




Variation entry of sediment, organic matter and different forms of phosphorus and nitrogen in flood and normal events in the Anzali wetland

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ABSTRACT

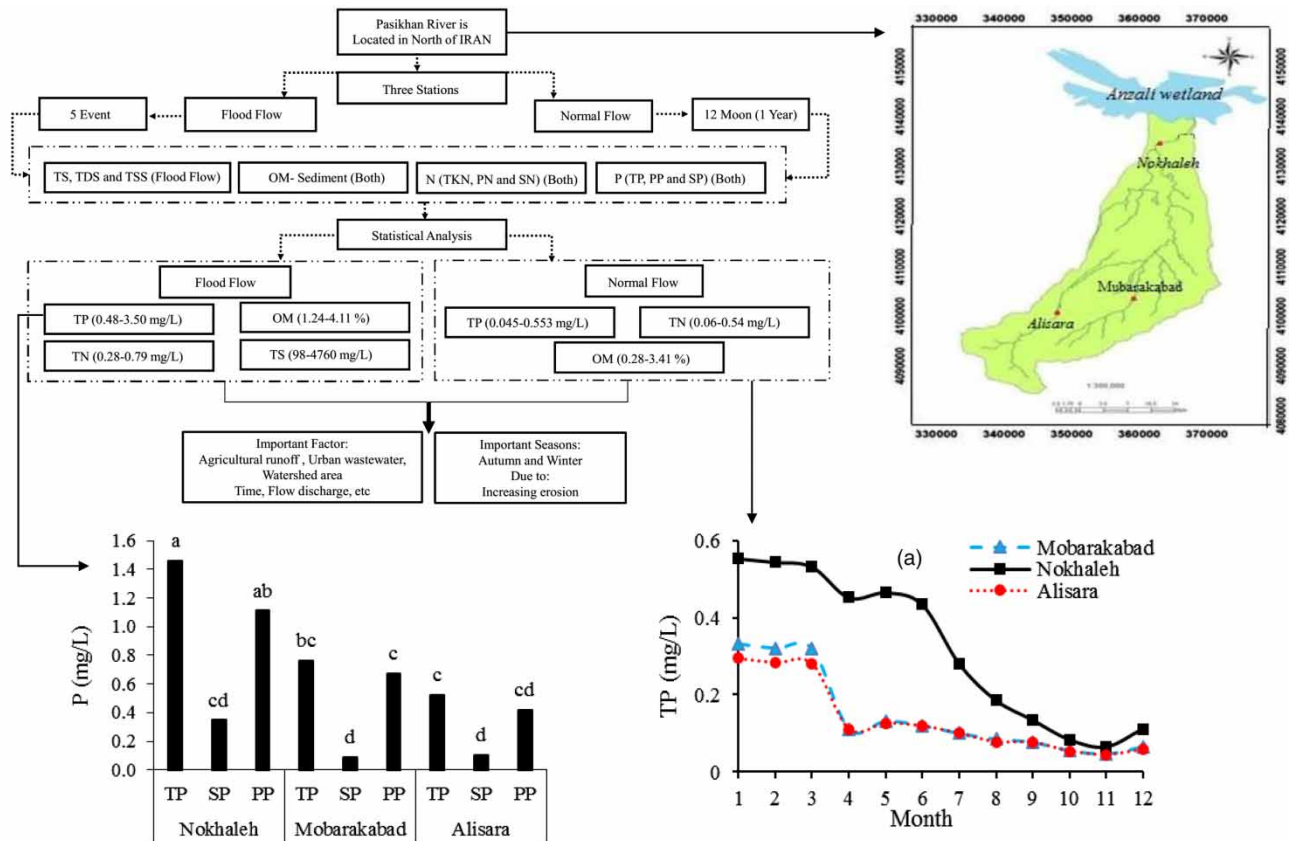
Phosphorus (P), nitrogen (N) and organic component are released from the soil into surface bodies by runoff and erosion, causing the pollution and eutrophication of water resources. This study aimed to investigate the seasonal changes in loads of N and P components, and organic matter (OM) in the Pasikhan River in flood and normal conditions. Sampling was performed monthly during normal flow conditions and for five flood events. The concentrations of P and N components were measured in the samples. The OM of the suspended sediments was determined by the combustion method. Under the normal flows, the maximum loads of total P and OM were about 0.553 mg l^{-1} (STD = 0.11) (November) and 3.41% (STD = 1.17) (November) in the autumn, respectively. The total N concentration of 0.533 mg l^{-1} (STD = 0.12) was observed in the winter. In the flood events, the TP, TN and OM ranged from 0.48 to 3.5 mg l^{-1} , 0.28 to 0.79 mg l^{-1} and 1.24 to 4.11%, respectively. The results indicated a high risk of eutrophication in the Pasikhan River. Also, the study revealed that in a severe flood event, some $113.9 \text{ tons h}^{-1}$ of OM can be released from the river watershed. Furthermore, there was a high correlation between the amount of P and OM losses with the concentration of suspended sediments in different flood events. Finally, it is concluded that if the floods are not controlled, they not only cause a rapid loss of soil nutrients and OM but also lead to severe eutrophication in the Anzali wetland.

Key words: Anzali wetland, flow, soil erosion, suspended sediment, water pollution

HIGHLIGHTS

- The Pasikhan River is at risk of eutrophication.
- Time, flow rate and area are the most important determinants of pollution.
- Nitrogen and phosphorus losses are the highest in autumn and winter.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Wetlands are considered as one of the most valuable natural ecosystems carrying a wide range of functions. Along with protecting biodiversity, they have other natural, economic and social values such as providing wildlife habitat, water treatment, climate change abatement, flood control, food supply, human health and tourism (Brander *et al.* 2006; Cao & Fox 2009; Costanza *et al.* 2014; Dwire *et al.* 2018; Zhong *et al.* 2020). Wetlands gain even more attention when we consider that more than a third of the world's population lives nearby wetlands, rivers, ponds and beaches. The maintenance of healthy wetlands is beneficial for human and ecosystem health as well as worldwide sustainable development (Sala *et al.* 2001; JICA 2005; Ramsar Convention on Wetlands 2018). However, these ecosystems have always been exposed to many hazards, including human disturbance, which disrupted their biological order and balance.

Severe soil erosion, due to human impacts on natural ecosystems, is a major environmental issue (Mohammed *et al.* 2020; Plambeck 2020) resulting in soil degradation, loss of soil particles and discharge of dissolved and particulate nutrients into water bodies (Quijano *et al.* 2020; Wang *et al.* 2020). Soil erosion mostly carries the finest soil particles (63–125 μm), which contain the majority of the bioavailable nutrients (Angulo-Martínez *et al.* 2012; Quijano *et al.* 2020). Heavy rainfalls would cause soil erosion, particularly on steep slopes, which can wash away soil nutrients into the downstream surface waters and rivers (Villa *et al.* 2014). On the other hand, significant concerns have been raised over nutrient wash-off from agricultural lands to surface waters (Koiter *et al.* 2017; Martínez-Mena *et al.* 2020). Nitrogen (N) and phosphorus (P) are the most important nutrients that can enter water bodies by runoff and in particulate form by suspended sediments, causing the deterioration of water quality (Bertol *et al.* 2010; Toor *et al.* 2017). Organic matter (OM) is also transported along with suspended sediments during the erosion process, as OM is usually less dense than other suspended sediment components, including minerals. As a result, OM may form a large portion of all suspended sediments during the flow. In addition, organic substances are among the major water pollutants, especially causing a reduction in the dissolved oxygen content of water

bodies. In fact, OM is considered as one of the main pollutants of aquatic environments due to the elements and substances which are bound to it (Aufdenkompe *et al.* 2007; Sharpley *et al.* 2015). The presence of P and N is necessary for eutrophication (Dauvin *et al.* 2007). However, since P concentration is often less than N concentration, the growth of algae and the onset of eutrophication are usually controlled by the content of P in water. If such conditions exist, P is said to be a limiting factor. In marine ecosystems, N controls the eutrophication and is considered to be a limiting element, although in many studies, P is a primary limiting nutrient in both freshwater and aquatic ecosystems as well (Howarth & Paerl 2008; Dubrovsky & Hamilton 2010; Chislock *et al.* 2013; Jarvie *et al.* 2013; Cao *et al.* 2014; Ngatia *et al.* 2019).

