The ITRAX core scanner, a useful tool to distinguish anthropic *vs.* climatic influences in lagoon of Aveiro (N Portugal)

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ABSTRACT

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The main goal of this work is to distinguish anthropic and climatic influences in sediments from the lagoon of Aveiro (Portugal). This study is based on a core (240-cm long) collected in Murtosa Channel. Optical and X-radiographic images and high-resolution elemental profiles were acquired with ITRAX micro-X-ray fluorescence (XRF) core scanner. Samples collected at each $\approx$3 cm along the core were analysed for grain size and total organic carbon. Furthermore, the fine fraction of selected layers was subjected to geochemical analysis by ICP-MS, after total acid digestion of the sediments, and mineralogical analysis, by XRD techniques. A radiocarbon age was determined by AMS, using molluscs shells collected at a depth of 90 cm.

Sediments along the core are composed by fine and medium sand, with several mud layers. Sediments composing the first 100-cm may have been deposited after 1950, as it is indicated by the radiocarbon data, the increasing trend of Zn/Al, Pb/Al and Cu/Al and total concentrations of Zn, Pb, Cu, V, Cr, As and Ni in this interval that therefore might be linked with industrial activities of Chemical Complex of Estarreja. The progressive increase of Si/Al, Cl/Al, Rb/Al, K/Al and Br/Al and reduced Al concentrations, from the base to the top of this core, are interpreted as being related to higher marine influence and greater differences in tidal currents with longer exposition to air of the sediments with the consequent formation of brines favouring minerals precipitation in the area (e.g. anhydrite). These results seem to be a consequence of several works developed over time like: i) dredging to improve the navigation access to the harbour, located in the external sector of the lagoon; ii) the control of the course of some rivers influencing the supply of sediments. The tendency of sea level rise may have also emphasized the gradual increase of marine influence in this area. Fine-grained sections, related to an increase in Al, phyllosilicates, organic matter, pyrite and siderite contents would be attributed to phases of greater supply of fine-sediments during heavy rainfall events by the nearby Antuã river and other streams during negative phases of North Atlantic Oscillation. Higher deposition of organic matter enhanced diagenetic changes with pyrite and siderite formation. In the bottom of the core another record of pollution was unveiled to mining activities at the beginning of 20th century.

ADDITIONAL INDEX WORDS: *sediment sources; sedimentary dynamic; geochemical and mineralogical proxies; North Atlantic Oscillation, heavy metals pollution*

INTRODUCTION

Ria de Aveiro is a shallow coastal lagoon located in northern region of Portugal (Fig. 1). The lagoon has a very irregular and

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complex geometry, composed by long and narrow channels and an arborescent network system of small channels and by extensive intertidal and supratidal flats and salt marshes. The lagoon receives fresh water from several rivers and streams but mainly by the Antuã and Vouga rivers (Dias *et al*., 1999) and communicates with the Atlantic through an artificial inlet. The engineering works for opening the inlet began in 1802. The communication with the sea was established at 1808 (Dias *et al*., 2012). The outward water flux caused the development of a 264 m wide channel, with depths between 4 m and 6 m. Nevertheless the first inlet was instable. Therefore, several works were performed for navigation purposes, namely, the construction of two inlet breakwaters in the first half of the twentieth century, whose extension grew significantly since there (Dias *et al*., 2012). For instance, between 1949 and 1958, significant engineering works were done that kept the inlet feasible with relative easiness. The intervention carried out between 1983 and 1987 fixed the inlet width at approximately 350 m. The increase in length of the jetties in conjunction with the regular channel dredging, produced a generalised deepening of the inlet channel (Plecha *et al.*, 2010), and also affected the lagoon hydrodynamics.

The lagoon hydrographical regime is characterized by several periodic time-scales, the most important of which are the semi-diurnal tidal period and one-half the lunar month, the spring-neap cycle (Dias *et al*., 1999).The hydrodynamic pattern of the lagoon is, therefore, imposed by tides, being its effect detected at the far end of each channel (Dias *et al*., 2000a). The tidal cycle is also the main period characterizing the sediments transport in the lagoon (Lopes *et al*., 2006).

