



Behavior, toxicity and diffusive flux of metals in a sediment core and pore-water from Anzali wetland

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Abstract Concentrations of metals along with pH, potential redox (Eh), total dissolved solid (TDS), electrical conductivity (EC) and salinity were measured for sediments of different layers, pore and surface water in the Anzali wetland. Also, the diffusive flux of metals was calculated and compared with the values in other aquatic bodies. The abundance of metals in sediments was Al > Fe > Ca > Ti > Mn > Zn > V > Cr > Ni > Cu > Pb > Co > As > Mo > Ag > Cd, while the pore-water results indicated a different concentration profile: Ca > Mn > Fe > Al > V > Mo > As > Ni > Cu > Co. Anzali wetland is classified within a high ecological risk. Pore-water toxicity test showed it is in non-polluted condition. Eh–pH diagrams showed that all species of elements are in a stable state in surface and pore-waters. However, Mn and Co (in some layers) are in soluble form and free ions and thus are bioavailable to the organisms. V and As are also present in the form of hydrogen compounds and Ni in the form of hydroxides, therefore, they are toxic to aquatic animals due to their solubility and ionic forms. Diffusive fluxes for As, Al, Fe, Ca, Cu, Mn, Mo, Ni and V are 0.43, 1.80, 48.52, 43,147.50, 0.12, 1.47, 0.15, 1.28, 0.21 $\mu\text{g}/$

m^2/day , respectively. Cluster analysis showed that in a solid phase of sediments, elements such as Cr, As and Ti are of petroleum and terrestrial origin. In pore-waters, Cu is of petroleum and biological origin, and Mo, As, Cu and Co are controlled by pH.

Keywords Aquatic · Environment · Pollution · Aerobic · Geochemistry · Elements

1 Introduction

The industrial wastes and wastewaters which include metals in some countries are directly discharged into the river bodies. They eventually find their way into the wetlands, lakes, gulfs, and seas (Pourang et al. 2010; El Houssainy et al. 2020). These metals are either soluble in water or stick to suspended particles or gradually precipitate in the bed (Bastami et al. 2018). This has increased the probability of endangering animal and plant ecosystems (Li et al. 2007; Baramaki Yazdi et al. 2012; Pal and Maiti 2018; Volz et al. 2020; Sahu and Basti 2021), especially aquatic environments such as wetlands and lakes which don't have any connection with open seas (Zhang et al. 2010).

It is vital to investigate and analysis of sediment properties (Bai et al. 2011; al Naggat et al. 2018; Ahn et al. 2020) and their relationship with surface waters to know about the health of aquatic environment (Cohen 2003; Laxmi Mohanta et al. 2020). It would be very informative to study data related to different periods if the sedimentation rate is known (Vaalgamea and Conley 2008). The accumulation of contaminants, especially trace metals in sediments and the possibility of their release into the

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surface water column, brings out the need for detailed water–sediment interactions. Sediments in aquatic environments can act as a source through decomposition, dissolution and desorption and sink through precipitation and adsorption (Lerman 1979; Carling et al. 2013).

In geochemical studies of water zones, the role of pore-water cannot be ignored because diagenesis does not only occur in the solid phase, thus the fluid phase must also be considered (Schroeder et al. 2017). In this regard, measuring and determining the characteristics of pore-water and analyzing the results can provide a better view of the state of diagenesis and pollution of aquatic environment (Hammond 2001). For example, it must be determined at what depth and under what conditions metals are released from the solid phase into the pore-water, what are the predominant species of metal released into the pore-water, how much of them are transferred to the overlying waters and finally what effect do the released metals on the aquatic ecosystem?

Today, many wetlands have dried up and, in addition to disrupting plant and animal life, have damaged local employment (Jafari 2009). As a result of the drying up of the wetlands, their use has changed in some places, and these water bodies, which were once a place for waste disposal, are used for agriculture, and since its products are consumed by humans, it is necessary to evaluate the behavior of trace metals and pollution which they may take up.

Tang et al. (2016) investigated the metals in pore-water of Fuyang River sediments and found that the average concentrations of Cr, Ni, Cu, As, Zn and Pb were 17.06, 15.97, 20.93, 19.08, 43.72 and 0.56 $\mu\text{g/L}$, respectively. Also, the diffusive fluxes for Cr, Ni, Cu, As, Zn and Pb are -0.37 to 3.17 , 1.37 to 2.63 , -4.61 to 3.44 , 0.17 to 6.02 , -180.26 to 7.51 and -0.92 to -0.29 $\mu\text{g/m}^2/\text{day}$, respectively. The Nemerow index used in the pore-water toxicity test was found to range between 0.11 to 2.06 at different stations. Zhu et al. (2016) measured the concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the pore-water of Ziya river sediments as 0.373, 57.1, 37.7, 20.4, 14.0 and 9.6 $\mu\text{g/L}$, respectively. The diffusion fluxes of Cd, Cr, Cu, Ni, Pb and Zn were estimated to be -0.427 to 0.469 , -71.8 to 42.5 , 3.16 to 86.6 , 5.29 to 14 , 7.24 to 19 and -20.4 to 21.9 $\mu\text{g/m}^2/\text{day}$, respectively. The Nemerow index for the pore-water toxicity test ranges from 0.759 to 1.05. Louriño-Cabana et al. (2011) used geo accumulation index and enrichment factor to investigate sediment contamination with metals. The geo accumulation index showed that Cd, Pb and Zn were not heavily contaminated, while Cu and Ni fall within moderate to severe contamination category. They also examined the toxicity of pore-water and examined the Nemerow index in different layers of the sediment core and obtained values ranging from 0.15

to 19.52. El Houssainy et al. (2020) investigated the trace metals in the coastal sediments of the Mediterranean sea and based on enrichment factor found the pattern of $\text{Cr} < \text{Cd} < \text{Hg} < \text{Cu} < \text{Pb} < \text{Ag}$. They also examined the relationship between sediment and pore-water and found that Fe and Mn are important in the mobility of metals from the solid to the fluid phase.

Anzali wetland is registered in Ramsar Convention. This wetland is very important from an ecological point of view because it is a spawning ground for many fishes and birds. Despite the importance of this marine body, in order to assess pollution state, several research through analysis of solid phase of sediment and benthic community (Pourang et al. 2010; Esmaeilzadeh et al. 2016a, b) have been done but the role of sediment pore-water is ignored. Therefore, the main goal of present research is to bring out the toxicity and diffusive flux of metals in the sediments and pore-water of Anzali wetland. The results of present work help to know the ecological risk within the wetland.

2 Materials and methods

2.1 Study area

Anzali wetland is located in the southwestern part of the Caspian Sea with an area of 193 km^2 , which dates back to the Pliocene or Holocene period (Rasta et al. 2021). This wetland was registered in 1975 in Ramsar Convention as an important international wetland. Anzali wetland is a eutrophic brackish wetland with shallow ponds and seasonal flood levels (Esmaeilzadeh et al. 2016b; Panahandeh et al. 2018). This wetland is very important from an ecological point of view because it is a spawning ground for many fishes and birds. This wetland can be divided into 4 parts: eastern, central, southern (Siahkeshim) and western or Abkenar. Discharging sewage from surrounding cities, various industries and agricultural wastes directly or indirectly through the rivers leading to the wetland has disrupted the animal and plant life of the wetland (Hassanzadeh et al. 2014; Panahandeh et al. 2018). Parts of Anzali wetland have now dried up and have been used as agricultural land for planting crops such as rice, etc., and other parts of the wetland are experiencing a decrease in depth and are drying up.

2.2 Sampling

Sampling was carried out from the eastern part of Anzali wetland (Fig. 1) since it has the lowest sedimentation rate (which is 0.9 mm/year, utilizing Lead-210 method; Karbassi 2016) and thus such sediment core may provide useful information from the older years. For core sediment

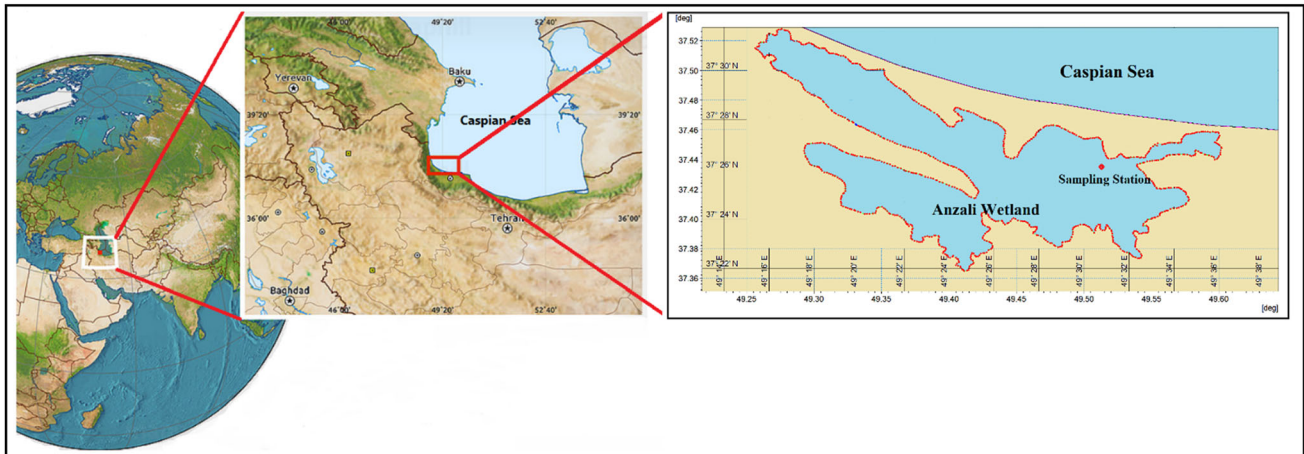


Fig. 1 Sampling station located in the eastern part of Anzali wetland (with the help of website: www.maphill.com) (2022)

sampling, PVC pipe with an inner diameter of approximately 5 cm was used and a clean polypropylene container was utilized for sampling of surface water. The important point in sampling is to prevent contaminants from entering the core sediment, so the pipe was cut through the middle of the section and reconnected with Adhesive tape. So that the sample could be removed by peeling off the glue without cutting the pipe. Figure 2, depicts the steps of the research work.

The length of the core sediment was 60 cm that was divided into 5 equal parts of 12 cm. The pieces were labeled as the first to the fifth layers from the surface to the depth and were transferred to the marked containers. To preserve any probable change in sample parameters, the samples were kept in containers immediately inside the icebox without any access to oxygen and sunlight until the time of analysis in the laboratory.

2.3 Sediment analysis

The sediment samples were centrifuged for 30 min at 10,000 rpm (US Environmental Protection Agency 2001) and therefore the pore-water was separated from the sediment. Subsequently, 10 g of sediment samples were mixed with 20 g of surface water of Anzali wetland and kept for 24 h. Finally, the parameters such as Eh, pH, TDS, EC and salinity of the sediments were measured by a portable multi-parameter probe.

