Title

On the Geochemistry of Venice Lagoon Sediments. Scripps Institution of Oceanography SEDiment Research Program – SIOSED. A Background Report

Authors

Gieskes, Joris M
Han, Seunghee
Rothwell, Guy
et al.

Publication Date

2011-10-09

On the Geochemistry of Venice Lagoon Sediments
Scripps Institution of Oceanography SEDiment Research Program – SIOSED
A Background Report

by

Joris M. Gieskes[1*], Seunghee Han[2], Guy Rothwell[3], Anthony Rathburn[4], Elena Perez[5], Fabrizio Perin[6], and Dimitri D. Deheyn[1]

1. Scripps Institution of Oceanography, La Jolla CA 92093, USA *jgieskes@ucsd.edu
2. Department of Environmental Science and Engineering Gwangju Institute of Science and Technology (GIST) Oryong-dong, Gwangju 500-712, Korea
3. British Ocean Sediment Core Research Facility, National Oceanography Centre Empress Dock, Southampton, SO14 3ZH, United Kingdom
4. Indiana State University, Department of Earth and Environmental Systems, Science Bldg 159, Terre Haute, IN 47809, USA
5. Department of Palaeontology, The Natural History Museum, Cromwell Rd., London, SW7 5BD,UK
6. Thetis SpA Castello 2737/f - 30122 Venice, Italy

1*: Primary contact jgieskes@ucsd.edu

This report presents information on the solid phase geochemistry of sediments in Venice Lagoon, obtained through the sponsorship of the SIOSED (Scripps Institution of Oceanography SEDiment research) program. Sediments were cored in a variety of environments as well as on artificial sediment banks constructed in the Lagoon.

The material will serve as a background for several papers to be written for publication in the reviewed literature.

1. Introduction

In order to understand the biogeochemical processes of contaminants involved in the relocation of dredged channel sediments in the Venice Lagoon, Italy, the SIOSED (Scripps Institution of Oceanography SEDiment research group) has carried out a research program from March 2005 to November 2007 (Deheyn and Shaffer, 2007). Sediments were cored at various locations in the Venice Lagoon (Figure 1). In addition sediments were dredged from a navigation channel (SSO) and transplanted directly into banks at two shallow sites (V1 and V2), in the vicinity of Sites SS1 and S2 respectively. The monitoring program was essential since sediment in the Venice Lagoon is often contaminated with various metals and organic pollutants in different concentrations; consequently, most of the sediment in the lagoon has been evaluated as potentially hazardous (MAV-CVN, 2004a,b; Apitz et al., 2007). The sediment classification of the lagoon is organized into three categories (A, B, C) based on the concentration range of various contaminants (Table 1; Figure 2), with the A category the least contaminated and C or higher the most. Concentrations of the categories are based on total concentration values and on potential toxicity of each single contaminant; therefore, the occurrence of only one contaminant above the range characteristic of a specific category associates the sediment to the next more contaminated category.

As part of this multi-disciplinary program, potential changes in the geochemistry of sediments were studied in relation to their dredging and reuse, including both the chemistry of solid phases and of interstitial fluids of the sediments.

The present program of studies has emphasized the study of both major elements and trace metals in the sediments. Results of SIOSED sponsored studies on the distribution of Hg and the processes involving the generation of pollutants such as methyl-mercury have been already been published (cf., Han et al., 2007; 2008; 2010a, b; 2011).

1.2. Previous studies on Venice Lagoon Sediments

Changes in sedimentation rates have affected the sediments of the central part of the Lagoon during the late 1990-ies (Sfriso et al., 2005a). These changes were mostly due to sediment suspension and removal during intensive clamming operations in recent years. A reduction of the macro-algal beds before and after the initiation of clam fishing by means of highly disruptive techniques has significantly contributed to the increase (~ one order of magnitude) of the fine sediment fraction re-suspension and spreading, favoring a loss of fine material and a homogenization of the surface sediments. For more information on sediment ages see also Appendix 1.

Various studies of trace metal contents have concentrated on the distribution in the upper few cm of the sediments throughout the Venice

Lagoon. As an example we reproduce three maps of the distribution of zinc (Figure 3; MAV-CVN, 2004a,b). It is evident that this distribution has changed over the period of 1978 – 1998. In part this may be related to the change in input of zinc in the last few years (Frignani, 1997; see below) as well as to the changes in sedimentation as discussed above. The distribution of 1998 does clearly indicate the enhanced values of zinc in the surface sediments in the areas of the industrial zones of Venice. An additional source of information on trace metals in Venice Lagoon sediments can be found in Bellucci et al. (2002; 2005).

Previous detailed studies of the chemical composition of the upper portions of the sediments (upper 30-40 cm), both of major elements and trace metals, have been combined with studies of sedimentation rates determined by radiometric techniques (Frignani et al., 1997; Cochran et al., 1998). Especially in the area to the northwest of the city of Venice it was established that since the mid 1930s trace-metal contamination became a significant problem, mainly as a result of the increased industrial activity in the Porto Marghera area. Only since 1980 has the increase in trace metal contamination been shown to indicate a reverse trend. For mercury the sediments have shown relatively large inputs as a result of local industrial activity, as well as from sources in the northern Adriatic, which has received inputs from mercury mine operations at least for a few centuries (Faganelli et al., 2003; Bloom et al., 2004; Piani et al., 2005; Covelli et al., 2008).