Aveiro region is densely populated. Industry and agriculture are intense and pressure on the Earth's resources and land grows constantly. The main vulnerable areas of the lagoon, from the water quality point of view, seem to be the far end of the main channels, where low dissolved oxygen concentration are observed (Lopes *et al*., 2005) and where eutrophication can occur (Lopes and Silva, 2006). These areas are also affected by chemical contaminants (Pastorinho *et al.*, 2012).

The study area is located at the northeast zone of the Ria de Aveiro, in Murtosa Channel (MC). This area was affected by mining activity in several zones of the Antuã River basin, namely in Pintor Mine. This mine has been licensed at 1897, having kept active till the end of the 1920s. Equipped with an important factory of chemical treatment, its business remained active even after shutdown of the mine until at least mid of 1930s. The abandonment of the mine without mitigation measures for environmental and landscape rehabilitation caused acute problems of pollution in Antuã River (Moreno, 2000). The existence of high levels of As in mobile phases and reactive sediments of the Pintor stream generate high environmental concern (Silva *et al*., 2002).

MC has been also affected for several years by industrial and urban effluents of the industrial parkland of Estarreja, the so-called 'Estarreja Chemical Complex (ECC) (Pereira *et al*., 2009 and references herein). ECC is composed of several chemical industries from which a chlor-alkali plant has been recognized as the most important source of mercury and other heavy metals input into this system. Factories of ECC used several streams as effluents to release wastes and pollutants. These effluents discharged high concentrations of several heavy metals in Laranjo Bay, the gateway of the Ria de Aveiro and the inner area of MC.

Discharge of pollutants by ECC plants reduced significantly since 1994. Therefore, higher heavy metals concentrations might be found in sub-superficial layers along the MC. The identification of subsurface levels with high concentrations of pollutants might be important to the management of this area, since traditional activity linked with professional fishing and molluscs catching and aquaculture in the lagoon are increasing in recent years.

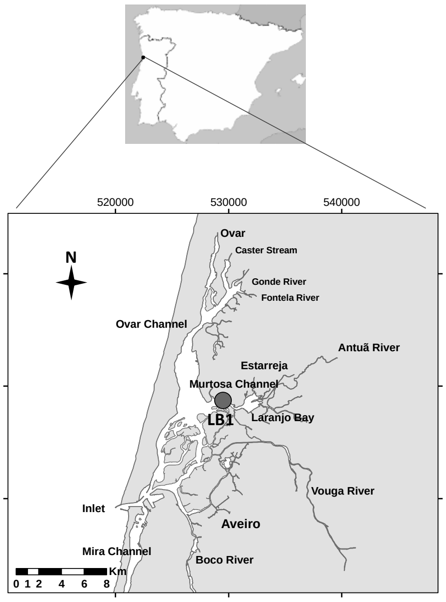

Figure 1. The study area in Ria de Aveiro. Core LB1 location in Murtosa Channel.

Climatic variations on an inter-annual to multi-decadal scale have an important geomorphological impact on Iberian river basins (Dias *et al*., 2004) and probably also leave a record in the sediments of the study area influenced by the Antuã river runoff.

In recent decades, it has been recognized that, in the North Atlantic, climatic variability has been largely driven by atmospheric forcing related to the North Atlantic Oscillation (NAO) which changed from positive to negative values since the end of 19th century, according the records of Hurrel (1995) (Fig. 2). NAO is the dominant mode of winter climate variability in the North Atlantic region. The NAO index is calculated as the normalised difference in winter sea-level pressures between Stykkisholmur in Iceland and Lisbon in Portugal (Hurrell, 1995). There is a strong pressure gradient between Iceland and Portugal during positive phases of the NAO, and a weak gradient during its negative phases. During the positive phases of NAO occurs the intensification of the westerlies across the sub-tropical Atlantic and the winter is cold and dry in Iberian Peninsula. A negative NAO index usually results in more rainfall, and subsequent flooding in the Iberian river basins during winter months (Dias *et al*., 2004).