The Anzali wetland is one of the most important wetlands globally, located on the southern coast of the Caspian Sea, the largest landlocked body of water in the world, in the north of Guilan province, Iran. The Anzali wetland is registered in the Ramsar Convention (June 1975) as an international wetland. The wetland suffers from severe pollution due to a range of human activities and is listed as a wetland which needs rehabilitation in the Montreux Record at 1993 (Khoshkam *et al.* 2016; Aghsaei *et al.* 2020; Rasta *et al.* 2020). The chemical and physical quality of the Anzali wetland has deteriorated in recent decades. A significant part of the Anzali wetland watershed is under agricultural activities ($\approx 1,273.7 \text{ km}^2$), which is responsible for the majority of destruction in the wetland quality (JICA 2005). Previous studies indicated that the agricultural sector can be considered as the most important cause of wetland degradation in different parts of the world (Beuel *et al.* 2016; Everard 2016; Mao *et al.* 2018).

Runoff from agricultural lands, especially paddy fields and disturbed pastures, would cause the discharge of P and N nutrients into the surface waters and finally the wetland. Arable lands' runoff contains the residue of chemical and organic fertilizers that can eventually enter the wetland and increase the growth of wetland plants. The accumulation of these nutrients in the wetland would lead to the eutrophication phenomenon. A better understanding of sediment and nutrient pollution in the Anzali wetland watershed would provide valuable information for a better management of wetlands and water resources located in the relevant climatic conditions or have similar vegetation cover, land-use diversity and topographic variations.

There is limited information available about the temporal changes of P and N, the role of land use and topography, and their interactions on the amount and forms of pollutants (such as P, N and OM) that are transported by flood events in complex watersheds like the Anzali wetland watershed. To the best of our knowledge, this is the first comprehensive study in the Anzali wetland watershed on different forms of transported P and N nutrients with a focus on the contribution of upstream and downstream lands as well as the role of flood events in the total amount of pollutants inlet to the wetland. Therefore, the objectives of this study were (1) to investigate the role of seasonal variations in the concentration of different forms of N, P and OM in the Pasikhan River as the biggest river entering the Anzali wetland, (2) to determine the dominant form of transported P and N to the Anzali wetland and the relative contribution of different land uses, (3) to determine the role of flood events in the transfer of these pollutants and (4) to estimate the total amount of P, N and OM transported into the Anzali wetland.

2. MATERIALS AND METHODS

2.1. Study area

The Anzali wetland (193 km^2 surface area) is one of the most important wetlands in Iran, which is located in the north part of Iran, along the southern coast of the Caspian Sea, in the Guilan province (Figure 1). It is internationally known as an important wetland for migratory birds and was registered as a Ramsar site in 1975 in accordance with the Convention on Wetlands of International Importance Especially as Waterfowl Habitat. However, the water quality of the wetland is deteriorating due to the inflow of wastewater and solid waste from neighboring cities, including the provincial capital, Rasht. The Anzali wetland is also shrinking due to the inflow of sediment from its catchment area (approximately $3,610 \text{ km}^2$). The annual mean discharge into the wetland is estimated at $76.14 \text{ m}^3 \text{ s}^{-1}$ (Asadi 2016). Rainfall of the region varies greatly (between 400 and $2,000 \text{ mm year}^{-1}$), with highest precipitation in the west side and gradual decrease towards the east. Evaporation in the region increases from west to east with an average of 800 mm. The temperature is mild, ranging between $-0.8 \text{ }^\circ\text{C}$ and $37.3 \text{ }^\circ\text{C}$ with an average of $17 \text{ }^\circ\text{C}$. Relative humidity varies depending on the location and season, which ranges between 24 and 100% with a regional average of 66%. The nine main rivers of the Anzali wetland watershed carry sediment and pollutants from rangelands, forests, agricultural lands and urban and industrial areas, and discharge them into the wetland. Pasikhan River (94.5 km length and 671 km^2 catchment area) is the main river drained into the wetland and has the highest

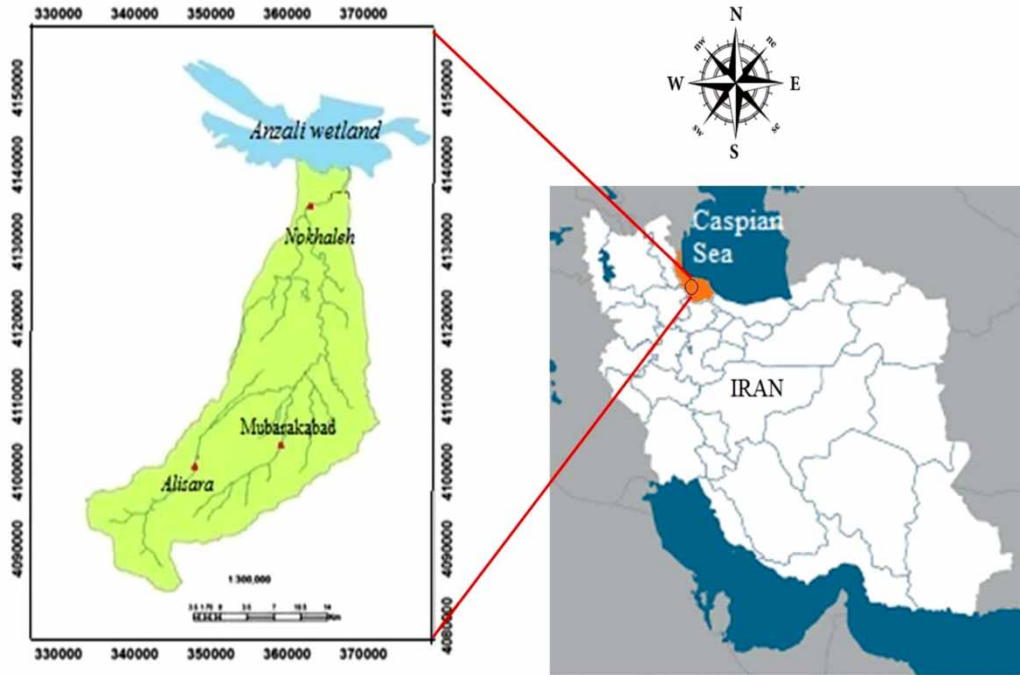


Figure 1 | Pasikhan River watershed and its hydrometric stations.

discharge (annual average of $20.70 \text{ m}^3 \text{ s}^{-1}$ equal to 27% of total discharge) among the entering rivers into the Anzali wetland (Figures 2 and 3 and Table 1). The annual sediment load in the Pasikhan River is approximately 0.2 million tons year⁻¹ (Table 1). Considering the Pasikhan River’s water flow, catchment area and amount of transported sediment, this river was selected as the index river of the Anzali wetland in this study.