1.3. Site Locations

In order to obtain a more detailed understanding of the nature of the problem of sediment dredging and relocation (Deheyn and Shaffer, 2007), several representative sites were studied, with the emphasis on coring in the most polluted areas near Porto Marghera (Site C) and the industrial zone of the lagoon (Sites S1 and SO), as well as in several areas both in the northern and southern parts of the lagoon (Figure 1). Note that Site SO is in a dredged channel, whereas S1 is located outside the same channel. In addition Sites A and B are essentially reference sites for this program. Figure 1 shows the locations of stations SS1 and S2 comprising the sites where the artificial sediment banks were constructed with sediments of station SSO (dredged canal) as the material for the bank construction. Site SS1 is located near the Malamocco Inlet of Venice Lagoon, whereas Site S2 is located in the middle of the basin south of Venice (*cf,* Figure 1).

2. Methods

We report data obtained through different means: (1) whole core scanning with X-Ray fluorescence, (2) whole sediment dissolution using a glass bead technique, and (3) partial extraction of metals from sediments by nitric acid digestion.

2.1. Whole cores X-Ray Fluorescence

We have chosen four cores from Venice Lagoon (Sites SS1, S2, SSO for the South Central lagoon, and Site C for the Porto Marghera area; Figure 1) for whole core scanning using the ITRAX micro-XRF core-scanner (Croudace et al. 2006; Rothwell and Rack, 2006). Such high-resolution XRF scanning methodologies have become a more widely used investigative technique in recent years (e.g., Rothwell et al., 2006, Boehning et al., 2007). ITRAX settings were at 200/500 microns step size and the count time was 60 secs to maximize response from trace elements. The ITRAX instrument does not yield data that are immediately quantitative in nature. Element data are recorded as peak areas that are roughly proportional to the concentrations of major and minor elements present in the sediment (all elements received the same counting time, but they have different sensitivities to X-Ray excitation). The data, however, allow measurement of the relative distribution of elements down-core. Elements that have high-energy X-ray responses (e.g., Fe, Ti, Rb, K) show good responses, whereas elements with low energy X-ray responses (e.g., Al, Si) show sometimes only a marginal response. Even though Ca X-rays are of relative low energy, the counts of Ca in the sediments of Venice Lagoon are significant, so the total counts for Ca and Fe are high (Ca mostly occurring as calcite and dolomite, often more than 50 % in Venice Lagoon; Frignani et al., 1997). The data obtained can be calibrated against data obtained on discrete samples by means of other analytical techniques, as will be described in this report. Though the XRF core is not exactly the same as the cores investigated for the wet chemical analysis of the cores obtained in the same area, precise calibrations are not necessarily expected, but generally the cores should have similar geochemistries.

As mentioned above, the value of the ITRAX technique is that geochemical trends can be studied down core, with the potential to distinguish features that may otherwise not be seen through a more limited sampling interval (e.g., Boehning et al, 2007). Because of potential shifts in the sensitivity of the instrument, it is advisable, however, to normalize the counts to a common reference. We have chosen Fe as the reference element, as it does produce data that are more comparable through this “normalization” procedure. In other studies normalization to Ti has been preferred (Thompson et al., 2006). However, even though normalization to Ti allows a reference to a truly lithogenic element, using Fe accomplishes virtually the same purpose, especially for trace elements that are often associated with Fe-bearing phases. In addition, high X-ray intensity of Fe and associated high count-rates makes it an appropriate element to use.

An example for the differences in counts for cores from SS1 and C is presented in Figure 4. It is evident that absolute counts are very different in the two cores; see, for example, the differences for Fe, Ca, and Ti. Ratios of Ti/Fe, however, are almost the same, thus justifying the comparative method for presentation of ratios. For comparison with actually measured values of Fe and Ti, we compared the data as adjusted to fit the same depth distribution as the experimental data on Fe_2O_3 and TiO_2 (see below).

2.2. Total Sediment Dissolution

In order to verify the concentrations of iron oxide, titanium oxide, as well as the determination of aluminum oxide, and phosphorus pent-oxide, we have used a wet chemical analysis based on a methodology originally developed by Shapiro and Brannock (1962) and Shapiro (1967), and subsequently modified by Donnelly (1980) as well as in the senior author's laboratory (e.g., Gieskes *et al.,* 2005). In this method sediment is fused with a lithium borate/metaborate mixture at 1070 °C. The resulting glass is dissolved in a 5 % sulfuric acid solution and the resulting solutions subsequently analyzed with colorimetric methods.

2.3. Partial metal extraction

The sediment samples were oven dried (90-100^{O}C), ground, and homogenized with a mortar and pestle, and sub-sampled for further analysis.

A number of metals, *inter alia,* Cu, Fe, Mn, Ni, Pb, and Zn, were simultaneously analyzed using an Induced Coupled Plasma Atomic Emission Spectrum (ICP-AES) spectrometer (Optima 3000, Perkin Elmer), available at the Scripps Institution of Oceanography Analytical Facility. Calibration of the instrument was done before every run by dilution of a 100 ppm Multi-Element Instrument Calibration Standard solution (Fisher Scientific).

All methods and protocols were modifications from Deheyn and Latz (2006). Sediment samples were digested in a 45 % nitric acid solution (Fisher Scientific) at 80°C for 20 minutes using an Ethos EZ Microwave Digestor (Milestone), in order to assess the leachable and bioavailable fraction of metals associated with the sediment, thus not including the metals constitutive of the geological matrix (Deheyn & Latz, 2006). A sub-sample of the resulting acid solution was then diluted by weight in MilliQ water for ICP analysis.

All manipulations during collection and sample preparation were done under clean controlled conditions to avoid metals contamination, using metals free solutions, nitric acid washed containers, disposable polypropylene or high-density polyethylene supplies, including forceps and tubes. Trace Metal Grade nitric acid (Fisher Scientific) was used in sample preparation with concentrations $< 10^{-7}$ mg/g for each metal, thus having a negligible effect on samples metal concentration (Deheyn, Gendreau, Baldwin, & Latz, 2005; Deheyn & Latz, 2006).