The main aim of this work is to identify the record of the anthropogenic and/or climatic influence in MC, an inner area of the Aveiro lagoon using results obtained by the ITRAX micro-X-ray fluorescence (XRF) core scanner and other supplementary proxies (total elemental concentrations analysed by ICP-MS and mineralogy) of selected layers.

METHODS

This work studies the sediment core LB1 collected with a suction corer in an intertidal zone of Murtosa Channel, (at Bico harbourage; 40°43'43.99"N; 8°39'2.48"W; 240 cm long), in 2010, outside of one of the most contaminated areas of the Ria de Aveiro, Laranjo Bay.

This core was firstly submitted to geochemical analysis by ITRAX micro-X-ray fluorescence (XRF) core scanner. This is a non-destructive technique for obtaining simultaneously optical and X-radiographic images, and provides high-resolution elemental profiles (microcompositional variations obtained by XRF) that are invaluable for guiding sample selection for further (destructive) detailed sampling. The equipment can supply elemental variations from sediment half cores up to 1.5 m long at a resolution as fine as 100 µm (Rubio *et al.*, 2011). A set of elements such as: Al, Ba, Br, Ca, Cl, Cu, Fe, K, Pb, S, Si, Tu, Mn, Rb, S and Zn were analyzed (with a resolution of 300 µm). With the aim of obtaining a better reading of the ITRAX elemental spectra, mean moving averages of 22 values were used in the graphs. Furthermore, samples were collected at each 3 cm approximately along the core to grain size and total organic carbon analysis. Grain size analysis was performed by classic sieving techniques. Total organic carbon (TOC) content was analysed using a LECO equipment. The sediments mineralogy was carried out by XRD techniques on the <63µm fraction (methodology described in Martins et al., 2007). Concentrations of the chemical elements were evaluated in the fine fraction (<63µm) of sediment samples collected in selected levels along the core. A strong multi-acid digestion that dissolves most minerals was applied. About 0.25g split was heated in HNO_3-$HClO_4$-HF to fuming and taken to dryness. The residue was dissolved in HCl. Solutions were analysed by ICP-MS at ACME Analytical Laboratories, Canada. A radiocarbon age using molluscs shells collected at a depth of 90 cm was carried out by AMS method in “Beta Analytic Inc.”, Miami, Florida, USA.

RESULTS

This core is composed by sand and sandy mud sediments. Sand fraction varies between 46-99%, including: 63-125 µm: 0.2 -21%; 125-250 µm: 1- 45%; 250-500 µm: 31-70%; 500-1000 µm: 4-44 %; >1000 µm: 0.01-10%. Medium sand is the most common sediments’ fraction. The sediments are in general relatively finer in the lower part of the core (90-240 cm). Several rich mud recurrent levels, positioned at: 35-40cm, 45-55cm, 65-75cm, 90-130cm and 180-220cm were found along the core (Fig. 3). These muddy levels have darkened colours due to higher content of TOC (Fig. 3).

Maximum, medium, minimum and standard deviation of total elemental concentrations (analysed by ICP-MS) and minerals percentage were included in Tables 1 and 2, respectively.

The most common and abundant minerals identified along the core are quartz, K-feldspars, phyllosilicates, rhodochrosite, pyrite, anhydrite, magnesite/maghemite, dolomite, plagioclase, opal-CT. Sporadic occurrences of analcime, jarosites, hematite, zeolites, goethite, basalunites and bassanite also were found. Qualitative analysis at the microscope reveals that sand fraction is essentially composed of quartz, whereas the XRD mineralogical analysis preformed in fine fraction reveals that the muddy levels, namely the section 90-130 cm, are punctuated by the increasing of K-feldspars, phyllosilicates, calcite, siderite, pyrite, anhydrite, plagioclase, dolomite, opal-CT and anatase (by decreasing order of percentage).

The depth plots of ITRAX results show that: i) the relative abundance of Al is higher in the lower section of the core (90-240 cm), decreasing toward the top where the sediments are in general coarser, however, this trend is interrupted in the muddy layers where Al peaks occur; ii) elements such as Br, Ca, Fe, K, S, Ti, Zr increase in the muddy sections while Si is reduced in those levels; iii) elements such as Cu, Pb and Zn tend to increase in the first 110 cm towards the top of the core.