The Siamazgi river (Alisara station; E 49°17' and N 37°2') and the Imamzadeh Ibrahim river (Mobarakabad station; E 49°24' and N 37°4') are the Pasikhan River’s main branches, which originate from the Lateberhne mountain with an altitude of 2,867 m. The Nokhaleh station (E 41°20' and N 36°27') is located at the exit point of the watershed. The watershed of Pasikhan River is located at the north latitude between 36°54' and 37°27' and the east longitude

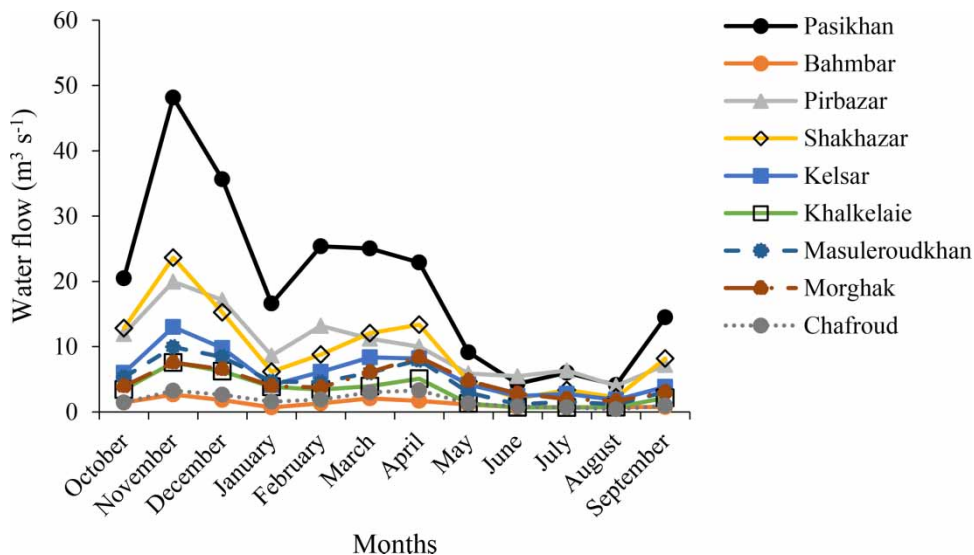


Figure 2 | Pasikhan River watershed and its hydrometric stations.

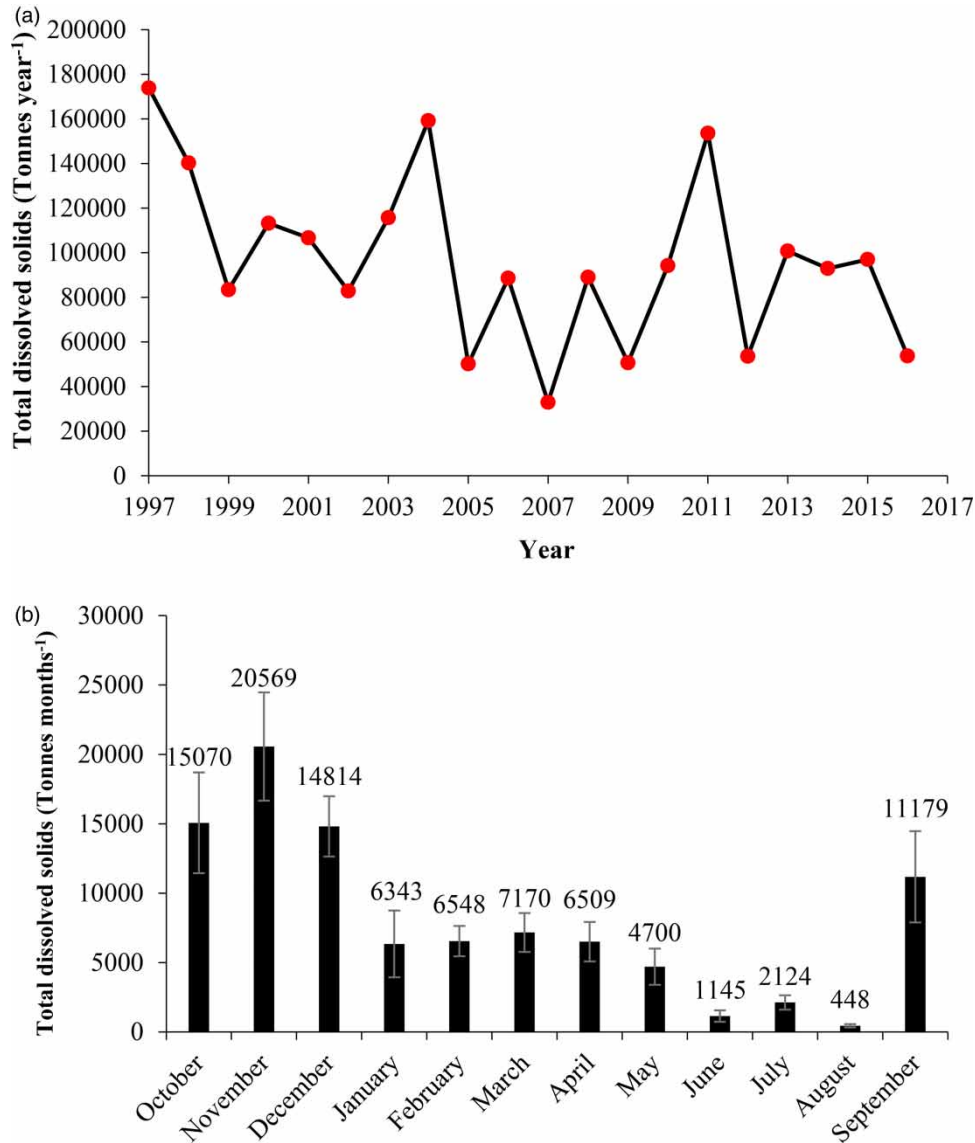


Figure 3 | (a) Annual changes and (b) monthly changes of suspended sediments in the Anzali wetland from Pasikhan River (from 1997 to 2016).

between 49°08' and 49°34'. The average slope of the watershed is 19.2 and it has a Gravelius index of 1.57. The Alisara (Upstream 1) and Mobarakabad (Upstream 2) stations are in the mountainous part of the region. Agricultural land use in these two stations has significantly damaged native pastures and forests. Therefore, the information generated from these two stations can determine the role of native pasture and forest in the mitigation of Anzali wetland pollution. The Nokhaleh station is located at the end of the watershed in the plain section (Downstream), which includes a large part of the upstream area of this station for agricultural and urban land uses. In general, by comparing the two stations in the mountainous part and the station in the plain part, we can determine the role of each different land use in supplying sediment and pollutants to the Anzali wetland.

The percentage of land-use areas in each of the studied sub-watersheds is presented in Table 2. The Alisara and Mobarakabad sub-watersheds are mainly covered by native forest, with limited agricultural and urban land uses. However, rangelands are located in the southern part of the Anzali watershed where the rivers originated. These pastures are located on steep slopes with low-density vegetation cover. Rainfall leads to high rates of soil surface erosion, and consequently, soil particles and nutrients are washed away to the rivers, which finally cause pollution in the Anzali wetland.