3. Results

3.1. Whole core XRF fluorescence

All the cores were obtained prior to the dredging, relocation, and building of the sediment banks and thus are considered representing a presumably undisturbed status of the sediment seafloor.

The results for the element to iron ratios are presented in Figures 5, 6, 7, and 8. Note that the mean standard error (MSE) is fairly large and that data with an MSE of less than ~ 40 % appear to be the most reliable.

Cores SS1 and S2 (Figures 5 and 6) are representative of the areas, where the artificial banks were to be constructed, using material of the upper 50-80 cm of sediments dredged from Site SSO. Core SS1 is characterized by a gradual decrease in the Ca/Fe ratio (Figure 5). Most of the other ratios indicate relatively constant Fe ratios. Of course, most of the elements show increasing concentrations of various elements (c.f., Figure 4), iron oxides/sulfides presumably serving as important carriers of trace metals. Core S2, notwithstanding relatively large errors, shows slightly increasing Ca/Fe ratios with depth, especially evident from the bottom section (Figure 6).

Core SSO (Figure 7) in a dredged canal shows almost constant ratios of Ca/Fe in the upper 1.15 meters, but below this large increases indicate much higher carbonate contents, with correspondingly lower ratios of trace metals to Fe.

Core C (Figure 8) is located in the sediments just off Porto Marghera (Figure 1) and thus typically high trace metal/Fe ratios characterize the sediments. Indeed the deeper sediment has relatively high Zn/Fe ratios, an observation that implies recent re-sedimentation, probably as a result of reworking during dredging operations.

An overview of the data on the element/Fe ratios from Figures 5 - 8 is presented in Table 2. On average the ratios K/Fe, Ti/Fe, Rb/Fe are constant within 10%, i.e., well within the estimated MSE error from the ITRAX. For the trace metal ratios, Zn/Fe shows the largest changes, mostly in Site C. Similarly, much smaller increases in Site C are detected for Pb/Fe, Co/Fe, and Ni/Fe. Cu/Fe ratios are considered too low to be useful in Cores SS1, S2 and SSO, but they do show higher ratios in Core C. In order to compare the data in a better fashion we have constructed diagrams obtained through averaging data from ITRAX over representative depth ranges. These data are discussed in a following section 3.2.

3.2. Total dissolution results

Data for Al_2O_3, TiO_2, Fe_2O_3, and P_2O_5 were obtained from the total sediment dissolutions of samples from cores SS1, S2, SSO, and C. In addition we determined the contents of Zn and Cu in these samples.

Data for Fe_2O_3 and TiO_2 are presented in Figures 9 and 10. Here we used data of XRF counts, adjusted to the dissolution data. It is evident that there is an acceptable correspondence between the two data sets

The major element count data estimated from the more detailed ITRAX data by means of averaging the data are presented in Figures 11, 12, 13, and 14. The data constitute the XRF derived counts for Fe, Ti, Ca, and Zn, as well as their ratios in the upper portion of the figures. Note that these data are based on XRF counts and thus do not represent actual concentrations. The ratios, however, are directly comparable with the information of contained in Figures 5-8. Though we have no data for the Ca and Mg contents of our samples, calcite concentrations in the Venice Lagoon are on average about 20-30 % in concentration (Bellucci et al., 2002; Cola and Simonini, 2002), with calcite/dolomite ratios varying between 0.36 and 0.41. Comparison with the data of Frignani et al. (1997) agrees with both high CaO and MgO contents of the Venice Lagoon sediments. Considering the variable Ca/Al ratios (representing Ca in both calcite and dolomite) in the XRF counts, the carbonate contents are not constant. The main point, however, is that carbonates are high, often more than 50 %. This, of course, reflects the source materials from the Dolomites mountain chain. The next principal contributor to the major constituents is silica (quartz and clays), with contents between 30 and 40 % (Frignani et al., 1997).

3.3. Trace metals in sediments

Trace metals were estimated both with the ITRAX methodology and with both the total sediments dissolution technique and the partial acid digestion methodology.

Table 2 summarizes the XRF derived ratios to the iron contents (element/Fe). As mentioned before, the count data are non-quantitative, unless they can be compared with other data. In Figure 15 the XRF counts for Zn at Core C are compared with the Zn contents obtained from discrete samples at this site. It is evident that the XRF trace allows the detection of more detail, but there is still reasonable agreement between actually measured concentrations and the XRF derived data. Note, of course, that changes in Zn are the largest observed in Core C (Table 2), i.e., in the area of Porto Marghera.

Data for the depth distribution of Zn and Cu are presented in Figure 16. Data in the upper part of this figure are those obtained from complete dissolutions of the sediments, whereas the data in the lower part are from the partial nitric acid extraction technique described above. Although similarly named cores are not necessarily physically the same for the two sets of data (i.e., they can be from two cores taken next to one another from the same site), similarities in the depth distributions are noticeable. Cores C and SO are located in the Porto Marghera industrial zone and in the more southern industrial area. In Core C and Core SO, both Cu and Zn increase with depth, an observation confirmed by the data for drill Hole SM3 (see below; Figure 19). Note that only cores C, SO, and SM3 indicate data classified as class B or C sediments, all other cores show data well within the limits of class A type sediments. Depth distributions are also not smooth, which may be the result of sediment disturbances as a result of frequent dredging operations at these sites. Data of Frignani et al. (1997) and Bellucci et al. (2002; 2005) in undisturbed sediments northwest of Venice indicate that trace metal enrichments do not extend much deeper than about 50 - 60 cm, whereas in Core C and SM3 they become enriched with depths to as deep as 4 meters.