Table 1. Maximum (Max), medium (Med), minimum (Min) and standard deviation (St. Dev.) of total elemental concentrations.

Element		Max	Med	Min	St. Dev.
Al	(%)	6.0	4.7	3.3	12
As	(mg/kg)	52	31	4.0	27
Ba	(mg/kg)	333	156	42	125
Ca	(%)	0.4	0.2	0.1	13
Ce	(mg/kg)	87	53	18	2.3
Cr	(mg/kg)	84	48	25	16
Cu	(mg/kg)	50	19	6	0.1
Fe	(%)	4.5	2.7	1.3	0.0
K	(%)	2.5	2.0	1.3	5.1
La	(mg/kg)	39	23	6.3	57
Li	(mg/kg)	137	95	53	0.9
Mg	(%)	1.1	0.6	0.3	0.8
Mn	(mg/kg)	296	169	103	26
Na	(%)	5.8	2.4	1.0	4.3
Ni	(mg/kg)	64	33	19	10
Pb	(mg/kg)	125	51	24	102
Rb	(mg/kg)	156	107	35	0.0
S	(%)	2.8	1.6	0.2	0.8
Th	(mg/kg)	22	13	6.8	0.9
Ti	(%)	0.3	0.2	0.1	19
V	(mg/kg)	80	55	31	2.9
W	(mg/kg)	5.3	2.7	1.5	2.5
Y	(mg/kg)	12	7.2	4.0	2.2
Zn	(mg/kg)	459	134	31	24
Zr	(mg/kg)	111	75	42	33

As the Al is generally related to fine fraction and increases where phyllosilicates also have higher relative abundance and the ITRAX values were acquired in bulk sediments, the elements ratios with Al were also analysed. Depth plots of those ratios (Fig. 3) evidence:

i) peaks of Al are in general followed by rising of Ti/Al; both variables have the same general pattern of fine fraction and TOC;

ii) muddy sections are punctuated by peaks of Fe/Al and S/Al which have a general similar pattern;

iii) the upper core section (0-90 cm) is marked by the progressive increase of values of Si/Al, Ba/Al, K/Al, Cl/Al, Rb/Al and Mn/Al;

iv) significant increases of Ca/Al, Br/Al, Cu/Al, Zn/Al and Pb/Al occur in several levels in the first 120 cm; the higher values of these ratios occur not only in muddy levels but also in coarser sediments.

Total concentrations of Al and Li, acquired by ICP-MS, have a similar pattern of Al, shown in Figure 3 (ITRAX results).

Table 2. Maximum (Max), medium (Med) and minimum (Min) percentages and standard deviation (St. Dev.) of minerals. Number of occurrences in 25 samples.

Minerals	**Max.**	**Med**	**Min**	**St. Dev.**	**N.º**
Quartz	67	36	9	13	25
K-Feldspars	64	11	0	12	24
Phyllosilicates	47	27	0	11	24
Rhodochrosite	36	4	0	10	14
Pyrite	18	4	0	4	24
Anhydrite	16	2	0	3	20
Magnesite/Maghemite	15	1	0	3	11
Dolomite	12	1	0	3	10
Plagioclase	12	6	0	3	23
Opal-CT	7	2	0	2	16
Alunites	6	1	0	1	7
Anatase	5	1	0	1	9
Calcite	3	1	0	1	9
Siderite	3	0	0	1	6

The total concentrations of Cu, Pb and Zn, evaluated by ICP-MS, also increase in the upper 110 cm of the core, reaching respectively 50 mg/kg, 90 mg/kg and 460 mg/kg. In this section, total concentrations of other elements also rise, such as: V up to 76 mg/kg; Cr up to 54 mg/kg; As up to 49 mg/kg; and Ni up to 33 mg/kg. Similar increases also were identified through the ICP-MS analysis at the core base, below 200 cm: Pb up to 125 mg/kg; Cr up to 84 mg/kg; V up to 80 mg/kg and; Ni up to 69 mg/kg; As up to 52 mg/kg; Cu up to 15.2 mg/kg and; W up to 5.3 mg/kg. Results of ITRAX do not evidence the enhancement of Pb in this section (Fig. 3).