Table 1 | Average flow and sediment load of the rivers that discharge into the Anzali wetland

River	Area (km ²)	Suspended load (tons year ⁻¹)	Bed load (tons year ⁻¹)	Annual sediment load (tons year ⁻¹)	Special sediment (tons year ⁻¹ . km ²)
Pasikhan	670.9	163,781	24,567	188,349	280
Shakhazar	443.1	68,353	10,253	78,606	177
Masuleroudkhan	400.4	76,046	11,407	87,453	246
Pirbazar	368.7	66,601	9,990	76,591	207
Chafroud	136.4	39,850	5,978	45,828	335
Kelsar	257.5	35,001	5,250	40,251	156
Khalkelaie	342.9	67,749	10,162	77,911	227
Morghak	308.8	64,284	9,643	73,927	239
Bahmbar	116.8	12,719	1,908	14,627	125

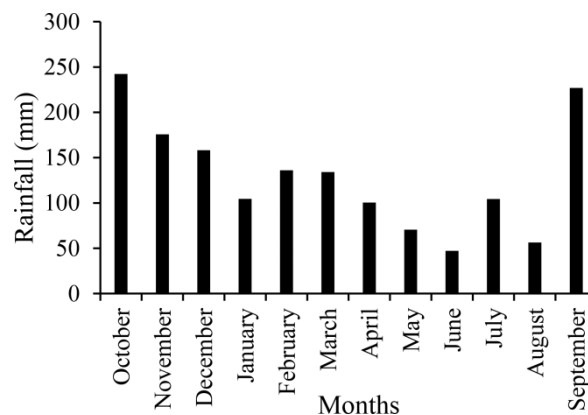
Table 2 | Land-use coverage (%) and slope in the Pasikhan River sub-watersheds

Land use	Nokhaleh	Mobarakabad	Alisara
Urban	1.67	1.45	0.33
Disturbed rangeland	8.30	24.20	16.19
Undisturbed rangeland	3.37	5.36	7.66
Dense forest	41.59	57.40	69.51
Moderately dense forest	1.49	3.61	3.34
Agriculture	38.68	5.92	2.74
Other	4.90	2.06	0.23
Average slope (%)	19.6	37.6	41.5

Figure 4 represents variations in average monthly rainfall for the study watershed. The highest and lowest rainfall occurs in October (242 mm) and June (47 mm), respectively. The mean annual rainfall (based on a 10-year period, 2005–2014) is approximately 1,557 mm.

2.2. Sample collection and analysis

Water samples were collected from the Pasikhan River at three stations of Nokhaleh (Downstream), Mobarakabad (Upstream 2) and Alisara (Upstream 1) during flood events and normal conditions. The sampling was performed monthly for 12 months

**Figure 4** | Rainfall in the Pasikhan River watershed (2005–2014).

and every 2 h during five flood events (13/11/2013, 20/11/2013, 13/3/2014, 22/3/2014 and 1/4/2014). The average values of 3 months were used to determine the values for each season. Overall, 111 samples were collected including 75 samples during flood events and 36 samples during normal conditions. Sampling was performed from the center of the river and at a moderate depth of flow from the bridge over the river. The average flow rate of the flood events is presented in Table 3.

The flow discharge and concentration of total solids (TS), total dissolved solids (TDS) and total suspended solids (TSS) were measured at each sampling time. The samples were filtered using Whatman filter paper No. 42 to determine the TSS. The TDS was measured by analyzing for TS and subtracting TSS (Standard Analytical Procedures for Water Analysis 1999). A measured volume (500 ml) of each sample passed through a pre-weighed filter paper. The filter paper was then dried at 104 ± 1 °C and the TSS was calculated by subtracting the total dry weight from the weight of the filter paper. In order to determine the loss of particulate P and N, in a subsample, total Kjeldahl nitrogen (TKN) was measured by the Kjeldahl method (Standard Analytical Procedures for Water Analysis 1999). The Persulfate digestion method was used to measure total phosphorus (TP). In this method, after adding sulfuric acid, 0.4 g ammonium sulfate was added and water samples were boiled in three repetitions for 30–40 min. Then the TP was measured using a spectrophotometer (Cintra 1010 UV/Vis model) at 880 nm by the Murphy and Riley colorimetric method. To measure TKN, 50 ml of water sample was collected and poured into digestion tube with 10 ml of digestion solution. The manifold tubes were then placed on the digester at 420 °C. The evaporation process continued until the sample became colorless or pale yellow. After that, evaporation continued for another 30 min. N digestion solution was prepared by dissolving 267 g potassium sulfate in 1,300 ml distilled water, 400 ml sulfuric acid and the addition of 50 ml 2% copper sulfate solution (20 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 500 ml water), and bringing the volume of the solution to 2 l. When cooled, 30 ml distilled water was added and then the TKN content in percentage in the samples was measured using a Kjeldahl device (K9840 model-IRAN). Measuring dissolved P and N was the same as TP and TKN, except that samples were filtered with Whatman 42 filter paper before digestion. The contents of particulate nutrients (with suspended sediments) were obtained from the difference in total and soluble contents (Standard Analytical Procedures for Water Analysis 1999). The OM content of suspended solids was determined by the combustion method (Onda *et al.* 2010). The dried sediment samples were incinerated in a furnace at 450 °C for 4 h. The difference between the initial weight and the final weight of sediments was considered as OM content. Also, the pH of the water samples was measured by Metrohm 744 pH meter (Standard Analytical Procedures for Water Analysis 1999).

2.3. Statistical analysis

All analytical procedures were performed with three replications. Sampling was done on a monthly basis (one sample was collected per month), so three samples were collected in each season. Monthly samples were used as replication to compare the mean between the seasons. The mean comparison and the correlation were performed using the IBM SPSS Statistics 23 software package (IBM Corp. Released 2013. IBM SPSS Statistics for Windows, Version 22.0. Ar-monk, NY: IBM Corp.). The differences at $P \leq 0.05$ (Duncan's test) between treatments considered statistically significant, and all variables were tested for normality of distribution using the Kolmogorov–Smirnov test. The diagrams and regression analysis were performed using Excel 2013 software.

3. RESULTS AND DISCUSSION

3.1. Changes in solid particles load in flood events

Figure 5 presents the mean comparison of solid load concentrations in flood events for the three studied gauge stations. The maximum TS concentration ($2,872 \text{ mg l}^{-1}$) was observed in the second flood event with the highest flow discharge at the Alisara station (Upstream 1) (Figure 5(a)). There was a significant ($P < 0.05$) difference among flood events at all three stations in

Table 3 | Average flow rate ($\text{m}^3 \text{s}^{-1}$) of each site in the studied events

Location	Event 1 13/11/2013	Event 2 20/11/2013	Event 3 13/3/2014	Event 4 22/3/2014	Event 5 1/4/2014
Upstream 1	8.6	26.0	6.0	5.7	4.5
Upstream 2	28.2	79.0	21.3	18.0	16
Downstream	171.8	309.5	126.0	85.1	92.9

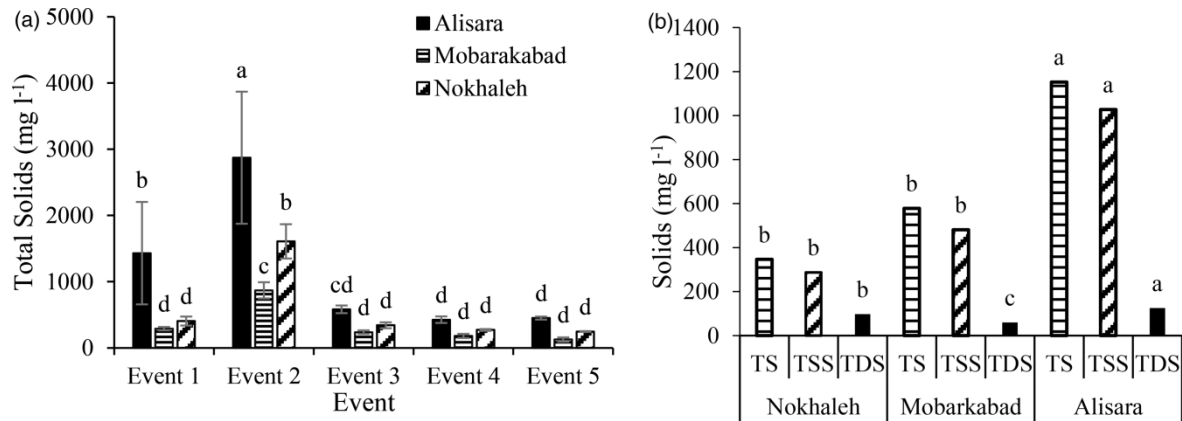


Figure 5 | Variations in the concentration of TS (a) and the concentration of TS, TSS and TDS (b) at flood events. Mean comparisons for each parameter were performed for different flood conditions and locations. TS, total solid; TSS, total suspended solid; TDS, total dissolved solids.

