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## Geochemical characterization of recent Nile Delta inner shelf sediments: Tracing natural and human-induced alterations into a deltaic system <sup>☆</sup>

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### ABSTRACT

The present study deals with the geochemical changes observed along Nile Delta inner shelf sediments over a period of 20 years (1995–2015). Major, minor, and trace constituents as well as rare earth elements (REE) were investigated in the surface sediments collected from seven transects along the inner shelf on five years intervals. Geochemical composition of sediments in Nile Delta inner shelf exhibits continuous changes over time due to the depositional and sediment transport processes. The sediments are generally enriched with Fe and Ti oxides, as well as Ta, Nb, Y in comparison to the Upper Continental Crust (UCC). These alterations signify the impact of processes such as erosion and sediment transport, as well as the impact of anthropogenic interferences such as damming the Nile River Flow. The reduction of the sediment input from the Nile River has somehow altered the geochemical signature of the inner shelf sediments. The REE patterns indicate weathering in areas subjected to erosion, while trace elements and major oxides spatial and temporal distributions concentrate eastwards under the influence of the easterly sediment transport pattern. Nile Delta inner shelf presented a typical case for understanding the link between geochemistry and sedimentary processes in nearshore and deltaic systems.

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### Introduction

The study of the sediments geochemistry is useful in characterizing their sedimentary environment and origin (McLennan, Hemming, Mcdaniel, & Hanson, 1993). The geochemical characteristics of sediments in coastal and estuarine areas are subjected to continuous changes due to the depositional and the post-depositional processes, such as mineral weathering, the precipitation of newly formed mineral phases (Singh, 2009). Moreover, some changes may also result from anthropogenic activities (Di Leonardo, Bellanca, Neri, Tranchida, & Mazzola, 2009; Tranchida et al., 2011), and the control of the sediment flux by barrages and dams (Padoan, Vezzoli, Garzanti, & Kammar, 2015). Elements generally thought to be immobile, such as High-Field-Strength Elements (HFSE) and Rare Earth Elements (REE), can be readily used as

tracers for many aquatic biogeochemical and sedimentary processes (McLennan et al., 1993).

The Nile Delta inner shelf, which is a part of the Mediterranean coast of Egypt, is subjected to significant natural and anthropogenic pressures, including vulnerability to climate change, sea level rise, coastal erosion, and pollution (El Banna & Frihy, 2009a; Elshanawany, Ibrahim, Frihy, & Abodia, 2018; Frihy & Dewidar, 2003; Soliman, Nasr, & Okbah, 2015). Currently, the Nile Delta is a wave-dominated delta, strongly influenced by erosion in some areas and accretion in others. The reduction of the sediment load, climatic change, and Nile Delta subsidence have had severe impacts on the geomorphology of the littoral zone of the Nile Delta (El Banna & Frihy, 2009b; Frihy, Nasr, & Raey, 1991). Limited attention was given to the geochemical features of the Nile Delta inner shelf sediments in terms of geochemical composition and processes. El-Kammar, Ragab, and Moustafa (2011) and Moustafa and Abdelfattah (2010) studied the geochemistry of rare earth elements in deltaic black sands. Arafa et al. (2015) applied neutron activation analysis to study the elemental geochemistry of the Nile Valley soils and the Nile Delta surface sediments. Siegel, Gupta,

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Shergill, Stanley, and Gerber (1995) studied the geochemistry of the subsurface Holocene sediments in the Nile Delta. Padoan et al. (2015) presented a large scale comprehensive account on the composition of the Nile sediments from its equatorial origins to the Mediterranean, including the Nile Delta.

The present study aims to illustrate some of the transformations that occurred in the geochemical characteristics of the Nile Delta inner shelf sediments by following up its spatio-temporal variations through a period of 20 years, to characterize the effects of some natural and anthropogenic influences that may affect a typical river delta.

## Materials and methods

### The study area

The study area represents the Nile Delta inner shelf (Fig. 1), located on the northern Mediterranean coast of the Nile Delta, Egypt. Since the late Miocene, the progressive sedimentation of the Nile Delta on the Nile Estuary formed the Nile Delta coast and its inner shelf (Said, 1981). The Nile River has been the major supplier of suspended sediments to the Eastern Mediterranean. However, since the damming of the Nile at Aswan, the Nile flood was held behind the Aswan High Dam and other structures including several dams and barrages that were built along the Nile River and on its promontories during the twentieth century (Frihy & Lawrence, 2004), thus the sediment supply to the Nile Delta coast has been greatly reduced from  $110$  to  $120 \times 10^6$  tons annually to just  $1 \times 10^6$  tons annually (Padoan et al., 2015). This resulted in drastic impacts on the geomorphology of the Nile Delta coastal area such as severe erosion and shoreline retreat (Pennington, Sturt, Wilson, Rowland, & Brown, 2017). This has motivated continual coastal protection projects to prevent further coastline degradation (Frihy, 2017). The sediment transport in the Nile Delta inner shelf is dominated by the general eastward longshore current (Fig. 1), which carries sediments from the Nile Delta to the Eastern coasts of the Mediterranean (Frihy, Lotfy, & Komar, 1995).