The rest of the sediment samples were dried and passed through a 63-micron sieve and then pulverized and prepared for bulk concentration analysis using strong acids such as HF, aqua regia and HClO₄. For this purpose, acetic acid (Simpson et al. 2005) was used at pH = 7 (which is

one unit lower than the pH of Anzali wetland water) to release the very loose bonded metals from sedimentary phase. Concentrations of major metals (Fe, Al, Ca, Mn, and Ti) and trace elements (Cr, Co, Ni, Cu, Zn, As, Pb, Cd, V and Ag) were measured by inductively coupled plasma mass spectrometry (ICP-MS 7500ce Zarazma Co., possessing ISO-17025). A standard sediment sample (MESS-1) was used to check the accuracy (better than $\pm 5\%$) of the analysis.

2.4 Water analysis

Immediately after separating the water from the sediments, the parameters Eh, pH, TDS, EC and salinity of the pore and surface water samples were measured by a portable multi-parameter probe. The water samples then passed through a 45 μ m filter and reduced to less than 2 mL by extra pure nitric acid to prevent the changes in the form and distribution of metals through different phases. Subsequently, ICP-MS 7500ce device was used to determine the concentrations of major metals (Fe, Al, Ca, Mn, Ti) and trace elements (Cr, Co, Ni, Cu, Zn, As, Pb, Cd, V, and Ag). It should be noted that the total hardness of the samples was measured by ion chromatography (model Metrohm 930 compact Flex).

2.5 Sediment toxicity tests

2.5.1 Geo accumulation index (I_{geo})

The geo accumulation index was introduced to compare the current concentration of metals with the concentration

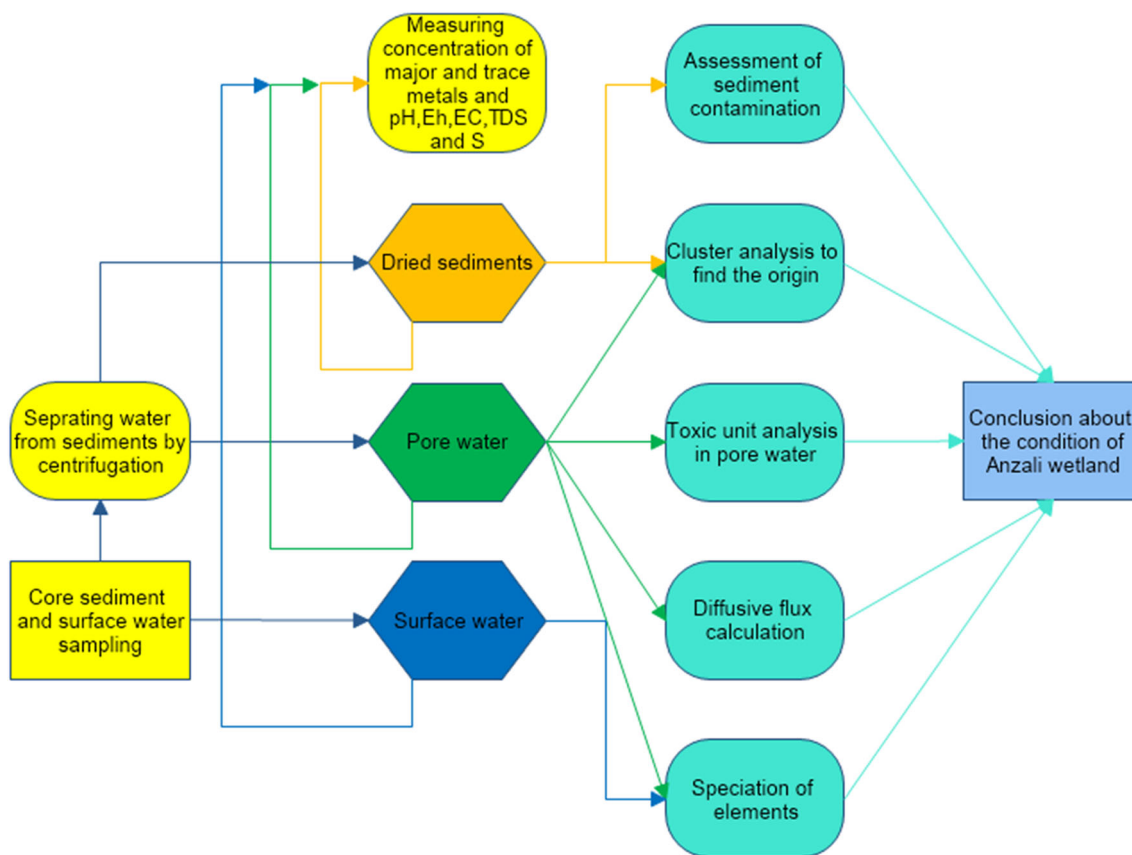


Fig. 2 Steps of conducting research to study the geochemistry of sediment core from Anzali wetland

before industrialization and to evaluate the severity of pollution, which was calculated according to Eq. (1):

$$I_{geo} = \log_2[C_n/1.5 * B_n] \quad (1)$$

where C_n is the present concentration of metal in sediments, B_n is the concentration of metal in shale and 1.5 is the correction factor for the concentration of metals in shale (Müller 1981). The concentration of metals in shale is listed in Table 1. Sediment quality status according to the modified geo accumulation index (introduced by Qingjie et al. 2008) for values less than 0.42, between 0.42 to 1.42, between 1.42 to 3.42, between 3.42 to 4.42 and for values greater than 4.42, classified as unpolluted, low pollution, moderate pollution, strongly pollution and extremely pollution, respectively.

2.5.2 Enrichment factor (EF)

The enrichment factor is a simple but effective tool for evaluating anthropogenic effects based on comparing the ratio of the current concentration of metal in the Earth's crust to its background level. The enrichment factor is calculated through Eq. (2):

$$EF = \left[\frac{(C_n/C_{Fe})_{\text{sample}}}{[(C_n/C_{Fe})_{\text{crust}}]} \right] \quad (2)$$

where $(C_n/C_{Fe})_{\text{sample}}$ is the ratio of the present concentration of the metal to the concentration of iron, $(C_n/C_{Fe})_{\text{crust}}$ is the ratio of the concentration of the metal to the element iron in the earth's crust. The concentration of metals in the earth's crust is listed in Table 1. Enrichment factor classification is as follows: for values less than 2, between 2 to 5, between 5 to 20, between 20 to 40 and for values greater than 40, respectively, Depletion to minimal enrichment, moderate enrichment, significant enrichment, very high enrichment and Extremely enrichment is considered (Sutherland 2000).

2.5.3 Modified hazard quotient (mHQ)

This index is a tool to assess the degree of danger of each metal to the aquatic environment and living organisms, which is based on the distribution of adverse ecological effects for the threshold levels and was calculated according to Eq. (3):

$$mHQ = [C_i(1/TEL_i + 1/PEL_i + 1/SEL_i)]^{1/2} \quad (3)$$

Table 1 Metals concentration in shales and Earth’s crust (mg/kg) (Bowen 1979)

Element	Cu	Zn	Ni	V	Cd	Co	Mn	Pb	Ca	As	Fe	Ti	Cr	Ag
Shales	45	95	68	130	0.3	19	850	20	22,100	13	47,200	4600	90	0.07
Crust	50	75	80	130	0.2	20	950	14	41,000	5	41,000	–	100	–

Table 2 Threshold, probable and severe values for each metal (mg/kg) (Persaud et al. 1993; Smith et al. 1996)

Element	Zn	Cr	Cu	Pb	Ni	As	Cd
TEL	123	37.3	35.7	35	18	5.9	0.596
PEL	315	90	197	91.3	36	17	3.53
SEL	820	110	110	250	75	33	10

Table 3 Effect ranges median for each metal (mg/kg) (Long et al. 1995)

Element	Cu	Zn	Cr	Ni	Pb	Cd	As
ERM	270	410	370	51.6	218	9.6	70

where C_i is the concentration of the target metal, *TEL* is the threshold effect level, *PEL* is the probable effect level, and *SEL* is the severe effect level. Threshold values are listed in Table 2. Degree of risk according to the modified risk index for values less than 0.5, between 0.5 to 1, between 1 to 1.5, between 1.5 to 2, between 2 to 2.5, between 2.5 to 3, between 3 to 3.5 and for larger values greater than 3.5, respectively, nil to very low, low, moderate, considerable, high, very high and extreme are considered (Benson et al. 2018).

2.5.4 Toxic risk index (TRI)

Toxicity risk index is a multi-element index that has been developed based on the threshold effect level and the probable effect level. To use this index, Eq. (4) was used:

$$TRI = \sum_{i=1}^n [((C_i/TEL_i)^2 + (C_i/PEL_i)^2)/2]^{1/2} \tag{4}$$

Table 4 Toxicity factor values for each metal (Hakanson 1980; Zhengqi et al. 2008)

Elements	Zn	Mn	Ti	V	Cr	Ni	Co	Pb	Cu	As	Cd
Tr	1	1	1	2	2	5	5	5	5	10	30

In the classification of TRI index, values less than 5, between 5 to 10, between 10 to 15, between 15 to 20 and values greater than 20 are considered as no toxic risk, low toxic risk, moderate toxic risk, considerable toxic risk and very high toxic risk, respectively (Zhang et al. 2016).

2.5.5 Mean ERM quotient (MERMQ)

This multi-element index was used to express the pollution status of several metals using Eq. (5):

$$MERMQ = \left[\sum_{i=1}^n (C_i/ERM_i) \right] / n \tag{5}$$

where C_i is the metal concentration, *ERM* is the average effect range for each metal and n is the number of elements. *ERM* values for each metal are listed in Table 3. According to the classification of this index, risk levels are divided into four categories: for values less than 0.1, between 0.1 to 0.5, between 0.5 to 1.5, and is greater than 1.5 low, medium, high and very high risk level, as well as 9%, 21%, 49% and 76% probability of toxicity, respectively were considered (Carr et al. 1996; Long and MacDonald 1998).

2.5.6 Potential ecological risk index (RI)

The potential ecological risk index was introduced by Hakanson to assess metal pollution and to determine the ecological risk that metals in sediments pose to aquatic. This index calculated using Eqs. (6) and (7):

$$E_r^i = Tr^i * (C_o^i/C_n^i) \tag{6}$$

$$RI = \sum_{i=1}^n E_r^i \tag{7}$$

In these equations, *Tr* is the toxicity factor for each metal, C_o is the current concentration of each metal and C_n is the concentration of the natural part of the metal. Toxicity factor values for each metal are listed in Table 4 and

Table 5 Background concentrations (the natural portion of the elements (total concentration = anthropogenic portion + natural portion) which estimated by chemical partitioning.) of metals in the eastern part of Anzali wetland (mg/kg) (Masoumi 2018)

Metal	Background ^a				
	0–12	13–24	25–36	37–48	49–60
Zn	23.8	10.8	13.5	17.8	18.2
Mn	285	224	256	285	304
V	18.1	11	9.6	10.6	11.4
Cr	14.1	15.5	11.7	8.1	6.35
Ni	6	15.6	3.6	6.5	6.3
Co	5.79	4.54	2.83	2.44	2.88
Pb	9.2	6.8	5.6	5	4.52
Cu	11.5	14.35	11.5	8.4	7.65
As	2.4	4.19	2.95	1.6	1.05
Cd	0.78	0.74	1.5	1.81	1.47

^aMetals concentrations at the selected depths were obtained by extrapolating other depths investigated in the previous studies

the background of the studied metal is also listed in Table 5. According to the classification of this index, values less than 150, between 150 to 300, between 300 to 600 and above 600 were considered low, moderate, considerable and very high risk, respectively (Hakanson 1980).