Another group of chemical elements also increase their total concentrations in the upper 110 cm of the core such as: Na from 1.4 up to 5.5 %; Mg from 0.37 up to 1.11 %; Ce from 39-87 mg/kg; Th from 8 up to 46 mg/kg; La from 18 up to 40 mg/kg; Y from 5 up to 12 mg/kg and; Mn from 134 up to 296 mg/kg.

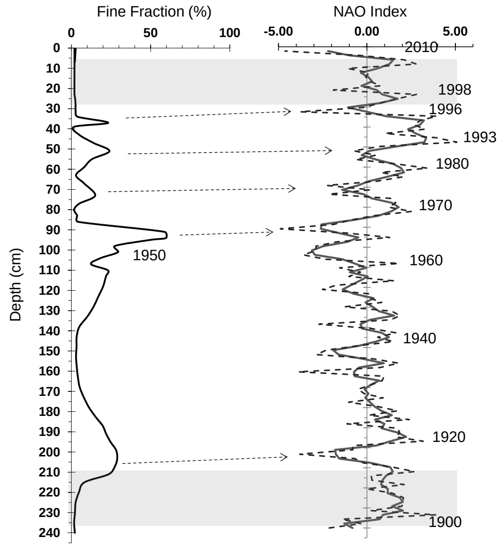

Figure 2. Depth plots of fine fraction (%) and NAO indexeswww.cgd.ucar.edu/cas/jhurrell/indices.html.

On the basis of the radiocarbon results, the uppermost 90 cm of the core represents the last 60 years.

DISCUSSION

Results of radiocarbon indicate an age recent than 60 years for the first 90 cm of the core. Peaks of As, Cr, Cu, Ni, Pb, Zn and V in the upper 110 cm of the core sign the industrial activity in Estarreja, one of the most important centre of the Portuguese chemical industry, that began the settlement in the 1930s, but especially after the end of World War II (Dias *et al*., 2012). ECC increased the discharging of pollutants essentially since the ‘50 (Pereira *et al*., 2009 and references herein). These pollutants were introduced by streams used as effluents in Laranjo Bay, an area significantly affected by tides. The hydrology of this area is ebb-dominant and during spring tides, approximately 75% of the water bay is renewed (Lopes *et al*., 2006), implying the resuspension and export of contaminated sediments by the tidal currents (Pereira *et al*., 2009). However, the tidal residual currents are generally small, leading to a significant deposition and consolidation of particles into the bed (Lopes *et al*., 2006).

Whereas Ca content is mostly related to biogenic contributions (molluscs shells and foraminifera) Al, Fe, Ti, Si, Rb, Ba, K, Cl, Br, S, Mn and Zr would mostly be lithogenic in origin, coming from metamorphic and igneous rocks weathering products of the Variscan basement. The weathered materials are introduced in the Ria de Aveiro mainly by the rivers run-off. Aluminium is commonly associated with aluminosilicates which are in general more abundant in muddy sediments. Values of Ti/Al also follow the same pattern of Al, indicating that Ti minerals, such as anatase, are being deposited mainly in fine grained sediments, even as phyllosilicates and other minerals. The general tendency to decrease of Al and the increasing of Si (and also Si/Al values; Fig. 3), in the upper section of the core (at the first 90 cm, but more clearly in the first ~35 cm) can be mostly related to the increment of quartz, the main mineralogical constituent of sand fraction, more abundant in this section. The tendency to the increasing of Ce and La (REE) and other elements such as Na, Mg, Th and Y might indicate increasing of erosion. In this section, the values of Cl/Al, K/Al and Rb/Al also rise. These elements can be concentrated in brines that may be related to higher marine influence in the area, leading to greater differences in tidal currents with periods of dry air sediments exposition favouring minerals precipitation.