### Sampling and analytical methods

Seven horizontal transects representing the Nile Delta inner shelf in the western (W1, W2), middle (M1, M2, M3), and eastern (E1, E2) sectors were studied (Fig. 1). The transects represent areas near land-based discharges of promontories and lagoon, and areas of erosion and accretion. Each transect included two

samples at fixed distances from the shoreline, namely: the near-shore (NS, 200 m from the shoreline) and the farshore (FS, 600 m from the shoreline). All transects were sampled on five years intervals of five years from 1995 to 2015 (1995 [referred to as 95], 2000 [00], 2005 [05], 2010 [10] and 2015 [15]). The textural analysis was done by mechanical sieving. The amount of the volatile components was determined through loss on ignition (LOI). The carbonate content was determined by calcimetry on 300 mg finely powdered samples, previously dried at  $105 \pm 5$  °C. Major and minor chemical components ( $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{Fe}_2\text{O}_3$ ) were determined using X-ray fluorescence (XRF) on powder pellets using an ARL 9400 XP + sequential X-ray spectrometer (Manufacturer: Thermo Fisher Scientific, MA, USA) under the instrumental conditions reported in Lezzerini and Tamponi (2014). Within the range of the measured concentrations, the analytical uncertainties were < 3% for all the components, except for  $\text{Na}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ , and  $\text{MnO}$ , which may attain < 10% for very low concentrations. The trace elements content of the bulk-sediment was determined by dissolving about 50–100 mg of each powdered sample in a mixture of superpure/ultrapure HF and  $\text{HNO}_3$  inside perfluoroalkoxy (PFA) vessels on a hot plate at 150 °C. The sample solutions were properly diluted with Mill-Q purified water ( $18.2 \text{ M}\Omega\text{-cm}$  at 25 °C) and then mixed with a solution containing 20 ng/mL of Rh, Re, and Bi (internal standards) for measurement on the Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) NexION 300x (Manufacturer: PerkinElmer Inc., MA, USA). Trace elements (Li, Be, Ga, Rb, Sr, Y, Nb, Cs, Ba, Ta, Th, and U), as well as REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb), were determined in standard mode. External calibration was done to determine the concentration of each of the selected isotopes using a solution of the BE-N (alkaline basalt) geochemical reference sample. Quality control was ensured through using a geochemical reference sample (Chinese sediment reference sample, CH-1), that was dissolved and analyzed along with the samples to check the accuracy of the results. The analytical precision and accuracy for all trace elements and REE were above 95% recovery, except for Ga, U, Th, Ta, Lu, Dy were above 90% recovery.

## Results

The Nile Delta inner shelf sediments are predominantly medium to fine grained well sorted sands with minor spatio-temporal heterogeneities. The NS sediments (mean size =  $0.15 \pm 0.06$  mm) are typically slightly coarser than the FS sediments (mean size =  $0.11 \pm 0.03$ ), exhibiting a relatively larger variation in the