2.6 Pore waters toxicity test

To evaluate the level of pore-water quality, the interstitial water criteria toxic unit was used, which described as:

$$IWCTU_{Me} = [Me]_{i.w.}/FCV_{Me} \quad (8)$$

where $[Me]_{i.w.}$ The concentration of total metal and FCV_{Me} is the final critical value depending on the hardness of each metal (Louriño-Cabana et al. 2011), which was calculated for each element according to Table 6. The total water quality of the pore-water was estimated using Nemerow index (NI), which is calculated according to Eq. (9). The classification of this index is as follows: for values less than 1, between 1 to 2, between 2 to 3, between 3 to 5 and greater than 5, respectively no impact, slight impact,

moderate impact, strong impact and serious impact were considered (Liu et al. 2003).

$$(NI) = \sqrt{\frac{(IWCTU)_{max}^2 + (IWCTU)_{mean}^2}{2}} \quad (9)$$

2.7 Diffusive fluxes

The quantitative diffusive fluxes of the metals from sediments to the water column were calculated by using the concentration gradient based on Fick's first law (Schulz and Zabel 2006):

$$J = -\varphi \cdot D_{sed} \cdot (\partial C / \partial X)_{X=0} \quad (10)$$

where J is the diffusive flux ($\mu\text{g}/\text{m}^2/\text{day}$), φ is the porosity, D_{sed} is the diffusion coefficient (cm^2/s) and $(\partial C / \partial X)_{X=0}$ the concentration gradient in the boundary between water and sediment ($\mu\text{g}/\text{L}/\text{cm}$). The diffusion coefficient was obtained using Eq. (11) (Schulz and Zabel 2006):

$$D_{sed} = D^{sw} / \theta^2 \quad (11)$$

where θ is the degree of deviation around the particles (tortuosity) and D^{sw} is the diffusion coefficient of the solution in seawater, the values of which for each metal are taken from the research of Yuan-Hui and Gregory (1974). Torsion was also calculated in terms of porosity from Eq. (12) (Boudreau 1997) and porosity from Eq. (13) (Berner 1980).

$$\theta^2 = 1 - \ln(\varphi^2) \quad (12)$$

$$\varphi = V_{iw} / (V_{iw} + V_s) \quad (13)$$

where V_{iw} is the volume of interstitial water and V_s is the total volume of dry sediment.

2.8 Speciation of metals

Chemically trace metals are found in different species in the aquatic environment and the effects they have on the environment vary depending on their chemical forms (Alabdeh et al. 2020; Ebraheim et al. 2021). Therefore, to understand the geochemical and toxicological effects of the environment, it is not only necessary to measure the concentration of metals but also their species must be identified. One way to identify metal species in the aquatic

Table 6 Final critical values for selected metals recommended by the United States Environmental Protection Agency (Hansen et al. 2005)

Metal	FCV
Cd	$[1.101672 - 0.041838 \ln(\text{hardness})][\exp(0.7852 \ln(\text{hardness}) - 3.490)]$
Cu	$0.960[\exp(0.8545 \ln(\text{hardness}) - 1.465)]$
Ni	$0.997[\exp(0.8460 \ln(\text{hardness}) + 1.1645)]$
Pb	$0.791[\exp(1.273 \ln(\text{hardness}) - 4.705)]$
Zn	$0.986[\exp(0.8473 \ln(\text{hardness}) + 0.7614)]$

environment is to use Eh–pH diagrams. These diagrams can display the area of thermodynamic stability of water and provide conditions for the study of metal hazards (Huang 2016). The stability zone of the metals in these diagrams is shown between the two lines, and outside this range, the metals are unstable and may be toxic in the aquatic environment.

In present investigation, HSC Chemistry software version 9.5.1 was used to prepare Eh–pH diagrams. The diagrams were plotted by entering data on temperature, redox potential, pH, atmospheric pressure, and concentration within the HSC program.

2.9 Cluster analysis

Pearson coefficient and cluster analysis were used to find correlations between metals and parameters, as well as similarities in the behavior and origin of metals in sediments and pore-water. The software used to calculate the Pearson coefficient was SPSS version 26 and cluster analysis was performed by multivariate statistical package (MVSP) software by a weighted pair group (WPG) clustering technique. In this technique, a linear correlation coefficient is used to measure the similarity and its ability to define clustering tendencies between different samples.

3 Results and discussion

3.1 Distribution of metals and diagenetic processes

The profiles of metals concentration in core sediment were not the same for all metals, but it can be stated that the average abundance of metals in sediments of different layers was $Al > Fe > Ca > Ti > Mn > Zn > V > Cr > Ni > Cu > Pb > Co > As > Mo > Ag > Cd$. As shown in Figs. 3, 4, 5 and 6, the order of abundance of metals on average in the pore-waters of different layers, illustrated a different trend from metal concentrations in sediments. Generally, the concentrations of Ti, Zn, Cr, Pb and Cd are almost negligible in all pore-waters' layers, indicating no release of sediment in the liquid phase. The other metals in pore-waters follow the trend of $Ca > Mn > Fe > Al > V > Mo > As > Ni > Cu > Co$. In other words, the trend of metal concentration in pore-water is not dependent on the concentration of metals in sediment core. The color of each layer of the core sediment is demonstrated in Figs. 3 and 4 (the cylinder which is located next to the vertical axis is the schematic form of the core which its color is altered with depth). The down sediment core color change from surface to depth (dark brown, black, and gray, respectively) confirms the prevailing anoxic conditions at the bottom of sediment core.

Ca in sediments and pore-water had a non-uniform downward trend and its highest (27,056 mg/kg in sediments and 531 mg/L in pore-water) and lowest (18,410 mg/kg in sediments and 112 mg/L in pore-water) concentrations belonged to the first and third layers, respectively. Mn in sediments had a uniform decreasing trend in depth and declined significantly, especially from the second layer onwards. But in water, its trend was completely different so that in the first layer its concentration was 0.02 mg/L but in the second layer, it reached 12.67 mg/L and then diminished with depth. Fe had a non-uniform increasing trend in sediments and pore-water with depth and its highest concentration was in sediments and pore-water in the fifth layer (54,826 mg/kg in sediments and 0.97 mg/L in pore-water) and the lowest (49,257 mg/kg in sediments and 0.79 mg/L in pore-water) concentration was in the sediments of the first layer and in the pore-water of the third layer. Al increased irregularly in sediments with depth and had the lowest (79,588 mg/kg) and highest (93,699 mg/kg) concentrations in the first and fifth layers, respectively. In pore-water, the concentration of Al in each layer enhanced compared to the upper layers except in the fifth layer and the highest release volume was observed in the fourth layer where whose concentration in sediment decreased. V increased in sediments unevenly with deep and grows uniformly in pore-water. The lowest and highest concentrations of V belonged to the first (116 mg/kg in sediments and 4.03 µg/L in pore-water) and fifth (140 mg/kg in sediments and 89.98 µg/L in pore-water) layers in both sediments and pore-water, respectively. The concentration of Mo in all sediment layers except in the fourth layer was the same and was equal to about 1 mg/kg. However, in pore-water, it had a different trend and its amount grew from the surface to the third layer, but then diminished. The fact that the concentration of Mo in some layers of pore-water was different, while its concentration was the same in sediments, indicates that factors other than increasing or decreasing the concentration in sediment were involved in the release of Mo in pore-water. As enhanced in sediments with depth except in the fourth layer, but in pore-water its trend was different, so that in the first layer it was 7.57 µg/L, but in the second layer it was so small that the ICP device could not measure it. But in the third layer, its concentration reached 30 µg/L. In the fourth layer, 10 units have been reduced compared to the previous layer, but in the fifth layer, the concentration again reached 30 µg/L. The trend of Ni concentration in sediments and pore-water was completely opposite to each other, so that in sediments the concentration grew from the surface to the third layer, reduced in the fourth layer and enhanced in the fifth layer compared to the fourth layer. The Ni concentration was constantly declining up to the third layer, increasing in the fourth layer and decreasing in

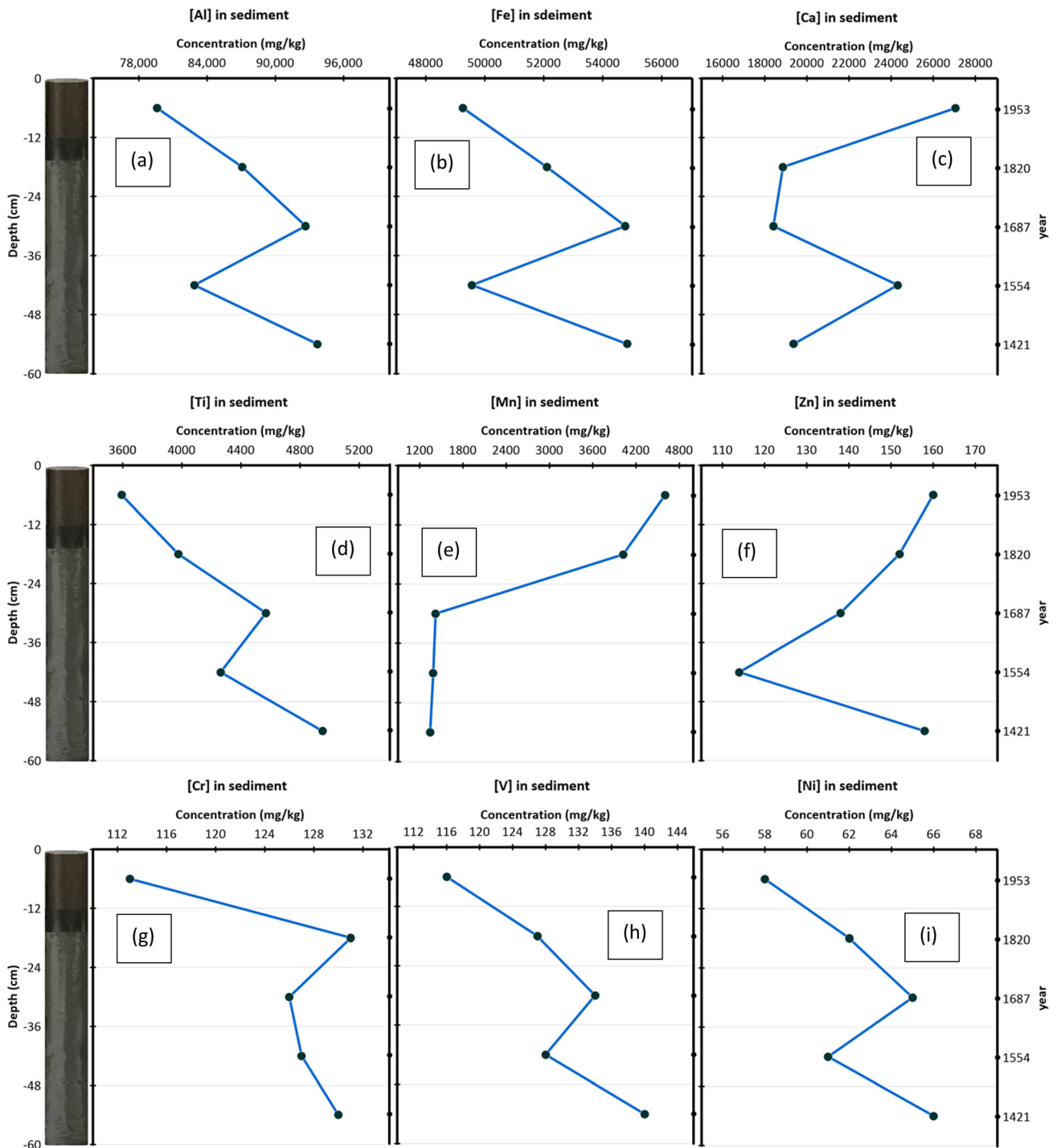


Fig. 3 Vertical profiles of metals [(a) Al, (b) Fe, (c) Ca, (d) Ti, (e) Mn, (f) Zn, (g) Cr, (h) V and (i) Ni] concentration in the solid phase of the core sediment belonging to the eastern part of Anzali wetland

the fifth layer compared to the fourth layer. Cu in sediments fluctuates in depth between 54 and 63 mg/kg and it did not show a definite trend, but in pore-water, its general trend could be described as downward increase. Co in sediments had an upward trend from the surface to the third layer, but in the fourth layer it dropped significantly, but it

grows in the fifth layer where highest amount of Co is observed. Also, Co concentration rises non-uniformly in pore-water with depth and the lowest (1.11 $\mu\text{g/L}$) and highest (1.74 $\mu\text{g/L}$) concentrations belonged to the first and fifth layers, respectively. Ti concentration in sediments has an increasing trend in depth except for the fourth layer. Zn