An alternative presentation is a plot of the measured Fe_2O_3 content vs. the trace metal contents. This is shown in Figure 17. Note that the Fe_2O_3 contents of the nitric acid dissolutions (Figure 17A) are about 50% lower than those of the total sediment digestions. However, the trace metal contents are very similar in magnitude, indicating that the samples dissolved in strong nitric acid also released all or most of the trace metals. In addition Figure 17B includes data in the area of the Industrial Zone previously reported (Frignani *et al.,* 1997; Cochran *et al.,* 1998; Bellucci *et al.,* 2005) indicating that especially in the sediments off Porto Marghera and the industrial zone are characterized by elevated Cu and Zn contents.

Figure 18 presents a map for drill hole SM3, located northwest of Venice at the edge of a dredged navigation channel. Data for zinc and copper from the upper 10 m of this drill hole are presented in Figure 19A. In the upper 4 meters of the drill hole maxima in Zn and Cu characterize this hole, suggesting significant disturbance of the sediments, presumably as a result of dredging activities (c.f., Core C). Data for the chemical composition of the sediments of the entire hole are given in Figure 19B. Any elevated Zn and Cu concentrations suggest that these sediments are relatively young in age, i.e., from after ~ 1930 or younger.

Figure 20 presents the Fe_2O_3 vs. Zn correlation for SM3, which also includes the data from Figure 17. Note the similarity of the Zn concentrations in the upper 4 m of SM3 to core C, whereas the lower 5 m fit with data from SS1 and S2.

Data for Ni and Pb (nitric acid dissolution) in the long cores are given in Figure 21, which should also be representative of these metal contents in the bulk samples. In general only the cores in the vicinity of the industrial zones show excess concentrations (above ERL, type B), especially for Zn, and to a much lesser extent for Cu, Ni, and Pb.

At this point it is important to present common information on the classification of the sediments with regard the potential pollution aspects of the various trace metals under consideration. Table 1 presents two sediment classifications. The system ERL/ERM is commonly used in the USA, whereas the classification into categories A, B, C, and >C is often used for sediment classification in Venice Lagoon. Where possible we have used both classifications (MAVCVN, 2004a,b; Apitz et al., 2007).

Figure 22 depicts data obtained from the extensive data obtained by our group on the total sediment content of Hg in Sites SS1, S2, SSO, and the bank sites V1 and V2. Concentrations in cores of SSO, V1, and V2 are usually higher than in the reference Sites SS1 and S2. This indicates that SSO samples came from a dredged channel, and that this material was superimposed on SS1 and S2 sediments. Thus, in principle, the sediments of the upper 50-70 cm of the bank sites should be classified as class B sediments. Han et al. (2010a) have shown that in the area of Porto Marghera (drill hole SM3) mercury concentration indicate values above 1000 ng/g dry sediment. The variability in the surface layers of the bank sites and their reference sites (SS1 and S2) is shown in Figure 23 (see also, Han et al., 2007, 2008). With the boundary for Class A to B at ~ 500 ng/g dry sediment, sites SS1 and S2 actually qualify for a Class A designation. Sites C and SO in the industrial area of the Venice Lagoon indicate substantially elevated concentrations, as does much of the sediment in Site SSO.

Previous studies have also shown that the Porto Marghera area is the most Hg-contaminated zone in the Venice Lagoon, together with the canals in the city of Venice (Bloom et al., 2004; Moretto et al., 2003). The total Hg concentrations determined in the surface sediment of open water sites (B, S0, S1, S2, SS0) ranged between 450 and 690 ng g^{-1}, which agreed with literature data (641 ± 260 ng g^{-1}; Bloom et al., 2004). This range corresponds to the upper range of total Hg concentrations found in several urbanized estuaries on the East Coast of the United States (200 – 700 ng g^{-1}; Mason and Lawrence, 1999). Surface sediments of sites A and SS1 showed the lowest total Hg concentration of 209 and 210 ng g^{-1}, respectively. However, this value is still almost twice as much as the background Hg level of 118 ng g^{-1} found in surface sediments of the Adriatic side of Lido Inlet (Moretto et al., 2003). It has been estimated that approximately 1100 kg of Hg was carried to the Adriatic Sea each year on suspended matter due to the natural and anthropogenic resuspension of surface sediments (Bloom et al., 2004).

Generally the Hg concentrations in the upper 2 - 3 cm of the surface sediments decreased with increasing distance from the Porto Marghera, following the trend of organic carbon content in the surface sediments. The total Hg concentration in estuarine sediment often has a positive correlation with the organic carbon content because of the strong association between sedimentary organic matter and Hg (Mason and Lawrence, 1999). The regression coefficient (r^2) increases from 0.55 ($n = 8$, $p = 0.036$) to 0.92 ($n = 6$, $p = 0.003$) when the data points of SS1 and S2 are not included in the linear regression, showing that the surface sediments of SS1 and S2 have low total Hg content in spite of high organic carbon concentration.

The mercury levels of V1 and V2 clearly reflect the source sediment of Site SSO (Figure 23). Small differences can be explained by the redistribution of sediments in the late 1990-ies.