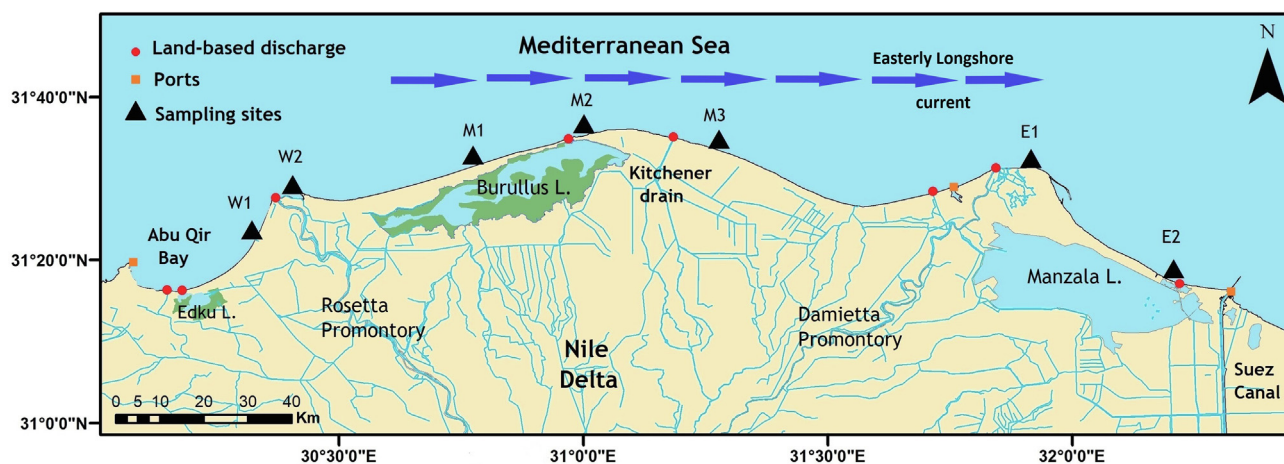


Fig. 1. The Nile Delta coastal area, the sampling locations (horizontal transects names) of the nearshore inner shelf sediments, and some coastal features.

mean grain size. This results from the wave effect on the NS sediments because they are located in the surf zone, while on the other hand the FS sediments are located further offshore in calmer conditions. The FS sediments are relatively more sorted, and the mean grain size is less prone to change over time. Depth is also another determining factor controlling the texture of the sediments, where the shallower nearshore area is more subjected to wave effect and characterized by coarser sediments. The total carbonate content is usually <2 wt% of the total sample weight; where higher CaCO<sub>3</sub> content is related to the presence of shell fragments, such as samples W1-FS-15, M3-NS-05, and E1-FS-05. The average LOI% is about 2.45%, which indicates that the organic content is generally low.

The spatial distributions of normalized concentrations of major and minor elements with respect to the Upper Continental Crust (UCC) values in the studied years are illustrated in Fig. 2. The average concentrations of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, CaO, MgO, TiO<sub>2</sub>, MnO, total iron as Fe<sub>2</sub>O<sub>3</sub>, and P<sub>2</sub>O<sub>5</sub> are 69.7 ± 7.4 wt%, 8.08 ± 2.09 wt%, 1.55 ± 0.39 wt%, 1.16 ± 0.3 wt%, 4.56 ± 1.7 wt%, 2.72 ± 0.82 wt%, 2.09 ± 1.03 wt%, 0.11 ± 0.03 wt%, 7.6 ± 2.3 wt% and 0.15 ± 0.03 wt%, respectively. SiO<sub>2</sub> is the most abundant among the major constituents. Excluding some exceptions, the NS sediments are more enriched in SiO<sub>2</sub>, particularly in the western sector. There is a noticeable drop in average SiO<sub>2</sub> during the second and third intervals (2000–2005). Al<sub>2</sub>O<sub>3</sub> is the second most abundant major constituent; however, it is quite depleted compared to UCC. Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and K<sub>2</sub>O behave similarly in spatio-temporal patterns. They are enriched in the eastern sector where SiO<sub>2</sub> shows relatively lesser concentrations than the rest of the coast. The FS sediments are usually slightly enriched in Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and K<sub>2</sub>O than the NS ones

and there is a general increase in those components especially in sediments from the second interval (2000–2005). The ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is quite high compared to UCC, reaching double or three times the UCC value. The patterns of CaO and MgO are strongly related as both are generally more abundant in the FS sediments and exhibit little variation over time.

All sediments are significantly enriched with Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, followed by MnO, when compared to UCC values they show a similar distribution. FS sediments are frequently more enriched in Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and MnO. They are commonly more abundant in the middle and eastern sectors, showing some steady increase eastwards. Additionally, an enrichment in Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and MnO over time is observed especially in FS sediments. P<sub>2</sub>O<sub>5</sub> is more abundant in the FS sediments and its average transect percentage shows a decline in W2 and E1. The P<sub>2</sub>O<sub>5</sub> concentration in NS sediments shows two spikes during 2000 and 2015, while in FS one concentration spike is observed during 2005. It is noticeable that P follows the same pattern as Fe, Ti and Mn oxides, indicating a strong correspondence.

