Recio (2007) for presenting a regional interpretation of paleosols has also used Fe_d to total iron ratio (Fe_d/Fe_t). Large content of Fe_d indicate more evolution in the soils. The range of electrical conductivity of saturation extract (Ece) changes of the horizons were between 0.92 to 2.63 dS m^{-1} and the average is 1.91 dS m^{-1}. In nearly profiles to the river, value of ECe is higher and away the river the ECe is less. Increasing of electrical conductivity during the first few weeks in submerged calcareous soils to the solution of $CaCO_3$ was done by accumulation of CO_2 and decreasing of it is done along the submerged by the partial pressure of CO_2 pressure and decomposition of organic acids. Total nitrogen in the surface horizons is variable between 0.067 (profile No. 2) to 0.12% (profile No. 1). Relatively high amount of total nitrogen in surface horizons of profile1 is related to high accumulation of fully decomposed organic matter (Humus) that creates a dark color in the surface horizon.

Table 2: Some chemical properties of profiles in the studied region

Horizon	P.av.	Al-d[1]	Fe-d	pH (paste)	ECe (dS m^{-1})	CEC (Cmol$_c$ kg^{-1})	CCE	O.C	T. N
	----------	(ppm)	----------				----------	(%)	----------
Profile NO. 1									
Apg	2.6	43	137	7.82	0.92	24	37.5	1.35	0.12
Bg1	-	56	155	7.88	0.49	24	40.1	0.76	-
Bg2	-	59	165	7.97	0.5	24	39.6	0.61	-
Bg3	-	54	207	8.08	0.44	22	41.6	0.30	-
2C	-	-	-	-	-	-	-	-	-
3Btkb	-	29	342	8.05	0.4	-	35.6	0.19	-
Profile NO. 2									
Apg	2.3	22	194	7.74	2.41	18	61.9	0.68	0.07
C	-	-	-	-	-	-	-	-	-
2C	-	15	91	8.05	0.82	10	88.6	0.08	-
2Cg	-	21	150	7.63	2.63	17	66.3	0.65	-
3Bgb1	-	40	181	7.63	2.84	20	54.5	0.76	-
3Bgb2	-	35	163	7.94	0.62	19	54.9	0.61	-
Profile NO. 3									
Apg	4.9	-	-	7.24	2.56	23	56.4	0.89	0.09
Bg	-	-	-	7.76	0.92	24	42.1	0.86	-
BCg	-	-	-	7.66	2.4	20	53.9	0.31	-
C	-	-	-		-	-	-	-	-
Profile NO. 4									
Ap	17	-	-	7.70	0.78	22	32.2	1.12	0.11
Bw1	-	-	-	7.70	0.71	21	33.3	0.67	-
Bw2	-	-	-	7.76	0.71	21	35.6	0.62	-
Bt	-	-	-	7.85	0.62	24	34.7	0.12	-
BC	-	-	-	7.98	1.46	17	49	0.08	-
Profile NO. 5									
Apg	4.6	22	349	7.62	2.06	19	46.5	0.91	0.09
Bg1	-	-	292	7.72	1.14	19	43.6	0.84	-
Bg2	-	15	142	7.8	0.78	20	49.5	0.61	-
Bg3	-	21	213	7.86	0.67	20	48.5	0.34	-
Bw	-	40	294	7.78	0.62	17	39	0.3	-
Profile NO. 6									
Apg	8.0	-	-	7.31	2.63	19	52	1.00	0.10
Bg1	-	-	-	7.69	1.14	21	41.6	0.64	-
Bg2	-	-	-	7.70	1.7	21	50	0.58	-
Bg3	-	-	-	7.67	0.67	18	40.9	0.32	-

[1]DCB-extractable Fe and Al (Dithionite Citrate Bicarbonate), EC: Electrical conductivity, CEC: Cation exchange capacity, O.C: Organic carbon, CCE: Calcium carbonate equivalent

Kyuma (1984) studies on 410 samples of wet land in tropical regions of Asia countries showed that 78% of the studied soils total nitrogen is less than 0.15% and its average is less than 0.13%. Range of available phosphorus changes in all surface horizons of studied is fluctuant between 2.3 to 8 ppm, while the mean of it is 4.48 ppm. If the content of soil phosphorus extracted by Olsen method is less than 10 ppm deficiency of phosphorus in paddy soils is expected, so it seems that studied soils are faced with phosphorus deficiency. Measured Phosphorus from 410 samples in paddy of Asian tropical countries soils showed that more than half of the analyzed samples contain available phosphorus less than 6 ppm that are much less for rice (Table 2).