parameters of TS, TSS and TDS (Figure 5(b)). In general, it was observed that by decreasing the flow rate in all three stations, the concentration of TS decreased significantly. The Alisara station (Upstream 1) showed the highest TS concentration during different flood events (Figure 5(b)). However, there was no significant difference between the Nokhaleh (Downstream) and Mobarakabad stations (Upstream 2), although the average TS concentration at the Mobarakabad station (578 mg l^{-1}) was higher than the Nokhaleh station (348 mg l^{-1}). The high TS concentrations in Upstream 2 and Upstream 1 can be related to the location of these stations, the presence of degraded pastures in their upstream (Table 3), their topography and slope of the sub-watersheds and the shorter transport distance of particles in the river (Table 2). Shu *et al.* (2019) reported the results that a large amount of sediment decreased as the slope decreased. The region is under intensive pasture cultivation, and overgrazing has caused severe destruction to grazing lands. Livestock grazing would reduce the infiltration rate of water into soil due to soil compaction, which can result in increase of runoff and soil erosion. As a result, the outflow of solid particles can increase from the soil surface (Milchunas & William 1993; Bayat *et al.* 2017). In addition, agricultural lands in the Alisara sub-watershed are dominated by tea gardens, which are mainly located on steep lands. Agricultural activities on high slope would make the soil unstable to rain and create runoff quickly after rain, which consequently transport solid particles downward. There are various reports on the role of agriculture and its slope on the exit of particles from lands (Tao *et al.* 2020). The trend of solid particles concentration was consistent with the overall slope of the sub-watershed. The Alisara sub-watershed has more severe topography (High slope) exhibiting the highest solids in the flood events mainly in suspended form. One of the reasons for the high TS in the Mobarakabad sub-watershed can be attributed to severe mass erosion (in the southern part). In this hill, a creep occurred 4-m deep and 10-m wide with a length of 50 m. This erosion has caused soil instability in this part of the sub-watershed. Chayle & Wayne (1995) in Argentina reported that soil mass movements upstream cause sedimentation downstream. The Nokhaleh station is located at the end of route (the end of the Guilan plain and before the river enters the wetland), where the slope of the watershed is generally low, therefore the solid particles are more likely to be deposited. The results (Figure 5(b)) also indicated that the concentration of TSS was higher than the concentration of TDS. The TSS accounted for 83, 82 and 89% of the solid particles at the Nokhaleh (Downstream), Mobarakabad (Upstream 2) and Alisara stations (Upstream 1), respectively. Zhu *et al.* (2007) also performed a similar evaluation for Longchuanjiang river in Southwest China, with an average annual rainfall of 800 mm, which mainly (86 ~ 94%) occurred in the wet season from May to October. They observed that 75–95% of TS was in the form of TSS. The similarity of the results of the current study (Figure 5(b)) with those of Zhu *et al.* (2007) could be related to the similar rainfall content and seasonal distribution in the two studied catchments.

3.2. OM and nutrient loads in flood events

Variations in the OM content and various forms of P and N are presented in Figure 6 for flood events at the studied gauge stations. Overall, it was observed that the OM percentage in the transported sediments increased with the increase of flow discharge (Figure 6(a)). The high percentage of the OM reported in this study was observed during the extreme and erosive rainfall events. In this regard, the average OM outflow from Mobarakabad (1.67%) was higher than Alisara (1.08%)

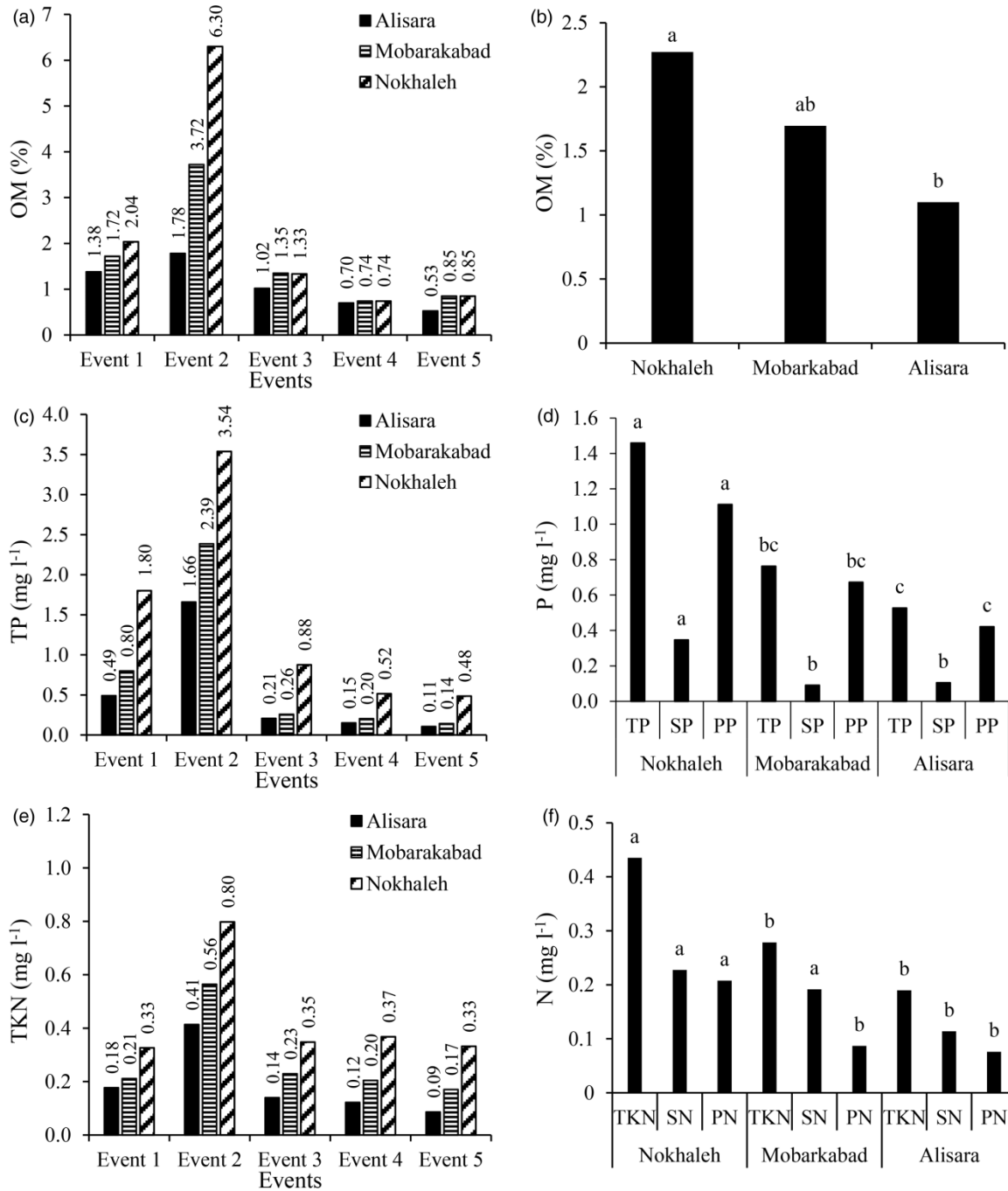


Figure 6 | (a) Variation in the concentration of organic matter in floods, (b) variation in the concentration of organic matter among the stations, (c) variation in the concentration of TP in floods, (d) variation in the concentration of phosphorus forms among the stations, (e) variation in the concentration of TKN in floods and (f) nitrogen forms among the stations. Mean comparisons were performed for different locations. TP, total phosphorus; SP, dissolved phosphorus; PP, particulate phosphorus; TKN, total Kjeldahl nitrogen; PN, particulate nitrogen; SN, soluble nitrogen.