The spatial distributions of normalized concentrations of trace elements with respect to the Upper Continental Crust (UCC) values in the studied years are illustrated in Fig. 3. The average concentrations of Li, Rb, Cs, Be, Sr, Ba, Ga, Y, Nb, Ta, Th, and U are 8.87 ± 3.3 µg.g<sup>-1</sup>, 28.1 ± 8.21 µg.g<sup>-1</sup>, 0.49 ± 0.18 µg.g<sup>-1</sup>, 0.97 ± 0.26 µg.g<sup>-1</sup>, 280.65 ± 66.35 µg.g<sup>-1</sup>, 3.45.36 ± 48.18 µg.g<sup>-1</sup>, 12.36 ± 3.35 µg.g<sup>-1</sup>, 23.7 ± 7.01 µg.g<sup>-1</sup>, 16.35 ± 6.51 µg.g<sup>-1</sup>, 1.03 ± 0.42 µg.g<sup>-1</sup>, 5.29 ± 4.11 µg.g<sup>-1</sup>, and 1.16 ± 0.63 µg.g<sup>-1</sup>, respectively.

Generally, FS sediments are relatively more enriched in Li, Be, Sr, Ba, and Ga with respect to the NS ones; however, NS sediments

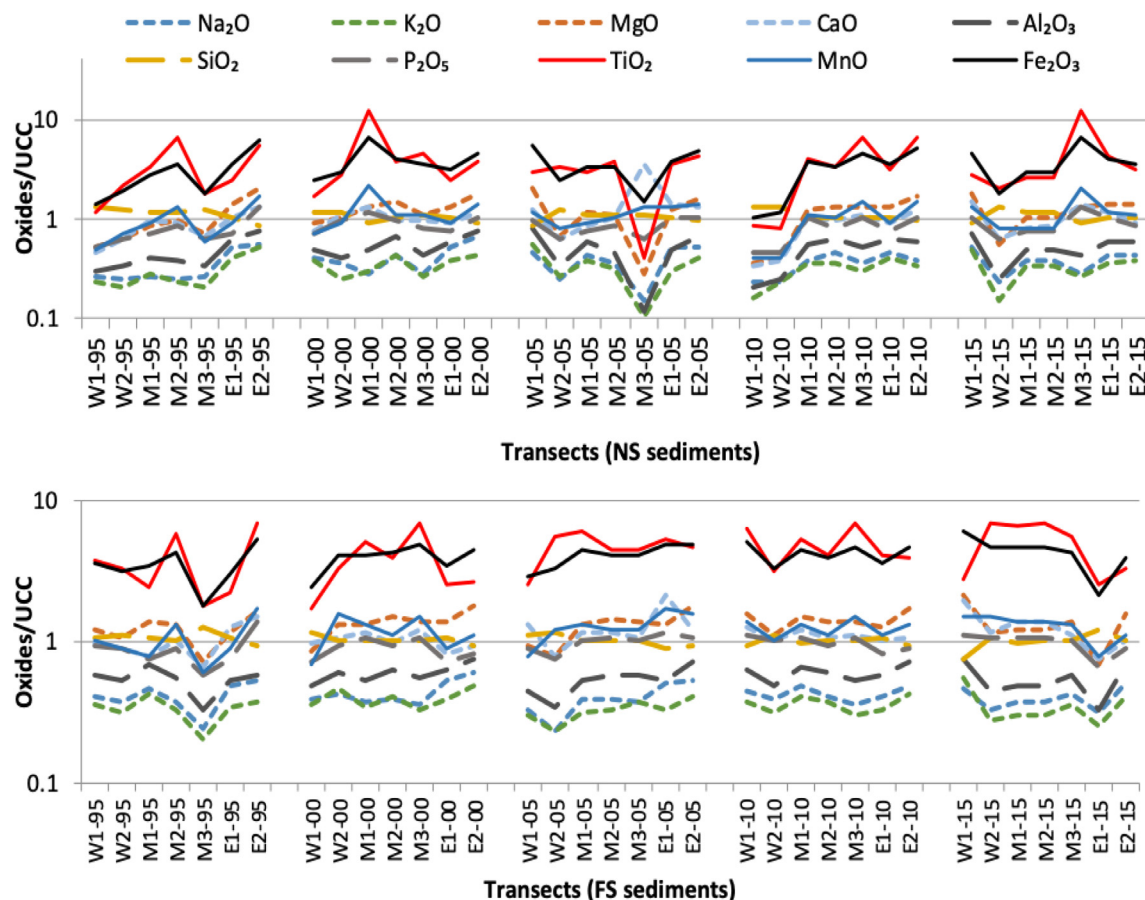
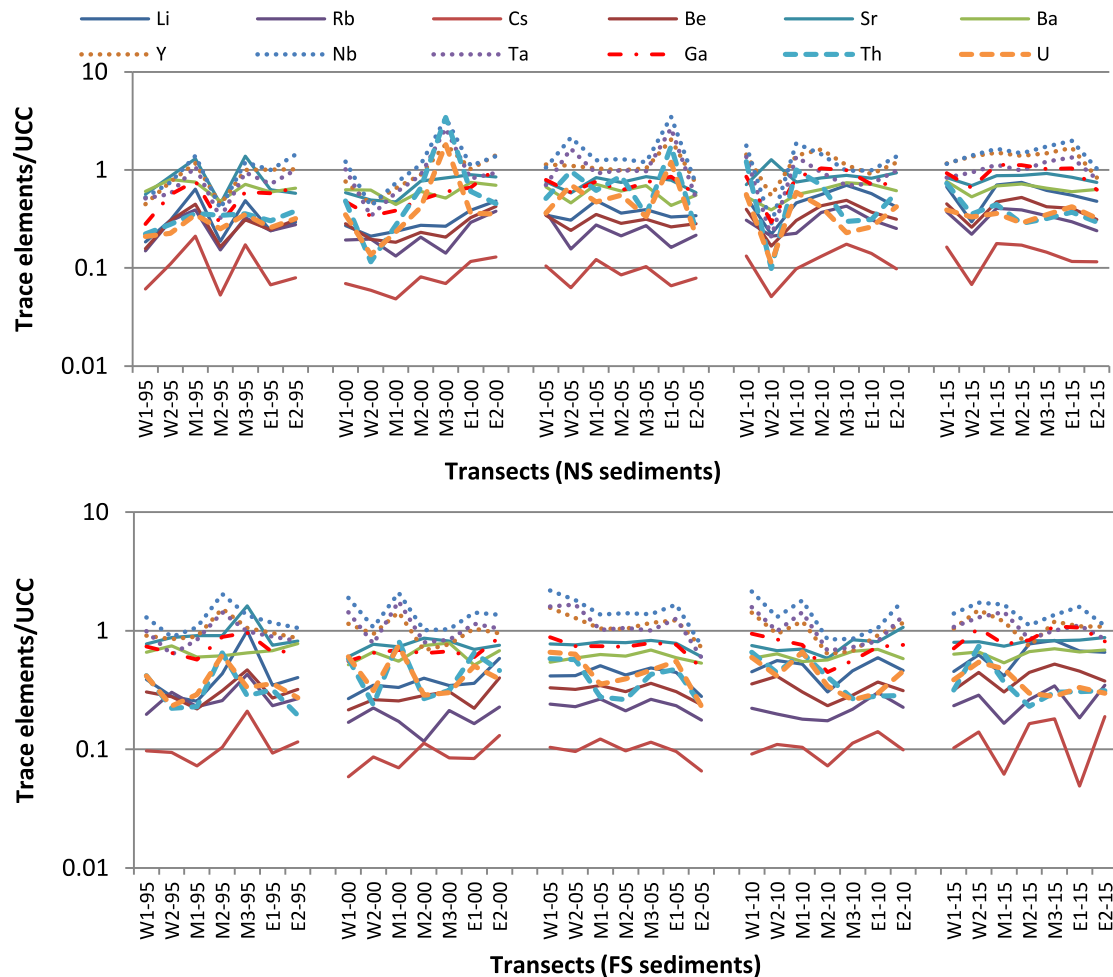