Two maps of sediment quality zones in Venice Lagoon, primarily based on the distributions of Hg and Cr, are presented in Figures 24 and 25 (MAV-CVN, 2004b). It is evident for these components that much of the central lagoon is classified as type B and C (c.f., Figure 2). However, for many of the trace metals the zonation is much more restricted. This, for example, is demonstrated for Zn and other metals in Figure 25 (MAV-CVN, 2004b; see also Apitz et al., 2007). The thought of the chromium distribution to be the source of the overall classification of the lagoonal sediments may not be entirely justified. Typically the distribution of chromium is rather uniform in Venice Lagoon, suggesting a relatively high, inherited, signal. Perhaps the input of sediments from the Dolomites Mountain range may be associated with enhanced concentrations in Cr. Other sources may be periodic inputs of Hg enriched sediments north of Venice.

3.4. Organic carbon distribution

The distribution of organic carbon has also changed considerably over the last few years, mostly as a result of changes in fisheries activities and bottom disturbances (Sfriso et al., 2005b). An older set of data has led to the organic C distribution map of organic carbon in Figure 26 (MAV-CVN, 2004b).

The organic carbon data of the various stations of SIOSED are presented in Figure 27. In addition to the SIOSED Sites A, B, C, S0, S1, S2, SS1, and SSO, we also report on stations D and E in the immediate vicinity of Sites S0 and S1. In addition data have been collected on Sites V1 and V2, both representing artificial banks constructed in the vicinity of Sites SS1 and S2. Though these sites may not present a representative overview of the sedimentary organic carbon levels of Venice Lagoon sediments, the data are of relevance to observations on the changes possibly taking place in dredged transplanted and reused sediments. Previously reported concentrations are generally slightly higher (c.f., Figure 26), but it is entirely possible that these differences can be understood in terms of methodologies.

The data reported in Figure 26 show large variability in the Venice Lagoon. Especially high in sedimentary organic carbon are the southwestern parts of the lagoon, i.e., the marsh and fish farm parts (MAV-CVN, 2004b). Also more enriched zones occur in the North-East part of Venice Lagoon.

For the purpose of the present study we utilize data from SIOSED/Thetis as well as our own data (Figure 27). Generally these data are less than 0.5 % at Sites A, B, and SS1, whereas most other sites indicate concentrations of ~ 1 % ± 0.2. These data, though somewhat less, do agree with the distribution of surface organic carbon data as presented in Figure 26. Data for Sites D and E (near S0 and S1) are roughly 0.8 %.

Of importance are studies of the distribution of organic carbon and associated components in the surface sediments, in the area where sedimentation rates were determined (Sfriso *et al.,* 2005a). These studies have shown substantial changes in organic matter distributions associated with the sediment disturbances caused by clam fishing operations (Sfriso et al., 2005b).

Acknowledgements

We would like to thank Christina Nasci, Andrea Barbanti, and Chiara Castellani. Special thanks are due to Andrea Berton, Matteo Conchetto, and Emiliano Molin for collecting field samples.

The material of this report has been produced in the framework of SIOSED Project, supported by Magistrato alle Acque di Venezia, Italy (Venice Water Authority) throughout Consorzio Venezia Nuova and Thetis S.p.A. Any opinions, findings, and conclusions or recommendations expressed in this report are those of the author and do not necessarily reflect the views of the Magistrato alle Acque di Venezia (Venice Water Authority), Consorzio Venezia Nuova or Thetis S.p.A.

References

Apitz, S.E., Barbanti, A., Bocci, M, Carlin, A., Montobbio, L., and Bernstein, A.G. (2007). The Sediments of the Venice Lagoon (Italy) Evaluated in a Screening Risk Assessment Approach: Part II—Lagoon Sediment Quality Compared to Hot Spots, Regional, and International Case Studies. Integr. Environ Assess. Manag., 3:393–41

Bellucci, L. G., Frignani, M., Paolucci, D., & Ravanelli, M. (2002). Distribution of heavy metals in sediments of the Venice Lagoon: The role of the industrial area. Science of the Total Environment, 295: 35–49

Belluci, L.G., Frignani, M, Lin, S., and Muntau, H. (2005). Accumulation and metal fluxes in the central Venice Lagoon during the last century. Chemistry and Geology, 21: 425-439

Bloom, N.S., Moretto, L.M., Scopece, P., and Ugo, P. (2004). Seasonal cycling of mercury and monomethyl mercury in the Venice Lagoon (Italy). Marine Chemistry 91: 85-99.

Boehning, P., Bard, E., Rose, J. (2007). Toward direct, micron-scale XRF elemental maps and quantitative profiles of wet marine sediments. Geochemistry, Geophysics, Geosystems, 8(5): Q05004, doi: 10.1029/2006GC001480

Cochran, J. K., M. Frignani, M., Salamanca, M., Bellucci, L.G., and Guerzoni, S. (1998). Lead-210 as a tracer of atmospheric input of heavy metals in the northern Venice Lagoon. Marine Chemistry 62: 15–29

Cola, S & Simonini, P. (2002). Mechanical behaviour of silty soils of the Venice lagoon as a function of their grading properties. Canadian Geotechnical J., 39 (4): 879-893.

Covelli, S., Faganeli, J., De Vittor, C., Predonzani, S., Acquavita, A., Horvat, M. (2008). Benthic fluxes of mercury species in a lagoon environment (Grado Lagoon, Northern Adriatic Sea, Italy). Applied Geochemistry 23, 529-546.

Croudace, I.W., Rindby, A., and Rothwell, R.G. (2006). ITRAX: description and evaluation of a new multifunction X-ray core scanner. In: Rothwell, R.G. (2006). New techniques in sediment core analysis. Geol.Soc. London, Special Publication 267: 51-63: 0305-8719/06. The Geological Society of London.