Whereas peaks of total concentrations of Pb, Cr, V, Ni, As, Cu and W below the level of 180 cm, might be related to mining activity in several areas of the Antuã River basin, namely in Pintor Mine until at least mid of 1920s. This mine explored W, As and Pb, which explain the enrichment in these metals in the core base and their decline since the level of 210 cm.

According to these results we can estimate an age of ~1920s to the level of 210 cm and ~1950s to the level 100 cm. According to this chronology a mean sedimentation rate of ~1.6 cm/year can be estimated to the core top (0-100 cm) and of ~3.6 cm/year for the section below 100 cm.

The increase of several redox-sensitive elements ratios such as, Fe/Al and S/Al, in TOC rich muddy sections, ~~suggests~~ suggest the occurrence of diagenetic changes related to organic matter degradation and sediments oxygenation: iron-sulphur and siderite precipitation in lower oxic conditions. Peaks of Mn/Al in the intervals indicate precipitation in oxic layers (coarser sediments). Muddy layers intercepting sandy sections are more frequent in the upper 150 cm of the core.

Records of Anthropic Influence

Two levels of higher concentrations of toxic heavy metals were identified in Murtosa Channel (at Bico harbourage) between 30-110 cm and 210-240 cm below sediments surface. The upper is a consequence of industrial discharges of the ECC mostly since the 1950s. The more ancient records the mining activity near the Antuã river basin at the end of 21th century and or at the beginning of 20th century. In order to know the position of these levels is important to prevent the reintroduction of pollutants in the system by stronger tidal currents or anthropogenic activities. The reintroduction and the dispersion of pollutants in the water column can affect the lagoon food chains including the riverine human population.

Coarser sediments (quartz rich, see Si/Al depth plot, Fig. 3) in the first 90 cm of the core also suggest deposition under stronger bottom currents, since currents control in great extent the sediments grain size and composition in this lagoon (Martins *et al*., 2011). The rise of lithogenic and brines associated elements in this section may be related to high marine influence in the area, increasing in tidal currents activity and erosion of lagoonal sedimentary deposits. These effects might be due to sea level rising tendency (Dias *et al*., 2000b), man intervention in the navigable channels through dredging and engineering works in the lagoon inlet.

Records of Climatic Influence

Considering the general chronology and depth plots of selected variables of grain size and geochemical composition of the sediments shown in Figs. 2 and 3, can be found some correspondence between the evolution of these variables and NAO indexes. The finer sediment layers are in general related to negative phases of NAO (Fig. 2). The NAO index was predominantly negative from 1960–1970 and predominantly positive from 1970 to the present (Fig. 2). A notable exception during the current positive phase was a severe reversal to a negative value in the winter of 1995–1996, which was followed by a switch back to strongly positive values by 1998. Fine grained sediments enriched in TOC should have been supplied by the rivers runoff during periods of rainfall, such as between 1960-1970 (130-85 cm). The coarser layers should be related to periods of more frequent positive phases of NAO, for instance the periods between 1920-1930 (210-240 cm) and between 1998-2010 (90-0 cm). The declining of sedimentation rate in the core top might be related to a decline in the terrigenous supply due to climatic dry conditions but may have been also influenced by anthropogenic actions on hydrographical basins (Dias *et al*., 2004) and in the lagoonal harbours area (Plecha *et al*., 2010).

CONCLUSION

This study is based on a core collected in an inner area of Ria de Aveiro. It represents a sedimentary sequence with probably less than one century, since the beginning of 20th century. Results of ITRAX provided high resolution data allowing us the identification of variations in terrigenous and anthropogenic elements used as a proxy of sedimentary dynamic. Furthermore results of ITRAX also were supported by elemental total concentrations evaluated by ICP-MS, TOC, mineralogical and grain size analysis in some selected levels of the core.

Sediments record two distinct sources of pollutants, an older one resultant of mining activity and a more recent due to effluents discharged by chemical plants. Man interventions in the lagoonal harbour area as well as climatic changes in a decadal periodicity related to NAO, and thus changing in wind and rainfall patterns and intensity, also leave a record in the sediments of the study area.