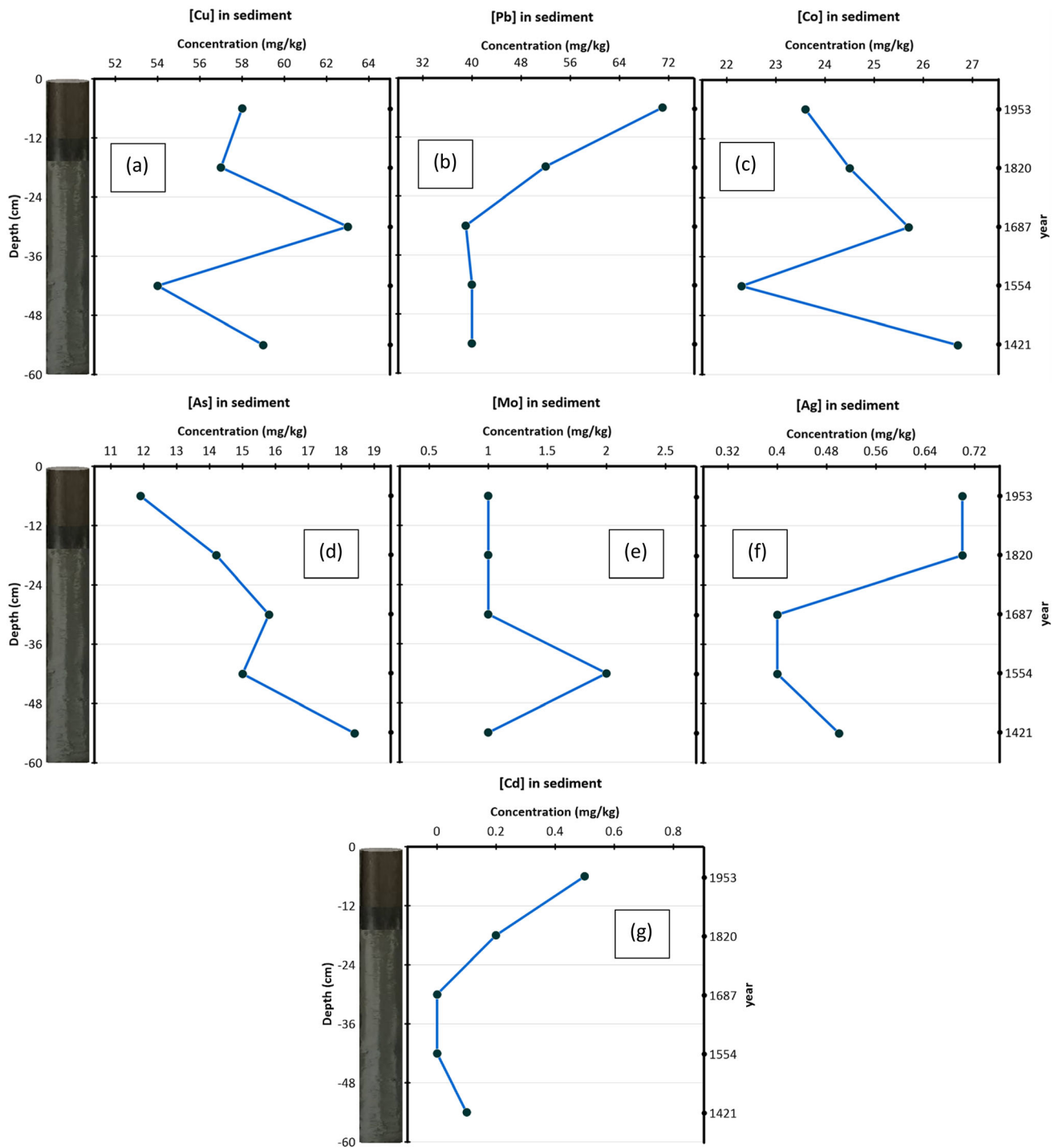


Fig. 4 Vertical profiles of metals [(a) Cu, (b) Pb, (c) Co, (d) As, (e) Mo, (f) Ag and (g) Cd] concentration in solid phase of the core sediment related to the eastern part of Anzali wetland

in sediments had a uniform downward decreasing trend from the surface to the fourth layer, but it suddenly increases in the fifth layer. The highest (160 mg/kg) and lowest (114 mg/kg) Zn concentrations belonged to the first and fourth layers, respectively. The lowest (113 mg/kg) and highest (131 mg/kg) concentrations of Cr in sediments

were observed in the first and second layers, respectively, and in other layers the amount of concentration fluctuated between the above cited ranges. Pb in sediments had a decreasing trend from the surface to the third layer and had constant values from the third layer to the bottom of core. Cd in the first layer of core sediment had the highest value

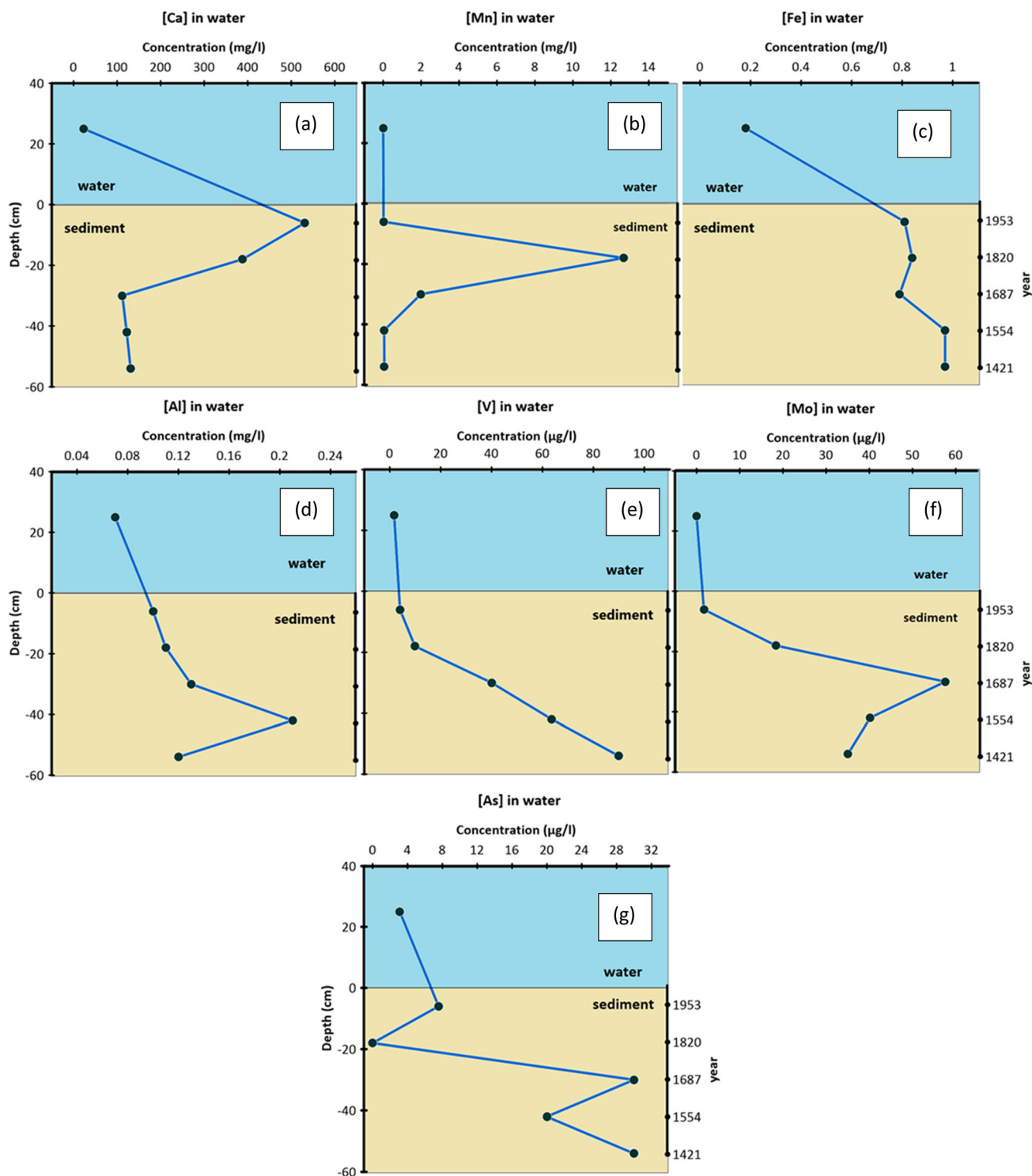


Fig. 5 Vertical profiles of metals [(a) Ca, (b) Mn, (c) Fe, (d) Al, (e) V, (f) Mo and (g) As] concentration in surface water and pore-water of the core sediment belonging to the eastern part of Anzali wetland

at 0.5 mg/kg and then decrease. The concentration of Ag in the first two layers was 0.7 mg/kg, in the next two layers it was 0.4 mg/kg and in the last layer, it slightly rose to 0.5 mg/kg.