Deheyn, D.D., Latz, M.I. (2006). Bioavailability of metals along a contamination gradient in San Diego Bay (California, USA). Chemosphere 63: 818-834

Deheyn, D.D. and Shaffer, L.R. (2007). Saving Venice: Engineering and ecology in the Venice lagoon. Technology in Society 29: 205-213

Deheyn, D.D., Gendreau, P., Baldwin, R, and Latz, M.I. (2005). Evidencefor enhanced bioavailability of trace elements in the marine ecosystem of Deception Island, a volcano in Antarctica. Marine Environmental Research 60(1): 1-33

Donnelly, T.W. (1980). Appendix. Chemical composition of deep sea sediments - Sites 9 through 425, Legs 2 through 54, DSDP. Initial Reports of the Deep Sea Drilling Project, 54, 899-949

Faganelli J, Horvat M, Covelli S, Fajon V, Logar M, Lipej L, Cermelj B.(2003). Mercury and methylmercury in the Gulf of Trieste (northern Adriatic Sea) Sci. Total. Environ., 304: 315-326

Frignani, M., Belluci, L.G., Langone, L., and Muntau, H. (1997). Metal fluxes to the sediments of the northern Venice Lagoon. Marine Chemistry, 58: 275-292

Gieskes, J., Mahn, C., Day, S., Martin J.B., Greinert, J., Rathburn, T., and McAdoo, B. (2005). A study of the chemistry of pore fluids and authigenic carbonates in methane seep environments: Kodiak Trench, Hydrate Ridge, Monterey Bay, and Eel River Basin. Chemical Geology 220 (2005) 329– 345

Han, S., Obraztsova, A., Pretto P, Gieskes, J., Choe, K-Y, Deheyn. D.D., Tebo, B. (2007).Evidences of biogeochemical factors affecting mercury methylation in sediments of the Venice Lagoon, Italy. Environmental Toxicology and Chemistry 26(4): 655-663

Han S., Obraztsova, A., Pretto, P., Deheyn, D.D., Gieskes, J., and Tebo, B. (2008). Sulfide and iron control on mercury speciation in anoxic estuarine sediment slurries. Marine Chemistry 111 (3-4): 214-220

Han Seunghee, Priya Narasingarao, Anna Obraztsova, Joris Gieskes, Aaron C. Hartmann, Bradley M. Tebo, Eric E. Allen and Dimitri D. Deheyn (2010a). Mercury Speciation in Marine Sediments under Sulfate-Limited Conditions. Environ. Sci. Technol., 2010, 44 (10), pp 3752–3757

Han Seunghee, Magali Porrachia, Elisa Volpato, Joris Gieskes, Dimitri Deheyn (2010b). Mercury Concentration and Monomethylmercury Production in Sediment: Effect of Dredged Sediment Reuse on Bioconcentration for Ragworms. Water, Air, & Soil Pollution (24 November 2010), pp. 1-10.

Han Seunghee, Joris Gieskes, Anna Obraztsova, Dimitri D. Deheyn, and Bradley M. Tebo (2011). Relocation effects of dredged sediments on mercury geochemistry: Venice lagoon, Italy. Estuarine, Coastal and Shelf Science, 93: 7-13

Magistrato alle Acque di Venezia-Consorzio Venezia Nuova (MAVCVN; 2003). MELa1-Attività C.2.1 – Indagini sperimentali sui rilasci dei sedimenti e biodisponibilità dei microinquinanti. Rapporto finale sui dati raccolti nel corso delle due campagne sperimentali.

Magistrato alle Acque di Venezia-Consorzio Venezia Nuova (MAVCVN; 2004a). Evoluzione temporal dell'inquinamento antropico dei sediment, Technical Report A.2.1. Venice, Italy.

Magistrato alle Acque di Venezia-Consorzio Venezia Nuova (MAVCVN; 2004b). ICSEL A.1. Valutazione integrata dello stato qualitativo attuale dei sedimenti lagunari superficiali. Technical Report

Piani, R., Covelli, S., Biester, H. (2005). Mercury contamination in Marano Lagoon (Northern Adriatic sea, Italy): Source identification by analyses of Hg phases. Applied Geochemistry 20: 1546-1559.

Rothwell, R.G. (2006). New techniques in sediment core analysis. Geol.Soc. London, Special Publication 267: 51-63: 0305-8719/06. The Geological Society of London.

Rothwell, R.G. and Rack, F.R. (2006). New techniques in sediment core analysis: an introduction. In: Rothwell,R.G. (2006). New techniques in sediment core analysis. Geol.Soc. London, Special Publication 267: 1-29: 0305-8719/06. The Geological Society of London.

Rothwell, R.G., Hoogakker, B., Thomson, J., Croudace, I.W. and Frenz, M. (2006). Turbidite emplacement on the southern Balearic Abyssal Plain (western Mediterranean Sea) during Marine Isotope Stages 1-3: an application of ITRAX/XRF scanning of sediment cores to lithostratigraphic analysis. In: Rothwell,R.G. (2006). New techniques in sediment core analysis. Geol.Soc. London, Special Publication 267: 79-98: 0305-8719/06. The Geological Society of London.

Shapiro, L. (1967). Rapid analysis of rocks and minerals by a single solution method. U.S. Geol. Survey Prof. Paper 575B.pp.B187-191

Shapiro, L. and Brannock,W.W. (1962). Rapid analysis of silicate, carbonate, and phosphate rocks. U.S. Geol. Survey Bulletin, 11144-A.

Sfriso A , Facca C., and Marcomini A. (2005a). Sedimentation rates and erosion processes in the lagoon ofVenice. Environment International 31: 983-992

Sfriso A., Favaretto M., Ceoldo S., Facca C., and Marcomini A. (2005b). Organic carbon changes in the surface sediments of the Venice lagoon. Environment International 31: 1002-1010

Thompson, J., Croudace, I.W., Rothwell, R.G. (2006). A geochemical application of the ITRAX scanning of a sediment core containing eastern Mediterranean sapropel. In: Rothwell,R.G. (2006). New techniques in sediment core analysis. Geol.Soc. London, Special Publication 267: 51-63: 0305-8719/06. The Geological Society of London.