(Figure 6(a) and 6(b)). The highest OM outflow (6.3%) was related to the second flood event with the highest flow discharge at the Nokhaleh station (Figure 6(a)). The average OM outflow from the Nokhaleh station (Downstream) was equal to 2.25%. The results showed that the differences among sub-watersheds in outflow OM (%) were higher in the first two events than those in the last three events (Figure 6(a)). The outflow of OM (%) in the last three flood events was similar at the Nokhaleh and Mobarakabad stations. Based on our field observations, this could be in part due to the dominance of surface erosion in

these two sub-watersheds. In the first two flood events, due to the high flow rate of the floods, the situation was more complicated, and the difference between the Nokhaleh and Mobarakabad sub-watersheds was higher than the last three events (Figure 6(a)).

Specific loss (mass per surface area per flood event) of OM in the studied watershed was calculated based on the measurements at the Nokhaleh station and resulted in a loss rate of $0.32 \text{ tons km}^{-2} \text{ event}^{-1}$. Predicting the OM loss for the low land parts of the watershed resulted in the value of $0.445 \text{ tons km}^{-2} \text{ event}^{-1}$, due to the land use of the study area and the frequency of agricultural use in the Nokhaleh sub-watersheds. Therefore, this means that the agricultural lands under rice cultivation are the main sources of OM entering the Anzali wetland. In paddy field, after the harvest of the main crop, some parts of the plant shoot and roots remain in the soil. Over time, these parts are decomposed and added to the soil as an OM. During the leaching and runoff processes, these substances are washed and discharged into the river.

Figure 6(c) presents the changes in TP concentration at the studied stations in different floods. The Upstream station (Nokhaleh) has a lower TP concentration than the downstream stations. Figure 6(d) represents the comparison among the stations in terms of average TP, particulate phosphorus (PP) and soluble phosphorus (SP) concentrations. The highest TP concentration was 3.53 , 2.38 and 1.65 mg l^{-1} in the Nokhaleh, Mobarakabad and Alisara stations, respectively, which was observed in the second flood event. Generally, the P concentration decreased by decreasing flow discharge. Also, the results showed no significant difference ($P < 0.05$) between TP concentrations in the Mobarakabad and Alisara stations (Figure 4(d)). In all three sub-watersheds, the SP concentration was lower than the PP concentration. The source of PP supply in the river can be from degraded pastures, surface erosion in forests, gully, landslides and agriculture.

The changes in TKN at the studied stations are presented in Figure 4(e) for the flood events. Similar to P and OM contents, N also had the highest concentration in the second flood event at the Nokhaleh station, which was 0.79 , 0.55 and 0.24 mg l^{-1} for TKN, particulate nitrogen (PN) and soluble nitrogen (SN), respectively. The trend of TKN changed with flood events and was similar to TP at all stations. In the case of TKN, in all events, there was a large difference among the stations, which can be attributed to the entry of agricultural, industrial and municipal wastewater into the river (Figure 6(e)). According to Figure 4(f), the concentration of SN was higher than PN. SN accounted for 52, 69 and 60% of average TKN transport in flood events at the Nokhaleh, Mobarakabad and Alisara stations, respectively. The results showed that the outflow of various forms of N at the Mobarakabad station was higher than the Alisara station.

The reason for these observations could be in part due to the soil erosion types in the Mobarakabad and Alisara sub-watersheds. It seems that channel erosion including gully and stream bank are dominant in the Alisara sub-watershed due to its rough topography and higher watershed slope (Table 2), which consequently resulted in higher erosion rates (Figure 5) and coarser sediment particles which have less OM and nutrients (Kalbitz *et al.* 2005). In contrast, the Mobarakabad sub-watershed consists of lower slopes (Table 2) and more agricultural lands (Table 2) resulting in lower channel erosion rates. This can also be attributed to the existence of less degraded rangelands in the Alisara sub-watershed (Table 2). Degraded rangelands usually have more sheet erosion, which can result in more OM, N and P losses from this land use. The flow rates of flood events were also higher in the Mobarakabad sub-watershed than those in the Alisara sub-watershed, which provide conditions for the transfer of more sediment from the Mobarakabad sub-watershed. With increasing rainfall and flow discharge, the rate of erosion increases, which leads to a significant increase in the outflow of nutrient compounds. Agriculture land use has covered most of the Nokhaleh sub-watershed area, i.e. low land parts of the watershed between the Mobarakabad and Nokhaleh stations (Table 2). Paddy fields and tea orchards are the main agricultural activities in the studied watershed, where the tea orchards are located at sloping lands. In these agricultural lands, OM, P and N are washed away with runoff due to heavy rainfall and steep slopes as a result of the overuse of chemical and organic fertilizers during the fall and spring. Therefore, runoff is created quickly after rainfall and increases the discharge of OM, N and P from these lands. When the activities like plant cultivation or grazing are increased, the sediment production rate and loss of OM increase (Wei *et al.* 2003). Alexander *et al.* (2008) conducted a similar study on a watershed in the Gulf of Mexico and reported that 70% of P contamination was due to agricultural activities in the western part of the Gulf. Overall, erosion in the Mobarakabad and Nokhaleh sub-watersheds was mainly in the form of surface erosion, which causes the release of fine particles from these sub-watersheds that can play a major role in the transfer of OM, N and P. As the outflow of fine particles increases, the outflow of OM, N and P also increases. The results showed that changes in P and N are similar to the changes in OM in the flood events. This indicates that OM and soil fine particles play a significant role in the release of P and N. Accordingly, it is likely that most of the transported PP and PKN are in the form of organic P and N in the studied watershed.

In the southern part of the watershed, there are degraded pastures that have very poor vegetation. Forests are located after pastures, which are mainly in areas with high slopes. In the flat part of the watershed, the agricultural sector has the highest level. In the downstream of the region, vegetation cover decreased, which mainly included residential and agricultural areas. Also, the dominant type of erosion or, in other words, the origin of suspended sediments is of great importance, which is affected by topography, land use, the occurrence of rainfall and somewhat seasonal precipitation. Deforestation has also been observed in parts of the watershed, which plays an important role in erosion. [Towsend-Small et al. \(2008\)](#) in the Amazon Mountain area and [Brent et al. \(2007\)](#) in an agricultural catchment area in the United States reported the importance of rainfall events with high rainfall intensity and short duration in controlling the annual discharge of particulate OM.

In the flood events, PP accounted for 76, 88 and 80% of total P transport on average at the Nokhaleh, Mobarakabad and Alisara stations, respectively. P is stored in the soil by adsorption on soil particles forming a strong bond with aluminum silicate, oxides and metal hydroxides such as aluminum and iron, which is carried along with suspended particles by runoff due to high precipitation and erosion ([Jordan et al. 2003](#)). The results showed that there is no significant difference between the stations of Mobarakabad and Alisara in terms of the amount and type of P, while there was a significant difference between these stations and the Nokhaleh station (P of the Mobarakabad and Alisara stations lower than the Nokhaleh station). After extreme rainfalls, the soil is affected by erosion on the sloping lands. Soil particles that carry large amounts of P, along with runoff, are moving downstream. Laboratory studies have shown that phosphate concentrations that can provide a balanced growth of algae vary considerably from 0.003 to 0.8 $\mu\text{g l}^{-1}$ ([Grover 1989](#)).