3.2 Sediment toxicity assessment

The results of geo accumulation indices and enrichment factor are presented in Table 7. According to the results of

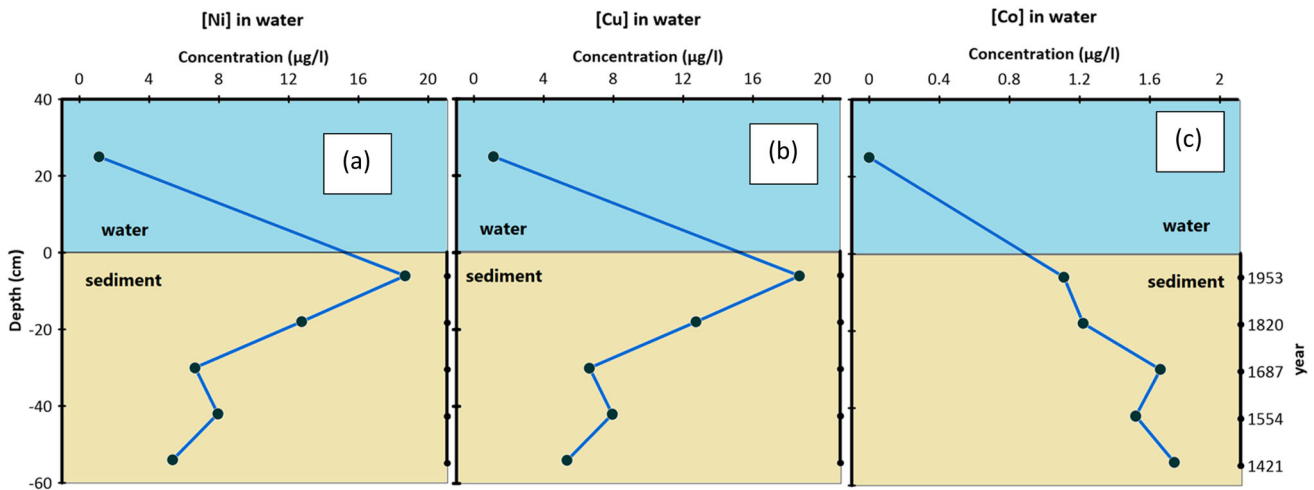


Fig. 6 Vertical profiles of metals [(a) Ni, (b) Cu and (c) Co] concentration in surface water and pore-water of the core sediment relating to the eastern part of Anzali wetland

Table 7 Geo accumulation index (I_{geo}) and enrichment factor (EF) in different core sediment layers from Anzali wetland

Element	I_{geo}					EF				
	Depth (cm)									
	0–12	13–24	25–36	37–48	49–60	0–12	13–24	25–36	37–48	49–60
Cu	-0.22	-0.24	-0.10	-0.32	-0.19	0.97	0.90	0.94	0.89	0.88
Zn	0.17	0.09	-0.05	-0.32	0.15	1.78	1.59	1.38	1.26	1.58
Ni	-0.81	-0.72	-0.65	-0.74	-0.63	0.60	0.61	0.61	0.63	0.62
V	-0.75	-0.62	-0.54	-0.61	-0.48	0.74	0.77	0.77	0.81	0.81
Cd	0.15	-1.17	-	-	-2.17	2.08	0.79	-	-	0.37
Co	-0.27	-0.22	-0.15	-0.35	-0.09	0.98	0.96	0.96	0.92	0.10
Mn	1.85	1.66	0.16	0.12	0.08	4.03	3.33	1.12	1.21	1.06
Pb	1.24	0.79	0.38	0.42	0.42	4.22	2.92	2.09	2.36	2.14
Cr	-0.26	-0.04	-0.10	-0.09	-0.05	0.94	1.03	0.94	1.05	0.97
As	-0.71	-0.46	-0.30	-0.38	-0.08	1.98	2.23	2.37	2.48	2.75
Ag	2.67	2.67	1.86	1.86	2.18					
Ti	-0.94	-0.80	-0.59	-0.70	-0.48					

Table 8 Modified hazard quotient of metals in different layers of the core sediment from Anzali wetland

Depth (cm)	TRI	State	MERMQ	State	Probability of toxicity (%)	RI	State
0–12	10.68	Moderate	0.35	Medium	21	283.04	Moderate
13–24	10.66	Moderate	0.35	Medium	21	218.97	Moderate
25–36	10.4	Moderate	0.34	Medium	21	316.93	Considerable
37–48	9.85	Low	0.3	Medium	21	325.34	Considerable
49–60	11.05	Moderate	0.35	Medium	21	437.45	Considerable

geo accumulation index, Mn in the first two layers and Ag in all layers caused moderate pollution. Pb in all core sediment layers except the third layer falls within low pollution class and other metals did not have a detrimental effect on the wetland environment. According to the results of the enrichment factor, Cd in the first layer, Mn and Pb and As in all layers except the surface layer had little

enrichment and the share of other metals was negligible. In Table 8, the results of the modified hazard quotient in different layers showed that Cd in the surface layer falls within low risk, in the second layer the risk was very low and then up to the fifth layer is risk free. As caused a moderate risk in the first, second and fourth layers and a considerable risk in the third and fifth layers. Ni had a

Table 9 Multi-elemental toxicity indices in different layers of the core sediment from Anzali wetland

mHQ					
Element	0–12 cm	13–24 cm	25–36 cm	37–48 cm	49–60 cm
Cd	1.01	0.64	0	0	0.45
As	1.76	1.92	2.03	1.97	2.19
Ni	2.41	2.49	2.55	2.47	2.57
Pb	1.69	1.44	1.25	1.26	1.26
Cu	1.7	1.69	1.78	1.64	1.72
Cr	1.37	2.56	2.51	2.52	2.55
Zn	1.26	1.23	1.17	1.07	1.26

considerable risk in the first, second and fourth layers and a high severity risk in the third and fifth layers. Pb exhibits moderate risk in the surface layer, and low risk in other layers. Cu had a moderate risk in all layers. Cr caused a low risk in the first layer but a high severity risk in the other layers. Zn had a low risk in all layers.

Table 9 lists the results of multi-element indices, which indicate that in terms of toxicity risk index, the fourth layer had a low risk and other layers had a moderate risk. The mean ERM quotient showed the medium risk level for all layers. The potential ecological risk index for the first and second layers was moderate, but for the other layers it was considerable.

3.3 Pore-water toxicity assessment

The IWCTU of Cd, Cu, Ni, Pb and Zn in the pore-water of all sediment layers are computed (Table 10). It is evident that the results of Nemerow index for all layers are less than 1 and thus they don't impose adverse impact on the eastern part of Anzali wetland.

3.4 Diffusive fluxes from sediments to overlying water

The diffusive fluxes to calculate the release of metals and their transfer from sediments to the water column in Anzali wetland have been calculated and the results are listed in Table 11. The highest diffusion rate was 43,147.5 $\mu\text{g}/\text{m}^2/\text{day}$ and the fluxes of Fe, Al, Mn, Ni, As, V, Mo, Cu and Co were 48.52, 1.8, 1.47, 1.28, 0.43, 0.21, 0.15 and 0.08 $\mu\text{g}/\text{m}^2/\text{day}$, respectively. Comparing the obtained values with other studies, it can be seen that the diffusive fluxes of Mn, V and As were relatively low and Fe, Ni, Cu and Co were not high compared to other aquatic bodies.

3.5 Speciation of dissolved metals

The parameters of water and sediment samples are listed in Tables 12 and 13, respectively. The chemical forms of metals for various pore-water layers and surface water were identified using Eh, pH, temperature, concentration and pressure values As displayed in the Figs. 7, 8, 9 and 10, all the marked points were between the two dotted lines and indicate that all metals were in a stable range.

Al in the water of the wetland was in the form of hydroxide and soluble ($\text{Al}_3(\text{OH})_4^{+5}$), which is of considerable biological importance and is toxic to organisms (ALabdeh et al. 2020). Fe is present in the water of the wetland in the form of magnetite (Fe_3O_4), which is in the oxidized form of Fe and in a colloidal or suspended state, and thus causes less peril to aquatic species than the free ion form. In Anzali wetland, Ca appeared in the form of hydroxides and ionic (CaOH^+), which due to its solution property is toxic and available to organisms. Mn existed in surface water and the first and second layers of pore-water in the form of free ion (Mn^{+2}), and because it was highly concentrated in the second layer of pore-water, it can be very toxic with high bioavailability. This form of Mn is available to plants and can be easily transported into root

Table 10 Interstitial water criteria toxic unit (IWCTU) and Nemerow index (NI) metals in pore-water in different layers of core sediment

Layer	Cd ^a		Cu		Ni		Pb ^a		Zn ^a		NI	Impact grade
	FCV	IWCTU	FCV	IWCTU	FCV	IWCTU	FCV	IWCTU	FCV	IWCTU		
1	8.37	0.119	130.21	0.017	1749.34	0.011	94.21	0.011	1171.34	0.001	0.093	No
2	6.80	0.147	102.43	0.019	1376.10	0.009	66.39	0.015	922.31	0.001	0.107	No
3	3.95	0.250	54.01	0.020	732.90	0.009	25.68	0.039	490.73	0.002	0.182	No
4	4.65	0.215	64.67	0.019	886.25	0.009	33.63	0.030	587.51	0.002	0.157	No
5	5.82	0.172	84.71	0.014	1149.40	0.005	50.18	0.020	762	0.001	0.125	No

^aConcentrations of Zn, Pb and Cd were less than ICP-MS detection limit. Thus, the highest probability was considered with respect to the detection limits (1 $\mu\text{g}/\text{L}$)

Table 11 Diffusive flux of dissolved metals ($\mu\text{g}/\text{m}^2/\text{day}$) in the eastern part of Anzali wetland and its comparison with other aquatic bodies

Area	Ca	Mn	Fe	Al	Ni	Cu	Co	V	As	Mo	References
Anzali Wetland	43,147.5	1.47	48.52	1.80	1.276	0.117	0.084	0.208	0.432	0.148	This study
Venice lagoon, Italy	158.4–252.12		– 47.04 to 84.67			4.45–7.68		– 102.84 to 15.93	– 3.25 to 4.5		Turetta et al. (2005)
Monteray Bay, CA	165–990		72.58–614.21			1.38–121.34					Berelson et al. (2003)
Daya Bay	2619.13		872.27		2.54	1.63					(Ni et al. 2017)
Myrtle Grove marsh	1115.07–5364.38		75.48–38,049.32					– 2.95 to 1.51	4.17–28.56		Telfeyan et al. (2017)
Vigo ria, Spain					0.26–2.73	– 0.03 to 1.93	0.05–0.39	2.07–6.08			Santos-Echeandia et al. (2009)

and branches cells, where it eventually accumulates (Marschner 1995). In the lower layers, Mn was present in the form of hydroxide ($\text{Mn}(\text{OH})_2$) in lower concentrations and in a colloidal or suspended state, which causes less damage to aquatic life. V appeared in combination with hydrogen ($\text{HV}_{10}\text{O}_{23}^{-5}$) in the water of the wetland and, due to its ionic and soluble nature, its toxicity was considered high. Cu existed in the wetland in elemental form (Cu), sediment and insoluble, so its toxicity was relatively low. Ni in Anzali wetland was in the form of hydroxide ($\text{Ni}_2\text{OH}^{+3}$) and soluble that has high bioavailability and is toxic to organisms. Co in the pore-water of the first layer of wetland sediments was present in the form of free ions (Co^{+2}), so it might be toxic with high bioavailability. But in other samples, it was found in the form of hydroxide ($\text{Co}_4(\text{OH})_4^{+4}$), which is less dangerous than its free ion, but is still available to organisms because it is soluble and ionic. As species in surface water and pore-water, except the first layer, was arsenate (HAsO_4^{-2}), which has less mobility and toxicity than the arsenite (As^{+3}). However, in the first layer of pore-water, As existed in the form of an insoluble oxide (As_2O_3) and has appeared in the form of colloid or suspended, which has less toxicity for aquatic life. Mo is seen as soluble and ionic oxide ($\text{Mo}_7\text{O}_{24}^{-6}$, MoO_4^{-2}) ones in all layers, thus it might be bioavailable and toxic to aquatic animals.