Reduction-oxidation potential of soil: The pH is measured under field conditions during the rice growing season and range of pH changes in different depths were: 1 cm (6.83-8.30), 5 cm (6.77-7.87), 10 cm (6.61-7.54) and depth 15 cm (6.78-7.56) (Fig. 3). Therefore redox parameter (pe + pH) was similar to reduction-oxidation potential, so discussion about the redox parameter is canceled. According to the soil properties the content of organic material, nitrate, iron, manganese and dissolved oxygen in water, need a few days or take several weeks to decreased oxidation-reduction potential and with oxygen depletion can apply the conditions of reduction. The results show that declining of soil studied in 1 cm depth occur in 17th day and in 5 cm depth occur in 14th day and in 10 cm depth occur at 12nd day and in 15 cm depth it started at 14th and decline to 70th days after the cultivation of rice and continued to about +100 mV and less than +100 mV. By approaching the end of the growing season and less irrigation in this stage will be stop and with soil drainage and air penetration into the soil, again it uptrends until near harvest stage. Later regenerate due to 1 and 15 cm depths can be related to contact between both the depth of soil with air and water underneath the surface that are containing dissolved oxygen. Despite being submerged soil, surface soil has higher aerobic status because of its close contact to the surface water with the atmosphere and surface water flow, which has soluble oxygen (Fig. 4).