Fig. 2. Major and minor chemical constituents in the sediments of the Nile Delta inner shelf transects (in NS and FS sediments) normalized to Upper Continental Crust (UCC); according to Taylor and McLennan (1985).



**Fig. 3.** Trace elements in the sediments of the Nile Delta inner shelf transects (NS and FS sediments) normalized to Upper Continental Crust (UCC); according to Taylor and McLennan (1985).

show variable concentrations both spatially and temporally. The sediments are strongly depleted in Cs compared to other elements. Ba and Sr display a lower spatial heterogeneity compared to other trace elements. Besides, alkali elements (Li, Cs, and to some extent Rb) follow the same spatial behavior of slight drop near Rosetta promontory in the West and a continuous increase eastward, even if their temporal distribution is slightly different.

The sediments are enriched with Nb, Ta, and Y with respect to UCC. Spatially, their concentration is variable to some extent increasing from West to East till the end of the middle sector, then a drop in concentration follows in E1 and then continues increasing in E2. This behavior is more noticeable in NS sediments, where the average concentrations of these metals are higher in M1-NS, M2-NS, and E2-NS, especially Ta and Nb. Nb and Ta concentrations significantly increase abruptly during the second interval in 2000–2015 (especially in the NS sediments), followed by a decrease in 2005 and 2010, then rise again in the most recent interval (2015). Strong variability in the Y, Nb, Ta, and Ga concentration is observed in NS sediments. Th is slightly more enriched than U and they are both more abundant in the NS middle sector (M1 and M2) than in the FS one. Both elements slowly accumulate in W1 and M1 transects with time, yet, strong spikes are detected. Geochemical ratios show that all sediments have a significantly low Rb/Sr (average =  $0.10 \pm 0.02$ ) ratio compared to UCC. Th/U ratio (average =  $4.3 \pm 0.9$ ) is occasionally high in FS sediments; however,

on the contrary, it is always significantly higher in the NS sediments; reaching up to two-fold of the UCC values.

Chondrite-normalized REE patterns are illustrated in Fig. 4. Chondrite-normalized REE patterns in FS sediments show smoother and more uniform patterns compared to NS sediments. In NS sediments, the averaged total REE concentration is quite similar in sediments from 1995, 2005, and slightly higher in those from 2010 and 2015. Relative enrichments in the total content of REE and particular light rare earth elements (LREE) are observed during the year 2000. Additionally, the inter-sample comparison shows a strong REE enrichment in M1-00-NS and M2-15-NS, exhibiting the highest Eu/Eu\* value. In the FS sediments, the results indicate a consistently increasing trend in averaged REE concentration from 1995 to 2015. Comparatively, the NS sediments are more enriched in LREE, while the FS sediments are more enriched in heavy rare earth elements (HREE). On the overall view, there is an enrichment in the middle sector (M1 and M2), followed by the eastern and the western sectors in the NS sediments, while there is a little and irregular disparity among transects in the FS sediments. The Ce anomaly is calculated as  $[Ce/Ce^* = Ce_N / (La_N \times Pr_N)^{0.5}]$ , while the Eu anomaly is calculated as  $[Eu/Eu^* = Eu_N / (Sm_N \times Gd_N)^{0.5}]$  (Leybourne & Johannesson, 2008). The average Ce/Ce\* is  $0.95 \pm 0.07$  and the average Eu/Eu\* is  $0.87 \pm 0.09$ . Though Ce displays trivial (in NS sediments) or no anomalies whatsoever, Eu becomes depleted with time, building up substantial negative