3.6 Cluster analysis

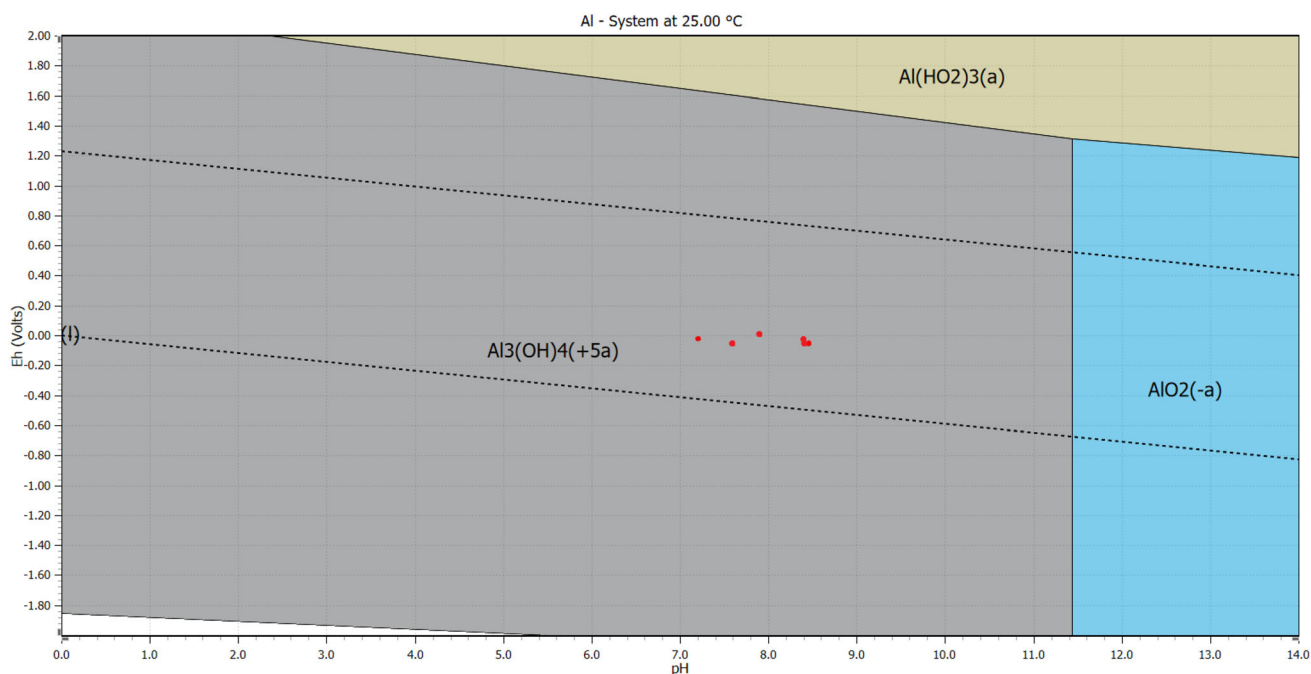
Correlation coefficient analysis (Table 14) along with cluster analysis (Fig. 11) after normalizing the data by SPSS for different layers of core sediments were done and as dendrogram depicts As, Ti, V, Ni, Fe, Al, and Cr are placed in one cluster (A), plus, there is a strong correlation between them. If V and Ni were considered as an indicator of oil pollution (Esmaeilzadeh et al. 2016a) and on the other hand Fe and Al as a lithogenic indicator (Vaezi et al. 2015), it might be concluded that Cr, As and Ti were partially derived from oil pollution and partly originated from the Earth's crust. Zn, Cd, Pb, Ag and Mn are placed in cluster "B" and there is a high correlation coefficient between them so they have similar behavior in the marine environment of the Anzali wetland. As cluster "C", shows there is a significant correlation between pH, Co, and Cu, it may be concluded that the behavior of mentioned elements is affected by pH. pH plays a crucial role in desorption and adsorption of the metals in sediment and in this research it has the non-uniform trend same as most of the metals in the core. However, as its lowest value is more than 6.5, so it seems other factors are effective too on release of metals and it does not depend only on pH value (Peng et al. 2009). It should be noted that pH itself is under control of the geology of area of study (Karbassi et al. 2018). Since there

Table 12 Physicochemical parameters of different layers of pore-water (P) and surface water (SW) of the eastern part of Anzali wetland

Layer	Eh (mv)	pH	EC (ms/cm)	Salinity (PSU)	TDS ($\mu\text{g/L}$)
SW	+ 17.5	7.86	0.335	0.17	167
P1 (0–12 cm)	+ 5.2	7.18	3.78	1.96	1849
P2 (13–24 cm)	– 11.2	7.57	3.71	1.96	1861
P3 (25–36 cm)	– 15.6	8.45	3.63	1.92	1817
P4 (37–48 cm)	– 13.1	8.40	5.18	2.78	2590
P5 (49–60 cm)	– 15.0	8.40	5.27	2.85	2640

Table 13 Physicochemical parameters of sediments of different layers of core sediment (S) belonging to the eastern part of Anzali wetland

Layer	Eh (mv)	pH	EC (ms/cm)	Salinity (PSU)	TDS (mg/kg)
S1 (0–12 cm)	– 20.7	7.32	2.66	1.37	1293
S2 (13–24 cm)	– 22.7	7.14	3.04	1.59	1525
S3 (25–36 cm)	– 20.7	7.42	2.43	1.26	1223
S4 (37–48 cm)	– 24.1	7.11	2.87	1.48	1436
S5 (49–60 cm)	– 23.5	7.60	2.57	1.32	1282

**Fig. 7** Eh–pH diagram of Al in pore-water samples of different layers and surface water of Anzali wetland drawn by HSC Chemistry software version 9.5.1

is not any considerable correlation between other parameters such as salinity, EC, TDS, Eh, Mo, and Ca which form clusters “D” and “E” it can not be found any significant relationship with other clusters.

Pursuant to Table 15, Pearson coefficient and dendrogram drawn in Fig. 12 which were drawn after normalizing the data by SPSS, for the pore-water at different core sediment layers, Cu, Ca and Ni and Eh are placed in cluster “A” and there is a high similarity coefficient between them. Since Ca might be considered as a biological index, so Cu in pore-waters of Anzali wetland could be originated

from oil and biological origin. In cluster “B”, there is a considerable correlation between pH, Mo, As, and Co so it might be concluded that the pH has effect on behavior of mentioned elements. Cluster “C”, shows that behavior of some elements such as V and Fe is influenced by EC, TDS and salinity. As cluster “D” indicates that Mn doesn’t have any significant correlation with other metals or parameters it is not possible to get any valuable information about its behavior.

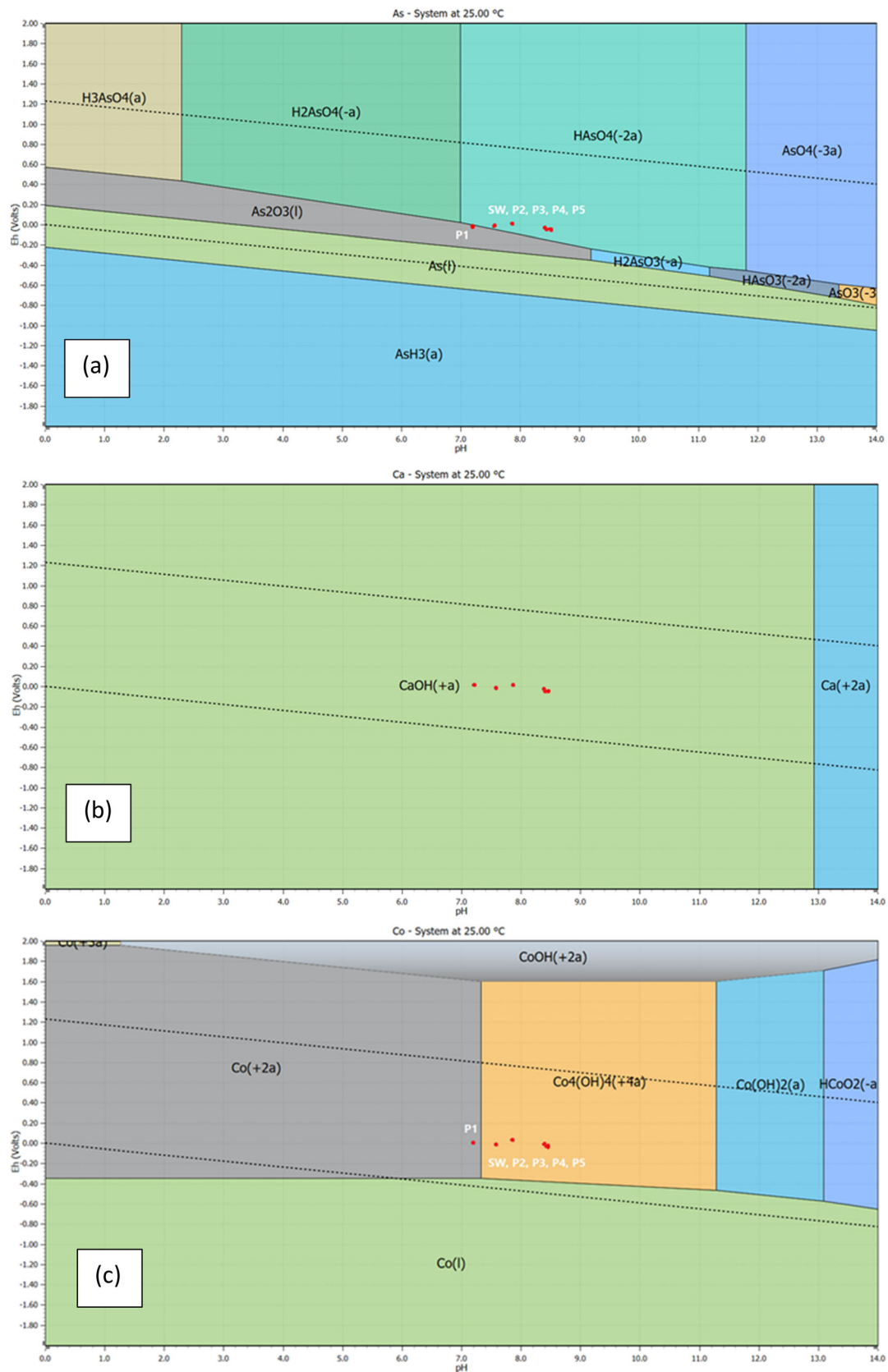


Fig. 8 Eh–pH diagrams of **a** As, **b** Ca, and **c** Co in pore-water samples of different layers and surface water of Anzali wetland drawn by HSC Chemistry software version 9.5.1