[Berihu et al. \(2017\)](#) stated that deforestation is one of the reasons for the increased N in runoff. The results of these researchers showed that the amount of carbon (C), N, P and potassium (K) losses in the degraded forest was 5, 10, 16 and 8 times more than the intact forest, respectively. Also, the concentrations of the above-mentioned nutrients in the intact areas were 3, 2, 1.1 and 1.4 times more than the degraded ones. In this regard, [Ma et al. \(2014\)](#) stated that water erosion is the main cause of soil degradation and the reduction of N and soil OM in forest areas. Studies show that dissolved mineral N in runoff is often in the form of nitrate. The eroded soil particles mainly contain high OM content that is rich in N. Therefore, N transport via sediments is associated with the runoff rate. Sediments released into surface waters often contain organic and ammonium N, and nitrate is usually soluble in runoff ([Follet & Delgado 2002](#)).

3.3. OM and nutrient loads in the normal flow

[Figure 7\(a\)](#) shows the seasonal changes in the OM content of suspended sediments measured during the normal conditions, and the comparison of means was performed among seasons separately for each station. As observed, there was no significant difference in the OM content between autumn and winter at all three stations, but it revealed significant differences compared to spring and summer ([Figure 7\(a\)](#)). The highest OM% in the suspended sediment were in autumn and winter in the normal flows. This was due to long-term rainfall in the area during these months increasing the rate of erosion, and consequently, further OM flowed out of the area, while from May to October, the depletion of OM has decreased due to the increased density of plant cover as well as the reduced rainfall and erosion ([Shinohara et al. 2016](#); [Starke et al. 2020](#)). A significant difference was observed between the outflow of OM at the Nokhaleh station and the two upstream stations (Mobarakabad and Alisara) in the normal flows ([Figure 7\(b\)](#)), while Aliasra and Mobarakabad did not have any significant differences.

[Figure 7\(c\)](#) shows the seasonal TP changes at all three stations. As shown, the seasonal values of TP at the Nokhaleh station were higher than the other two stations. The reason is that there are many agricultural lands where large amounts of P fertilizer are consumed annually ([Ebrahimi et al. 2020](#)). The maximum amount of TP at the Nokhaleh station was about 0.543 mg l^{-1} (STD = 0.008) in the autumn ([Figure 7\(c\)](#)). The reason for the high level of P in the autumn for the Pasikhan River can be attributed to the decrease in the vegetation and land cover in this season compared to spring and summer. In general, the trend in the P changes was similar to OM. The Nokhaleh station is located at the end of the river route, which includes upstream pollution, and its pollution is higher than the other two stations. The lowest total P was observed in the summer at all three stations when the rainfall rate was low and there was a good vegetation cover. [Li et al. \(2017\)](#) stated that P concentration in runoff from agricultural fields could reach up to 1.2 mg l^{-1} . Generally, the trend of P changes has decreased significantly from autumn to summer, and another reason for this can be attributed to rainfall, which mainly occurs in autumn and winter.

Some researchers (e.g. [Smith et al. 1993](#); [Foy & Withers 1998](#)) considered P concentrations in the range of 0.01–0.015 mg l^{-1} as a concentration that causes the growth of harmful algae in water bodies. A later study in New Zealand confirmed a concentration of 0.015–0.3 mg l^{-1} ([Nguyen & Sukias 2002](#)). [Sharpley et al. \(2003\)](#) suggested that if the

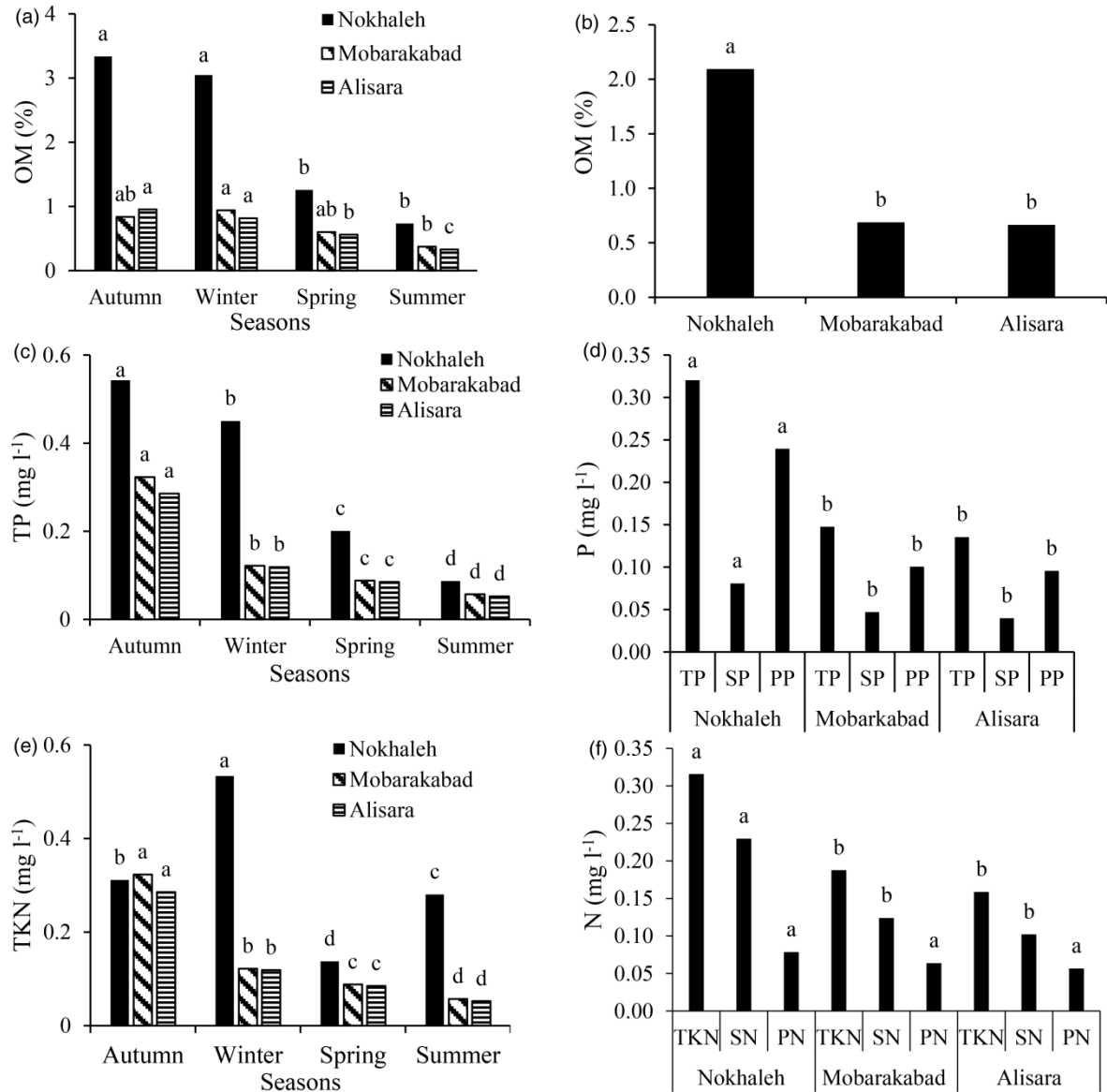


Figure 7 | (a) Variation in the concentration of organic matter in normal flow, (b) variation in the concentration of organic matter among the stations, (c) variation in the concentration of TKN in normal flow and (f) variation in the concentration of nitrogen forms among the stations. In the left figures, mean comparisons were performed among seasons for each location. In the right figures, mean comparisons were performed among locations for different P and N forms. TP, total phosphorus; SP, dissolved phosphorus; PP, particulate phosphorus; TKN, total Kjeldahl nitrogen; PN, particulate nitrogen; SN, soluble nitrogen.

concentration of P goes higher than 0.02 mg l⁻¹, the lake water eutrophication usually accelerates. According to the reported critical limits for P, it is observed that the water of the Pasikhan River is harmful to the Anzali wetland and causes the eutrophication phenomenon in the wetland.