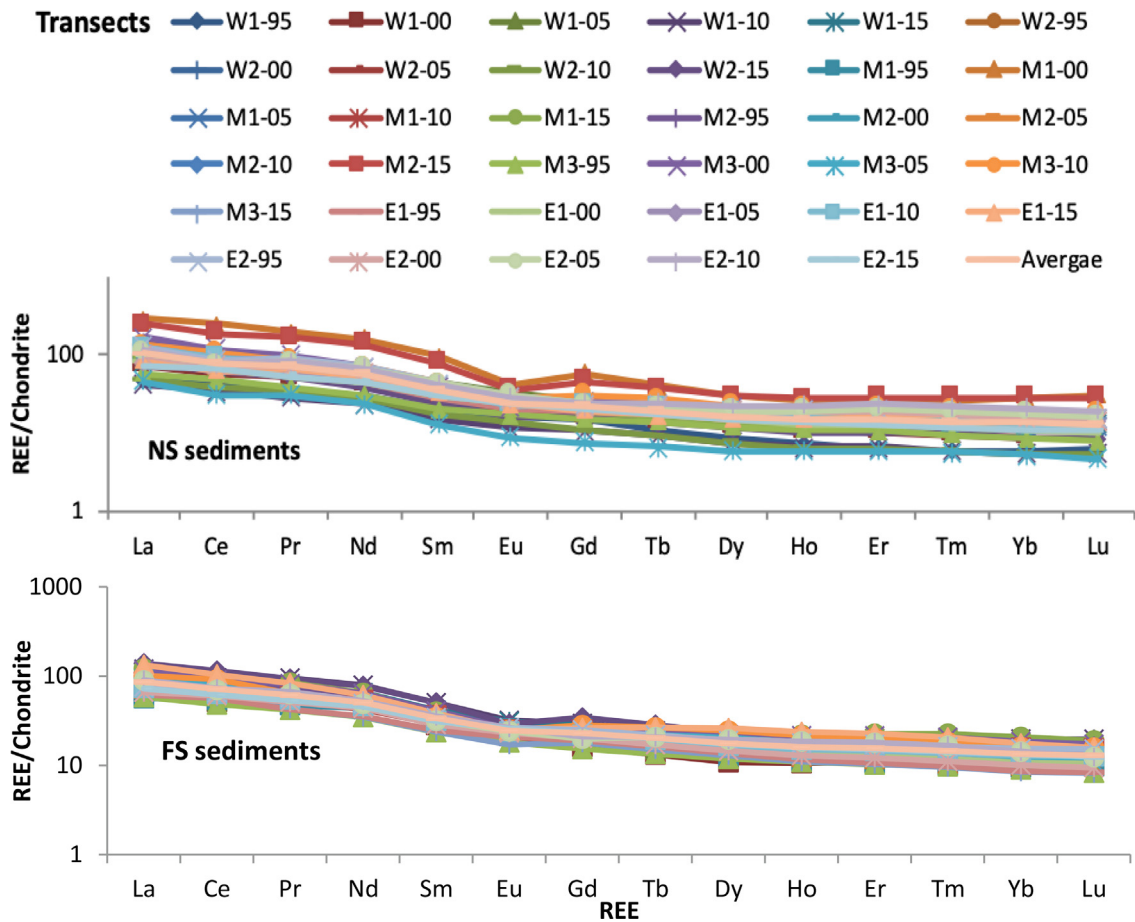


Fig. 4. Rare Earth Elements (REE) in the sediments of the Nile Delta inner shelf transects (NS and FS sediments) normalized to chondrite.

Eu/Eu\* anomaly. However, the europium anomaly is usually more evident in the NS sediments. Eu/Eu\* shows stronger negative anomalies in the Middle sector.

The highest Eu/Eu\* is observed during the second interval in the NS; however, it is quite constant in the FS sediments throughout the period of the study. The highest LREE enrichment with respect to HREE, given by the  $(La/Lu)_N$  ratio, occurs during the second interval (2000) in NS. On the other hand, in the FS sediments, it increases abruptly during the second interval, but there is a continuous increase to reach the highest  $(La/Lu)_N$  ratio in 2015.

## Discussion

Deltaic inner shelf sediments present a good case study on the impacts of natural and anthropogenic interferences in a typical deltaic system. Deltaic detrital sediments of the Nile Delta are mainly composed of quartz-feldspars, with a distinctive presence of heavy minerals of an igneous origin (El-Kammar et al., 2011; El Gamal & Saleh, 2012; Frihy & Dewidar, 2003). The geochemical data reflect the processes that occur before and after the deposition of the Nile sediments on the inner shelf. The presence of ferromagnesian and ferrotitanium minerals enriches the sediments with Fe, Ti compared to UCC values, especially in the FS. However, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and K<sub>2</sub>O are predominantly of quartz-feldspars origin. Chemical Index of Alteration (CIA) indicates the degree of weathering by using molecular proportions. It is calculated using the equation:  $CIA = Al_2O_3 / [Al_2O_3 + K_2O + Na_2O + CaO] * 100$  (McLennan et al., 1993). CIA values range between 40 and 60. Hence, the wave dominated Delta reports CIA values similar to those of the upper Nile

sands (Padoan et al., 2015); however, those values are more variable in the NS sediments, indicating that the immediate changes can be more commonly detected closer to the shoreline. Variations of CIA in NS sediments might be a result of wave breaking and turbulence effect in addition to changes in sediment origin and input. Furthermore, the variability of CIA values coincides with Eu/Eu\* negative anomalies, indicating moderate weathering. SiO<sub>2</sub> in NS sediments exceeds that of the FS sediments, thus, indicates that the NS sediments are diluted with quartz and feldspars, while the metal-rich heavy minerals are further transported away from the shoreline and become more concentrated in FS sediments. On the contrary, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and K<sub>2</sub>O behave similarly, probably due to mineralogical association in feldspars (alumino-silicates). CaO and to some extent MgO are likely to be affected by the rare presence of carbonate bioclasts. Spatio-temporal distribution of different trace elements illustrates the disparity between different sediment sources in the Nile Delta and their inputs. Consequently, trace elements discern three distinctive sectors of the Nile Delta inner shelf; East, West, and Middle. The Middle sector is more prone to show anomalies of enrichment and depletion than other sectors. Additionally, FS sediments are usually more enriched in most elements and show more stable spatio-temporal trends than the NS sediments. Rb tends to be depleted in the Nile sediments likely due to weathering and continuous local recycling as well as the contribution of volcanolithic grains (Padoan, Garzanti, Harlavan, & Villa, 2011). Contrariwise, Sr is usually enriched in coarser sandy sediments of the Nile sands, resulting in a distinguishable low Rb/Sr ratio. Y, Nb and Ta are slightly enriched due to possible anthropogenic inputs. Previous studies suggested the