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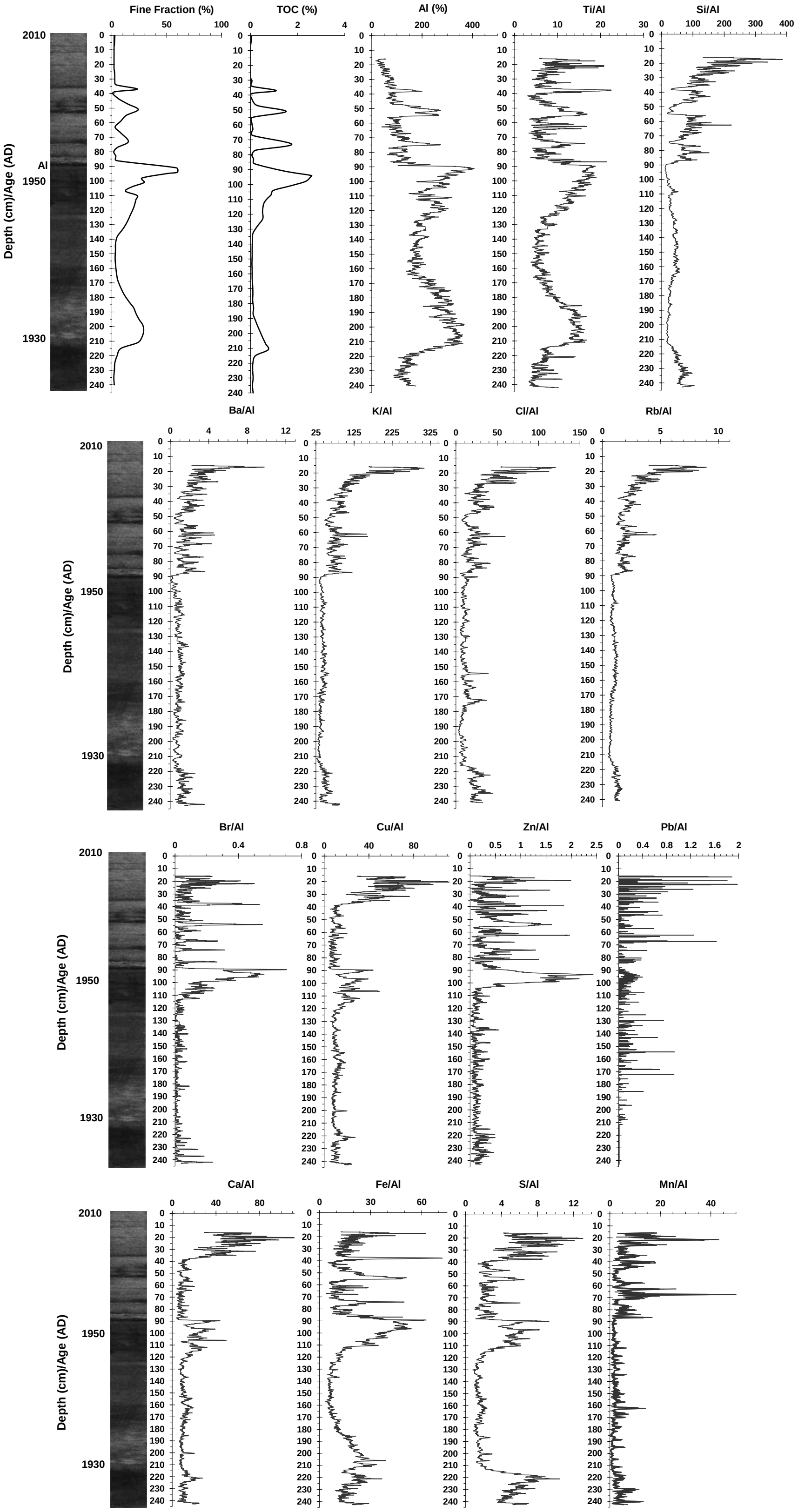

Figure 3. Depth plots of percentage of fine fraction and TOC and results of ITRAX: elemental relative abundance of Al and ratios with Al of Ti, Si, Ba, K, Cl, Rb, Ca, Fe, S, Mn, Br, Cu, Zn and Pb.