Table 1

Sediment Classification for Trace Metals

Concentrations in mg/Kg dry weight

Element	ERL*	ERM*	Class A	Class B	Limit Class C
Zn	150	410	200	400	3000
Cu	34	270	40	50	400
Pb	47	218	45	100	500
Ni	21	52			
Hg	0.15	0.71	0.5	2	10

ERL = Effects Range Low; *ERM = Effects Range Median

For an understanding of ERL/ERM see:
www.gfredlee.com/Sediment/oconnor.pdf

Table 2

Average Element/Iron ratios Cores SS1, SSO, S2, and C SIOSED

	K/Fe	Ti/Fe	Rb/Fe	Zn/Fe	Pb/Fe	Co/Fe	Ni/Fe
SS1	0.031	0.021	0.032 to 0.027	0.004	0.003	0.007	0.004
SSO	0.033	0.020	0.030	0.006	0.004	0.012	0.0057
S2	0.032	0.022	0.029	0.006 to 0.0075	0.003	0.008	0.0033
C	0.030	0.020 to 0.017	0.029	0.020 to 0.10	0.006 to 0.0095	0.008 to 0.012	0.003 to 0.0033
Average	0.0315 ± 0.002	0.021 ± 0.002	0.030 ± 0.0015				

K, Ti, Rb Lithogenic – essentially constant ratios

Zn/Fe Major pollutant in C (up to 28 times SS1)
Pb/Fe Next major pollutant in C (up to 4.5 times SS1)
Co/Fe Small changes
Ni/Fe Small changes (less than 20 %)

Note: Elemental ratios are for XRF intensity counts and do not represent real elemental concentration ratios.

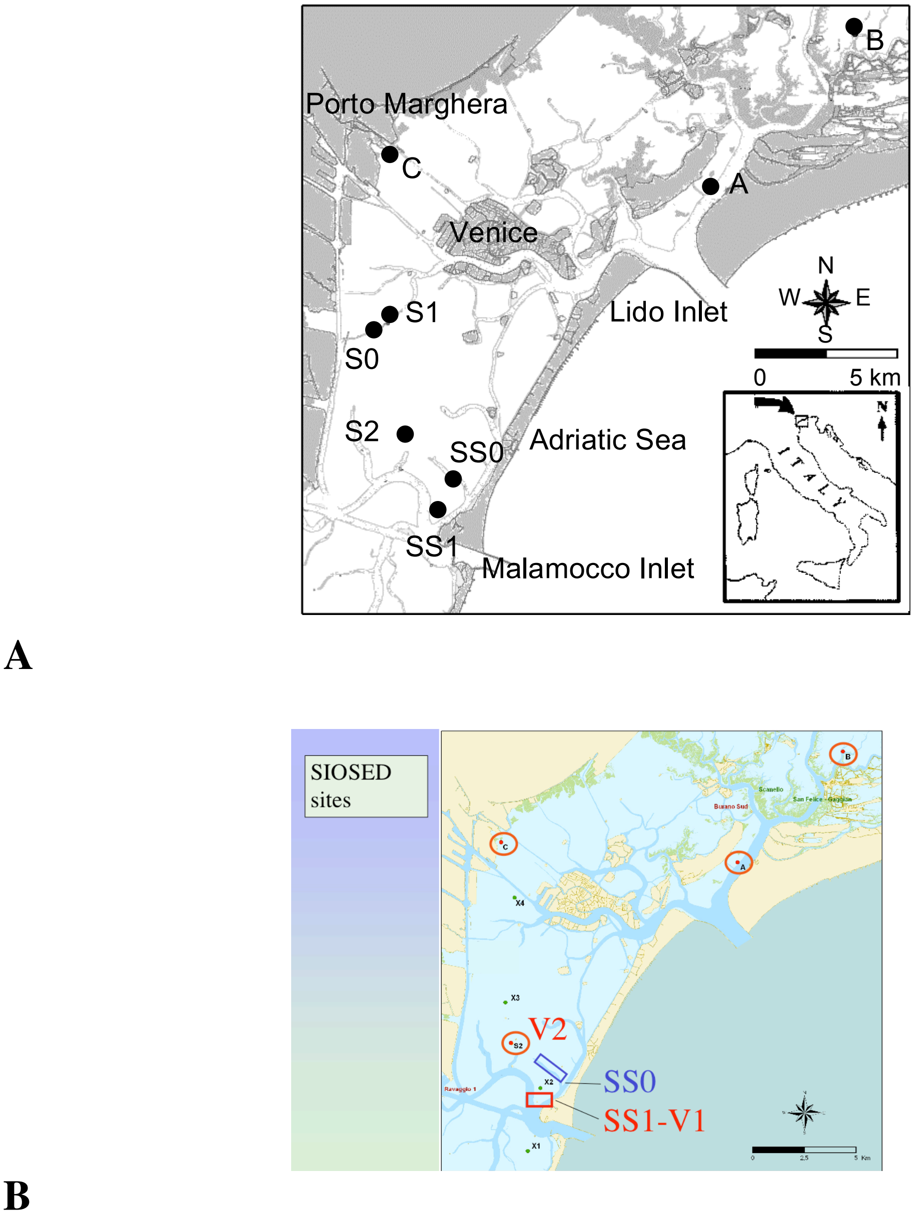


Figure 1

Map showing the principal coring sites in Venice Lagoon.
SSO: Dredged Canal near Malamocco Inlet; SS1 and S2: Sites of artificial banks V1 and V2