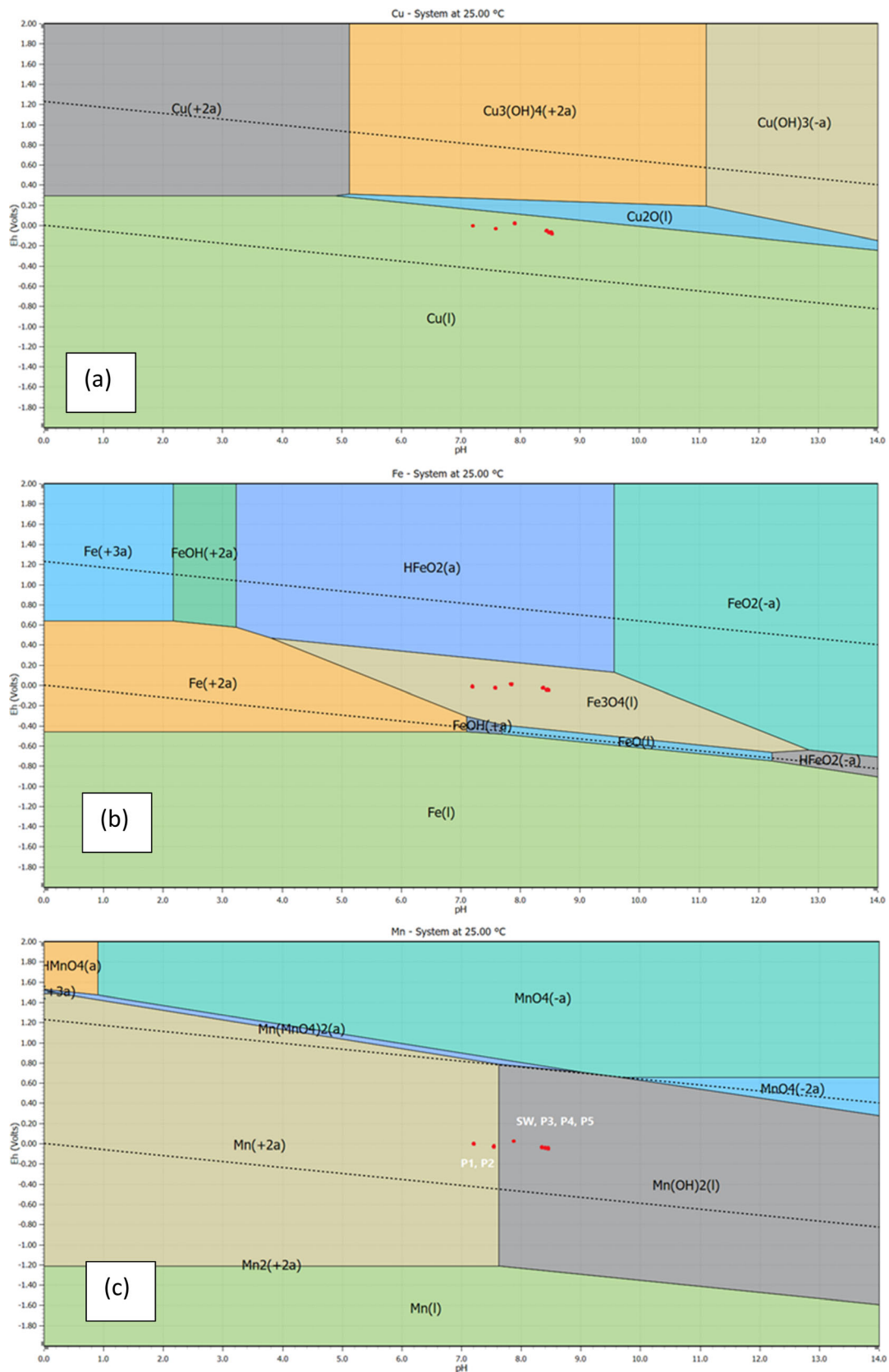


Fig. 9 Eh–pH diagrams of **a** Cu, **b** Fe, and **c** Mn in pore-water samples of different layers and surface water of Anzali wetland drawn by HSC Chemistry software version 9.5.1

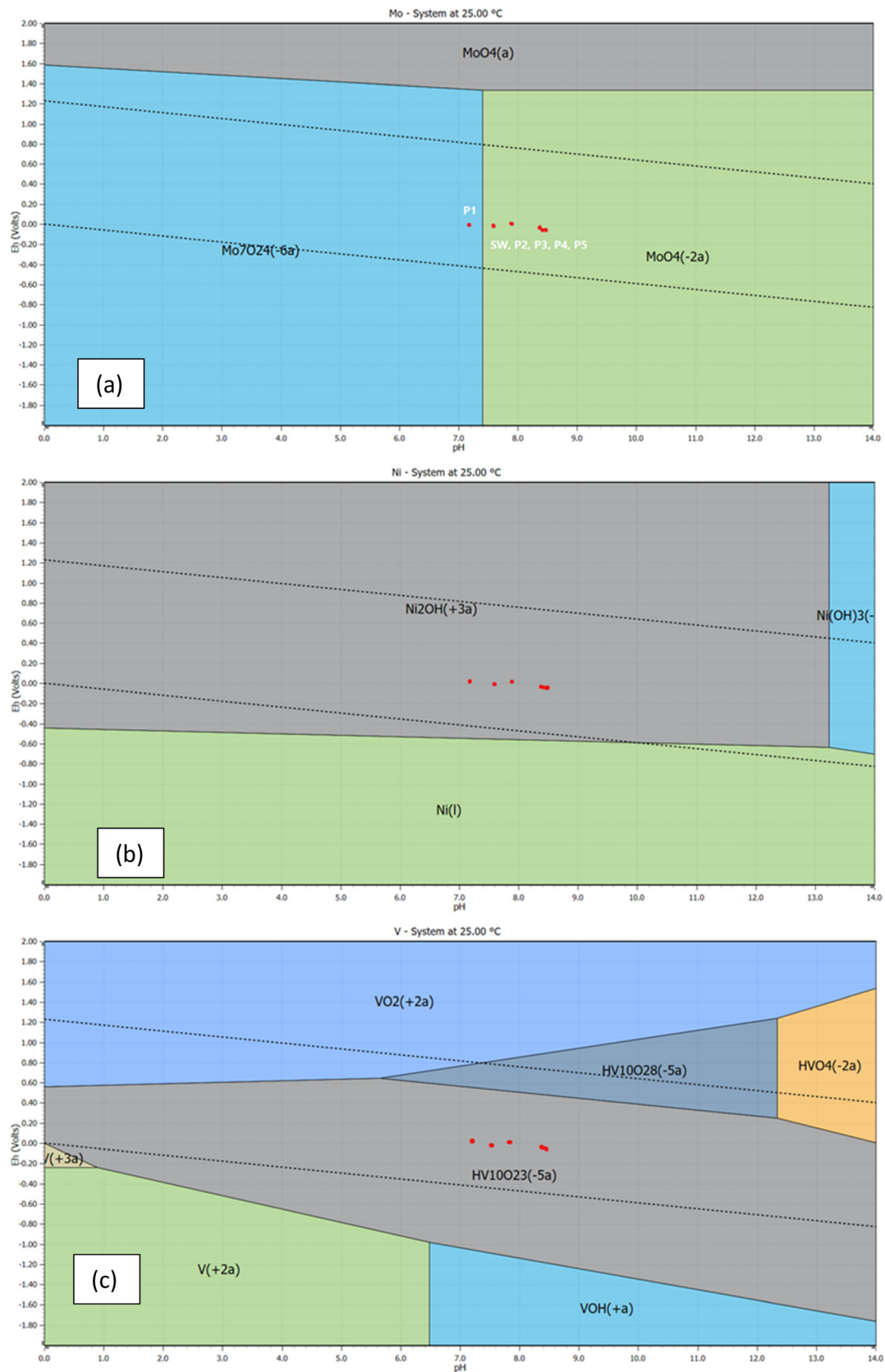


Fig. 10 Eh–pH diagrams of **a** Mo, **b** Ni, and **c** V in pore-water samples of different layers and surface water of Anzali wetland drawn by HSC Chemistry software version 9.5.1

Table 14 Pearson correlation coefficients of metal concentrations in solid phase of core sediment from eastern part of Anzali wetland

	Al	Fe	Ca	Ti	Mn	Zn	V	Cr	Ni	Cu	Pb	Co	As	Mo	Ag	Cd	Eh	pH	EC	TDS	S
Al	1																				
Fe	0.99**	1																			
Ca	-0.90	-0.89	1																		
Ti	0.88*	0.81	-0.66	1																	
Mn	-0.63	-0.53	0.41	-0.88	1																
Zn	0.14	0.26	-0.10	-0.13	0.56	1															
V	0.93*	0.86	-0.79	0.98**	-0.82	-0.10	1														
Cr	0.68	0.58	-0.81	0.66	-0.54	-0.26	0.78	1													
Ni	0.99**	0.95*	-0.87	0.94*	-0.74	0.01	0.98**	0.73	1												
Cu	0.64	0.74	-0.52	0.36	-0.17	0.38	0.36	-0.05	0.54	1											
Pb	-0.72	-0.61	0.66	-0.86	0.93*	0.56	-0.88	-0.80	-0.82	-0.14	1										
Co	0.88*	0.93*	-0.74	0.69	-0.30	0.57	0.71	0.37	0.82	0.75	-0.33	1									
As	0.87	0.79	-0.68	0.99**	-0.82	-0.07	0.98**	0.73	0.93*	0.26	-0.84	0.69	1								
Mo	-0.39	-0.53	0.39	-0.01	-0.40	-0.89	-0.06	0.12	-0.24	-0.72	-0.34	-0.73	-0.01	1							
Ag	-0.45	-0.36	0.25	-0.70	0.95*	0.72	-0.63	-0.36	-0.55	-0.17	0.84	-0.09	-0.61	-0.52	1						
Cd	-0.63	-0.52	0.61	-0.76	0.89	0.68	-0.78	-0.77	-0.72	-0.10	0.98**	-0.19	-0.72	-0.43	0.86	1					
Eh	-0.09	0.06	0.10	-0.39	0.43	0.42	-0.41	-0.65	-0.22	0.70	0.52	0.17	-0.50	-0.62	0.28	0.48	1				
pH	0.67	0.71	-0.32	0.65	-0.36	0.53	0.57	0	0.63	0.68	-0.20	0.86	0.61	-0.57	-0.20	-0.04	0.21	1			
EC	-0.47	-0.53	0.12	-0.48	0.44	-0.18	-0.36	0.27	-0.44	-0.79	0.19	-0.57	-0.35	0.36	0.46	0.12	-0.51	-0.81	1		
TDS	-0.36	-0.43	0	-0.37	0.33	-0.24	-0.24	0.40	-0.32	-0.75	0.06	-0.51	-0.25	0.38	0.36	-0.02	-0.56	-0.80	0.99**	1	
S	-0.44	-0.50	0.08	-0.48	0.45	-0.16	-0.35	0.29	-0.42	-0.75	0.18	-0.54	-0.36	0.32	0.47	0.11	-0.48	-0.82	1**	0.99**	1

*Correlation significant at the 0.05 level (2-tailed)