Figure 7(d) presents the results of comparison of mean changes of different forms of P in the three studied stations. The results show that P is mainly transported in particle form (PP). In the flood events, PP accounted for 75, 62 and 71% of total P transport on average at the Nokhaleh, Mobarakabad and Alisara stations, respectively. PP in the Mobarakabad sub-watershed is higher than that in the Alisara sub-watershed. Some researchers stated that there is a strong correlation between the transport of nutrients and OM due to soil erosion and sediment transport (Ikeda *et al.* 2009). Napoli *et al.* (2017) studied soil erosion and the transport of elements in Italian vineyards. These researchers stated that many more

nutrients will wash away by increasing rain erosivity. Also, Cheng *et al.* (2014) investigated the relationship between P and N with sediments in the Dianbai region, China. They concluded that sediments can act as a sink and release elements into the water, increasing the pollution.

According to Figure 7(e), the highest amount of TKN (0.53%) was observed in the winter. N changes revealed a declining trend in the winter, autumn, summer and spring, respectively. Furthermore, Figure 7(e) shows that the minimum amount of TKN (0.047%) was obtained in the spring at the Alisara station. The spatial variation of N was similar to that of P, showing the highest contents in the downstream of the Nokhaleh station, and also, the N content was higher in the Mobarakabad station than that in the Alisara station. It is also observed that the SN concentration was significantly higher than the PN concentration. The results showed that N is mainly transported in SN form (Figure 7(f)). SN accounted for 73, 66 and 64% of the average transported TKN in flood events at the Nokhaleh, Mobarakabad and Alisara stations, respectively. Also, there was no significant difference between the Mobarakabad and Alisara stations in different forms of N.

3.4. Comparison of parameters in the normal and flood conditions at the Nokhaleh station (hydrometric station in the outlet of watershed)

Figure 8 shows the results of mean comparison of the studied parameters in the normal and flood conditions at the Nokhaleh station (as a final station in the outlet of watershed and the entrance to the Anzali wetland). The results showed that the changes in TP, PP and SP were significant in both normal and flood flows, and naturally, these parameters are higher in flood conditions than normal ones due to the higher flow and erosion rates. It was also observed that the content of OM (2.3%) in the flood event was higher than its content (2%) in the normal flow, although this difference was not significant. The results showed that there was no significant difference between TKN and SN in the normal and flood conditions, but the value of PN (0.2%) in the flood event was significantly higher than the normal flow (0.07%). Liu *et al.* (2016) stated that there is a high correlation between TP and SP with P in paddy fields water. In other words, these researchers indicated that the major parts of P in runoff come from P of rice cultivated regions. According to Yousefifard (2004), P is mostly found in organic form; therefore, the OM losses cause an increase in the P losses, which was due to the occurrence of sheet erosion in the area (particularly paddy fields) leading to the removal of the large amounts of OM containing P from the soil. In a study conducted by Adeymo *et al.* (2008) on physical and chemical properties of the sediment, the highest rate of P losses in sediments was observed in rainy seasons, whereas the highest rates of N and OM losses occurred in dry seasons.

4. CONCLUSION

The results of this study revealed that the concentration of nutrients such as P and N has increased significantly with increasing flood discharge, and in the erosion process, there was also a sharp increment in the OM loss from the land with increasing flood discharge. As expected, as the flood discharge increases, higher amounts of solids will be transported, which plays a negative role in filling the Anzali wetland and reducing its depth downstream. The average TP of the river upstream in flood conditions (mean of two stations, Mobarakabad and Alisara) was lower than the average TP in the river downstream

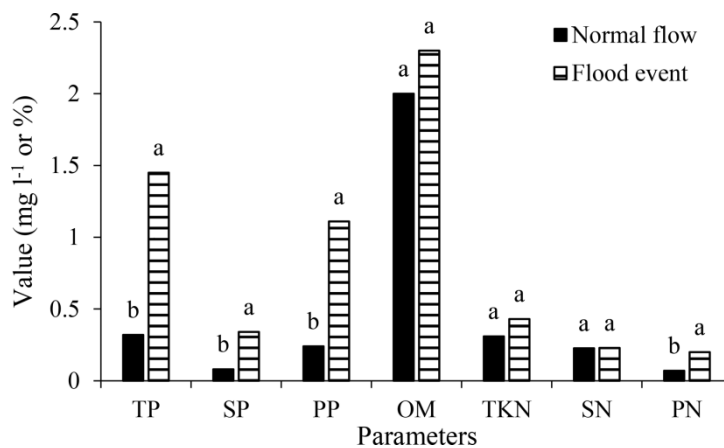


Figure 8 | Mean comparison for each parameter in the normal and flood conditions. TP, total phosphorus; SP, dissolved phosphorus; PP, particulate phosphorus; TKN, total Kjeldahl nitrogen; PN, particulate nitrogen; SN, soluble nitrogen; OM, organic matter.

(Nokhaleh station). As mentioned in the results section, according to the P contamination limit, and comparison of the measured values of P in this study, the status of P output in the Pasikhan River was critical. Regarding SP, it has increased from the upstream to the downstream. The same trend was observed for TKN in both upstream and downstream. Based on the value reported by the United States Environmental Protection Agency (U.S. EPA 2000) as the critical N limit for surface water, the N concentration in the watershed is below the critical value. But it starts to become a problem in the same way as P if not controlled.

The amount of OM in the river also followed a similar trend to P and N, and in the upstream, the mean value of two stations (Alisara and Mobarakabad) was equal to 1.38%, which reached 2.25% in the downstream at the Nokhaleh station. Also, the results showed that in the normal flow, the maximum TP and OM outputs at the Nokhaleh station were about 0.543 mg l^{-1} and 3.336% in the autumn, respectively, and the value of 0.533 mg l^{-1} was reported for TKN in the winter. The reason for the increment in P, N and OM in the river water can be attributed to an increased agricultural land use, the application of fertilizer as well as the discharge of rural and municipal wastewater into the middle and lower parts of the watershed. According to the results of this study, it can be concluded that the suspended sediment in rivers and streams affects the transport of OM and nutrients such as P and N in watershed, which will cause unpleasant consequences at the regional, local and even global scales. Furthermore, soil erosion plays an important role in the loss of these materials, and the suspended sediment is an appropriate estimator for the loss of these materials, which can easily be used to estimate the loss of OM.

According to the status of the study area, it is essential that some measures should be taken into account to control the sediment load and reduce the discharge of the contaminant into the Anzali wetland. Finally, the results of this study can be applied to the issues related to water quality, soil and water resources management, as well as the need for erosion control, and proper management of agricultural lands. It can also be used for training farmers on the proper application of farm pesticides and fertilizer.

AUTHOR CONTRIBUTIONS

E.E., H.A., M.J. and M.R.R. conceived the presented idea. E.E., H.A. and M.B.F. developed the theoretical framework. E.E., H.A., M.J. and A.A. developed the theory and performed the computations. H.A., M.R.R., M.B.F., A.A. and M.K. verified the analytical methods. E.E. and M.J. carried out the experiments. All authors discussed the results and contributed to the final manuscript.

COMPETING INTERESTS

The authors declared no competing interests.

ETHICAL APPROVAL

The subject of plagiarism has been considered by the authors and this article is without problems.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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