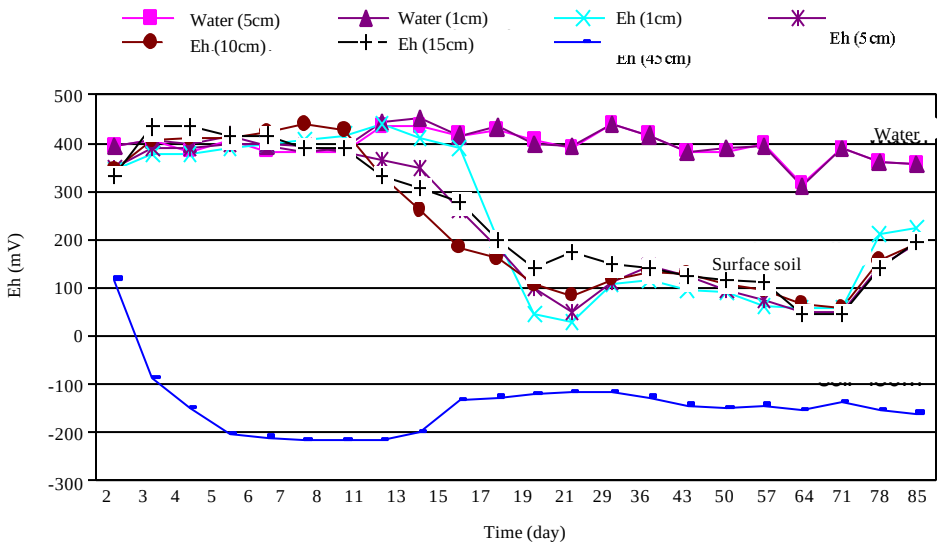

Fig. 4: Changes of pH at soil and water depths during rice-growing season

Trend of a sharp decreasing in 1, 5 and 10 cm depths started at 29th to 22nd and a relative enhancement observed in Eh, so that this increase continues until 36th and then partial decreasing is started. This decreasing reached to its minimum in 71st day. In 15 cm depth, the trend of partial increasing started at 22nd day and then its decrease started from 29th day with faster slope, so that at least decreasing in 71st days were higher than others depths. Some oscillations that occur in the trend of Eh changes can be related to frequency of irrigation courses and changes in the environment of field, whereas under laboratory conditions that a certain head of water applied to the soil such oscillations are not observed. In Bartlett and James view (Bartlett and James, 1993), the effect of photochemistry phenomena in surface water of Paddy land can be lead to Eh changes In 71st day, to prepare the field for harvest, farm irrigation stopped. So with gradually decreasing of water level, it is expected to increase in Eh, this increase occurs more in 1 cm depth. Of course in 5 and 10 cm depth the results are similar, but in 15 cm depth increasing trend has happened much slower in this time. In other words, in 15 cm depth and in final days of growing season, reduction is more. The Shirvan paddy fields are terracing and irrigation water transferred from field to another field. This is the constant cause of surface water flow. It will effect on Eh increasing in surface. Values of Eh in the 45 cm depth are different from the surface depths, as can be seen in Table 2 this depth by submerging is a reducing layer that its Eh values quickly decreased and the slope of reduction in the first days was very sharp, so that in the second day Eh s +115 mV and in 8th day was 222 mV. The trend of its changes almost constant since 5th to 13rd days and from 13rd day had increased and in 15th day it was -133 mV and it had a constant trend up to end of growing season, so that, the average of Eh was equal to -144 mV. The most reducing conditions in 45 cm depth in the paddy in 8th day is Eh = -222 mV and in surface depth and in 15 cm depth and in 64th day Eh is +4.5 mV. Bostani (2009) reported all value of redox potential in all studied soils after 40th days past satiate in the range of -220 to 5 mV. On the other hand in the range of 10 to 40 days, redox potential changes are small for each soil that it expresses the achieving of relative constant potential in the redox potential. Torabi *et al.* (2002) was measured Eh values in 5, 10, 25, 50 and 100cm depths in the paddy soils of Langarood land in Gilan province. They reported that the value of Eh changes in the surface depths (5 and 10 cm) have changes as like other three depths but the amount of it, is higher. In this study, the Eh range of 5 and 10 cm depths is positive, but during the rice growing season is negative, so that in the 50 cm depth layer was completely reducing and numeric value is -210 mV. The results of Torabi (2001), Torabi *et al.* (2002) and Bostani (2009) are in agreement with the results of this manuscript.

Pearson correlation analysis of data related to the Eh and pH at different depths and times shows that between the time of submerged and Eh and pH values in surface depths there is a significant reverse relationship at the level of 1%. It means that over time of submerged Eh value and pH decrease. So that the correlation coefficients between the mean of Eh and pH in the time of submerged were -0.747 and -0.600, respectively. The results of Pearson correlation coefficients data analysis for Eh and

pH in different depths, indicating a positive and significant relationship between Eh and pH in any depth, in other words by decreasing or increasing Eh in any depth, pH also will decrease or increase. The correlation coefficients between Eh and pH at 1, 5, 10 and 15 cm depths are: +0.765, +0.796, +0.611 and +0.918, respectively. The highest correlation was in 15 cm depth which has the most reduction. As a result, between the Eh mean in all surface depths with the pH mean there is a direct and significant relationship ($r = +0.897$, $p = 0.000$).

CONCLUSION

Irrigation of paddy fields with high level of ground water has influenced on the cochemical characteristics of soil in the Shirvan plain. The results of measured Eh values show that the variations in the surface Eh and in depths of 1, 5, 10 and 15 cm are more intensive than ones in depth of 45 cm. Most aerobic conditions in depth of 1 cm is Eh = +440 mV and in non-aerobic conditions in the most surface depth and in depth of 15 cm is Eh = +4.5 mV and in depth of 45 cm is Eh = -222 mV. By submerging and prepare the conditions of reduction, the soil pH will decreased and it continues until pH be equal to 6.61. Results of Pearson correlation coefficients data analysis for Eh and pH in different depths, indicating a direct and significant relationship between Eh and pH at any depth and there is a reverse and significant relationship between Eh and pH over time at any depth.

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