**Correlation significant at the 0.01 level (2-tailed)

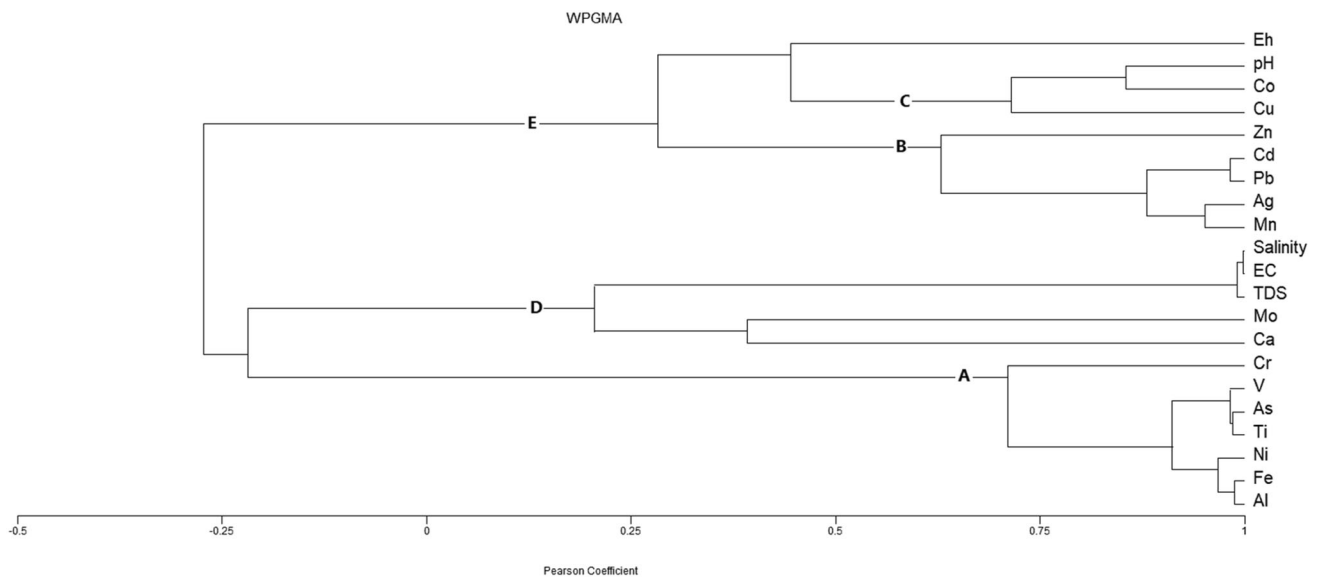


Fig. 11 Results of cluster or dendrogram analysis of elements in sediments of the eastern part of Anzali wetland

4 Conclusions

In the present research, behavior of trace metals in different core sediment layers in solid and liquid phases were investigated. For this purpose by performing various analysis was carried out on sediment core, pore-water and bottom water of Anzali wetland. The results of TRI multi-element toxicity test, showed that in all layers except the fourth layer, the rest of the layers were classified in the moderate pollution class. The MERMQ index, which is based on the range of effects, indicated all layers in the medium pollution class. However, the RI depicted that the first and second layers were moderate but 3rd to 5th layers had a high ecological risk. The results of pore-water toxicity test illustrated that all layers had no pollution impact.

Moreover, the status and properties of the metals were also studied separately. The results indicated that Al had the largest share in sediments but was released in relatively small amounts in pore-water and also its diffusive flux was insignificant. Al in the water of Anzali wetland was in the form of hydroxide, soluble and bioavailable, which is hazardous for organisms. Fe in the pore and surface water of Anzali wetland was in the form of magnetite, which is the oxidized state of Fe and was present in a colloidal or suspended state, which is not dangerous for aquatic animals when compared with free ions forms. Also, its diffusive flux was not very large compared to other water zones. Ca was present in the water of Anzali wetland in the form of hydroxides and ionic so it is available to organisms due to its solubility and had toxic properties. In addition, its diffusive flux was significant compared to other elements. Though Ti is present in high concentration in the sediments, but according to EF and I_{geo} indices, it does not

cause any contamination. The rate of release of Ti in surface and pore-waters was almost zero and its concentration in water samples was too small that the ICP device was not able to detect it. I_{geo} and EF indices indicated that Mn in some layers caused pollution. Mn is significantly released in the second and third layers of the pore-water. Mn is present in the form of soluble free ion in surface water and the first and second layers of pore-water, which is indicative high bioavailability and high toxicity to animals and plants. I_{geo} and EF indices depicted that Zn did not cause any contamination and enrichment and, in terms of mHQ index in all layers, had low risk. Zn in the water had no release and its concentration was negligible. V in sediments had no contamination and enrichment effect. V was in the form of a hydrogen compound in water and had high toxicity due to its ionic and soluble nature, but its risk is reduced due to its low diffusive flux. Cr was evaluated pursuant to I_{geo} and EF indices without contamination and enrichment, and mHQ described this metal as low risk for the first layer and high risk for the other layers. Cr had no release in water and was of terrestrial and oil pollution origin in sediments. I_{geo} and EF indices showed the Ni did not cause any contamination and enrichment, but according to the mHQ index, it had a significant risk in the first, second and fourth layers and a high risk for the third and fifth layers. The diffusive flux of Ni in Anzali wetland was $1.276 \mu\text{g}/\text{m}^2/\text{day}$. Ni in the water of Anzali wetland was in the form of hydroxide and soluble with high bioavailability and toxicity to aquatic animals. Cu in the water of the wetland was in elemental form, and is not considered a danger to Anzali wetland because it has low toxicity. Pb caused low pollution according to the I_{geo} index in all layers except in the third layer and in terms of EF index in

Table 15 Pearson correlation coefficients for the relationships between the metal concentrations in pore-waters of the eastern part of Anzali wetland

	Ca	Mn	Fe	Al	V	Mo	As	Ni	Cu	Co	TH	Eh	pH	EC	TDS	S
Ca	1															
Mn	0.32	1														
Fe	-0.52	-0.32	1													
Al	-0.60	-0.32	0.60	1												
V	-0.84	-0.50	0.82	0.48	1											
Mo	-0.93	-0.21	0.18	0.49	0.60	1										
As	-0.85	-0.65	0.34	0.30	0.81	0.81	1									
Ni	0.97**	0.20	-0.53	-0.46	-0.86	-0.89	-0.83	1								
Cu	0.99**	0.41	-0.46	-0.56	-0.83	-0.94	-0.91	0.95*	1							
Co	-0.95	-0.41	0.48	0.36	0.89*	0.86	0.94*	-0.96	-0.96	1						
TH	0.94*	0.18	-0.28	-0.63	-0.61	-0.98	-0.74	0.89*	0.93*	-0.83	1					
Eh	0.88*	-0.14	-0.41	-0.42	-0.67	-0.85	-0.60	0.94*	0.83	-0.82	0.87	1				
pH	-1	-0.35	0.52	0.59	0.85	0.93*	0.87	-0.97	-0.99	0.96*	-0.94	-0.87	1			
EC	-0.57	-0.49	0.98**	0.60	0.87	0.24	0.48	-0.56	-0.53	0.56	-0.32	-0.38	0.57	1		
TDS	-0.59	-0.46	0.98**	0.61	0.89*	0.27	0.49	-0.59	-0.56	0.58	-0.35	-0.42	0.60	1**	1	
S	-0.59	-0.47	0.98**	0.60	0.89*	0.27	0.49	-0.59	-0.56	0.59	-0.34	-0.42	0.59	1**	1**	1

*Correlation significant at the 0.05 level (2-tailed)

**Correlation significant at the 0.01 level (2-tailed)

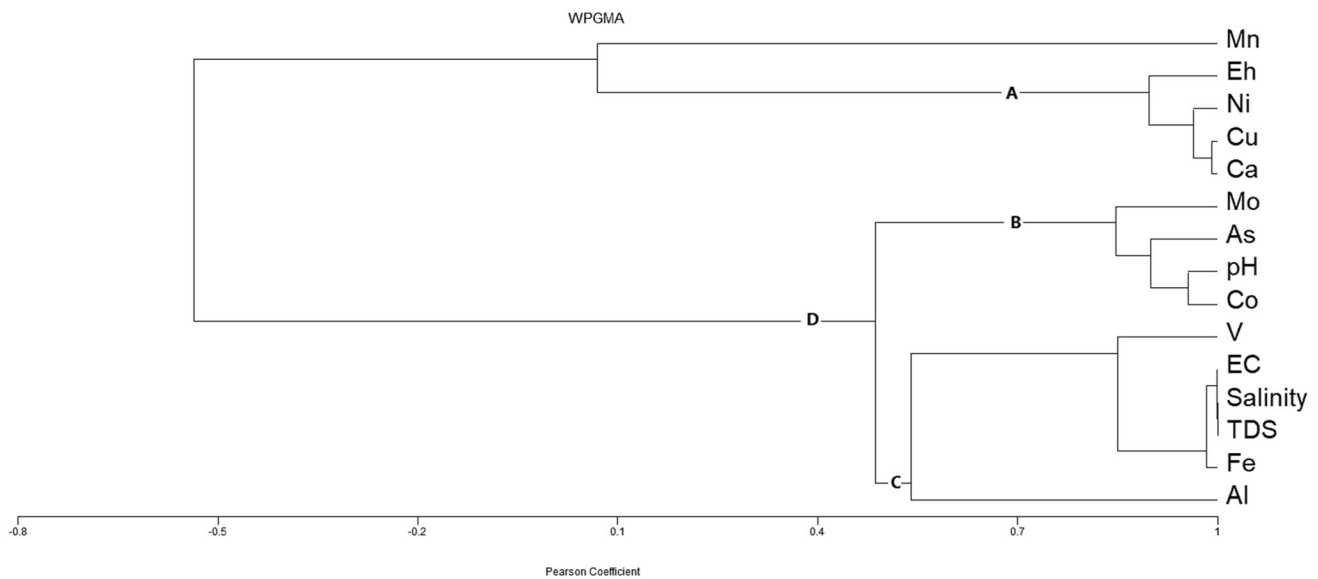


Fig. 12 Results of cluster or dendrogram analysis of elements in pore-waters of the eastern part of Anzali wetland

all layers had low enrichment. Also, in terms of mHQ index in the first layer had a moderate risk and in other layers had a low risk. The results of I_{geo} and EF indices illustrated that Co did not cause any contamination in the sediments and its diffusive flux was $0.084 \mu\text{g}/\text{m}^2/\text{day}$ and in the first layer of pore-water it was in the form of free ion which is the most dangerous form for aquatic life and also it has high bioavailability. Co is governed by pH changes in sediments (not completely) and pore-water. As was released in small amounts from the solid phase in the second layer of pore-water and the concentration in this layer was negligible. As, pursuant to the EF index in the second to fifth layers, had moderate enrichment. Additionally, according to the mHQ index, in the first, second and fourth layers, there was a moderate risk and in the third and fifth layers, there was a significant risk. As in surface water and pore-waters of the second to fifth layers was in the form of arsenate (As^{+5}), which has low mobility and toxicity. In the first layer of pore-water was also appeared in the form of insoluble oxide, which is less toxic to aquatic life. Mo in the second to fifth layers of pore-water had a concentration of more than $10 \mu\text{g}/\text{L}$. Its diffusive flux was $0.148 \mu\text{g}/\text{m}^2/\text{day}$ and in the water of Anzali wetland existed in the form of soluble oxide and ionic, which is toxic and bioavailable to aquatic life. Ag shows moderate pollution in all sediment layers based on I_{geo} . According to the I_{geo} index, Cd did not cause any pollution and EF showed low enrichment only in the first layer. Also mHQ index indicated that Cd had a risk in the first two layers.

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Declarations

Conflict of interest The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

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