role of easterly longshore transport towards North Sinai and the Eastern Mediterranean shores (Frihy & Dewidar, 2003). This longshore transport causes spikes of elemental concentrations in the eastern sector. Spatial variations among transects and temporal variations among different time intervals in trace elements and REE concentrations may also be attributed to waste discharge from the extensive Nile Delta drainage systems. REE may be incorporated into deltaic sediments via several probable processes; such as (i) inputs from the Abyssinian source rocks and other sediment contributors in the Nile tributaries, (ii) scavenging from overlying water (the Nile, its lagoons and the sea), mainly dependent on Fe and Mn oxides particulates (Elderfield, Whitfield, Burton, Bacon, & Liss, 1988), (iii) and some potential anthropogenic influences. The general enrichment of LREE in Nile Delta well sorted sandy deposits indicates that LREE are more likely to be related to coarser grains; however, in the middle sector, the embellishment of some heavy minerals content, such as xenotime and monazite, contributes significantly to the enrichment with LREE in particular. This is largely conformable with the upper Nile geochemical signature (Fielding et al., 2017; Padoan et al., 2011), which reflects the terrigenous origin of REE in the deltaic coastal sediments (Mejjad et al., 2016). However, there is a lot of distortion in such conformity resulting from various inputs to the sedimentary budget of the Nile including erosion of granitic rocks in the South of the Main Nile, which are more enriched in REE (El-TaHER, 2007). Major constituents, trace elements, and REE in NS sediments have variable spatio-temporal patterns. Although it is challenging to discern the causes of the abrupt geochemical spatio-temporal changes in nearshore zone neither to explain in detail the reasons for these variations, it is plausible to attribute these changes to the less than stable conditions closer to the shoreline. The sedimentary origin of the part of the inner shelf closer to the shoreline is subjected to more dynamic setting and anthropogenic influences from one side, while in the further part offshore, the sedimentary provenance is affected by sediment sorting during transport. Hence, the Nile Delta inner shelf sediments appear to be subjected to slow changes in the geochemical compositions as a result of multiple intertwining reasons. (i) The coastal dynamics associated with the local weathering and sediment transport processes control the erosion/accretion processes, which affect the geochemical composition of the deposited sediments. This is shown in the difference between NS and FS sediments and between different sectors of the Nile Delta inner shelf. (ii) Artificial damming and water-control systems within the River Nile and its promontories prevent a substantial amount of certain minerals from reaching the Mediterranean coast. (iii) This may be also enhanced by particular natural controls such as the dilution with quartzose aeolian sand from the Sahara as suggested in Padoan et al. (2015) and Woodward et al. (2015). (iv) Anthropogenic inputs can result in the enrichment of some trace metals such as Be, Nb, and Ta. (v) The onshore construction projects, especially coastal protection projects that started in 1998, have changed the composition of NS sediments through nourishment with alien materials. The construction operations may have brought about the dispersal of alien allochthonous materials on the inner shelf of the Nile Delta.

## Conclusions

Geochemical characteristics of the Nile Delta inner shelf sediments have proven to be good tools to trace and identify the spatio-temporal changes related to sediment origin and composition during the past 20 years. Natural and man-made interventions have had a noticeable effect on the provenance of the Nile Delta inner shelf. This is signified by the difference between NS and FS sediments and between sediments of different sectors of the Nile

Delta inner shelf, and anomalies in the REE patterns. Human activities may intervene in the geochemical provenance through the construction of dams that obstruct the sediment flow to the Delta shelf, which result in geochemical anomalies, or by the coastal protection projects, which might be responsible for the introduction of allochthonous materials. The discharge of anthropogenic wastes is likely to cause enrichment in some trace elements. Generally, the Nile Delta inner shelf is progressively subjected to ongoing changes with prospected sensitivity to some potential impacts.

## Author Contributions

All authors have contributed significantly to the research process and manuscript preparation. **Ahmed S. Mandour** is the main author and involved in technical and research stages as well as manuscript formulation. **Dr. Lisa Ghezzi** co-participated in ICP-analysis and data organization and recuperation, besides revising and editing manuscript. **Dr. Ahmed Elshazly** co-participated in revising data, data analysis and construction of the manuscript. **Dr. Marco Lezzerini** aided and participated in identifying major components using SEM-EDS examinations and manuscript editing. **Prof. Ayman El-Gamal** provided the samples and supervised grain size analysis and provided valuable notes on Nile Delta geology during formulating the manuscript. **Prof. Riccardo Petrini** supervised research stages, most importantly, the geochemical analyses, data interpretation of rare earth elements and manuscript formulation to its final form.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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