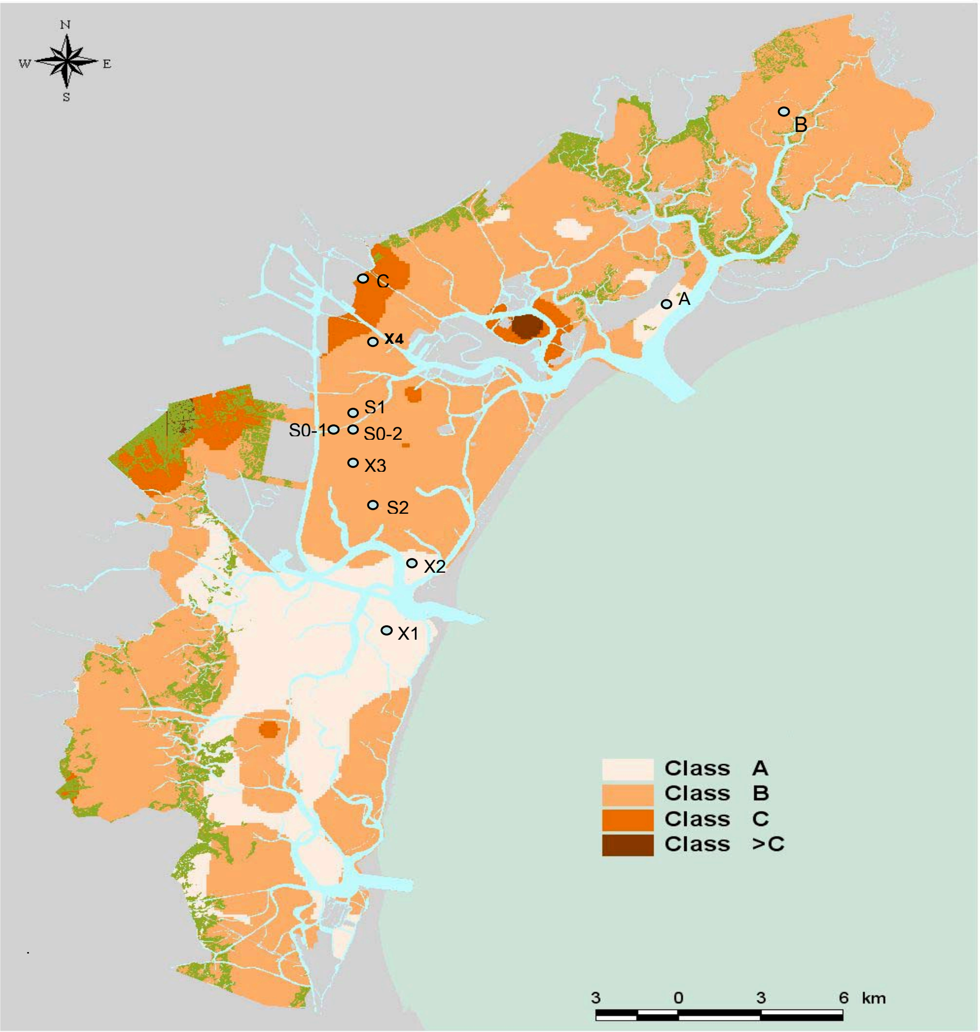
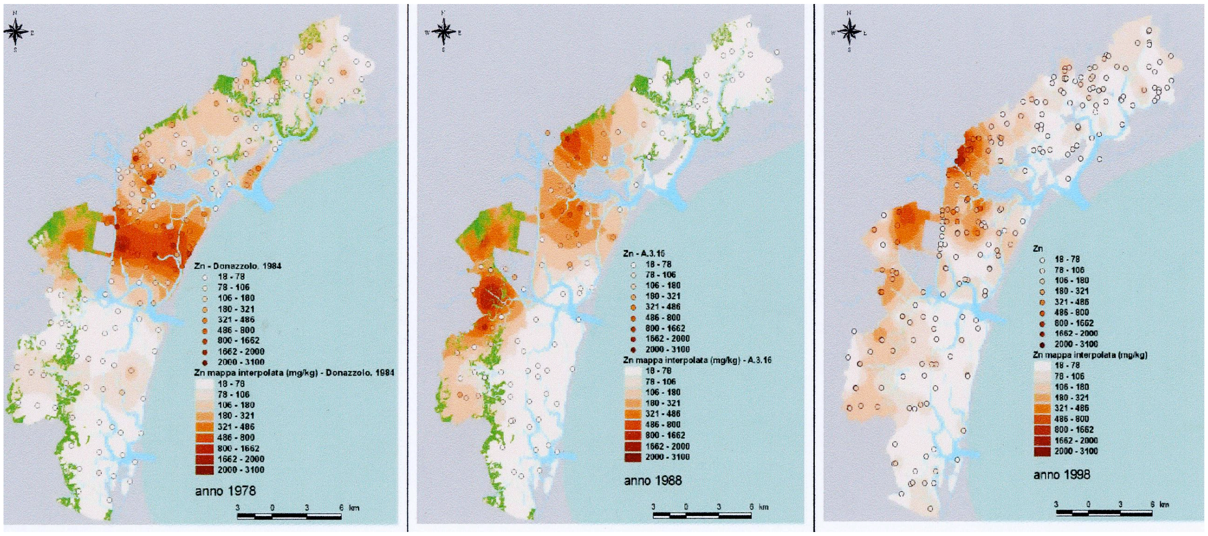


Figure 2

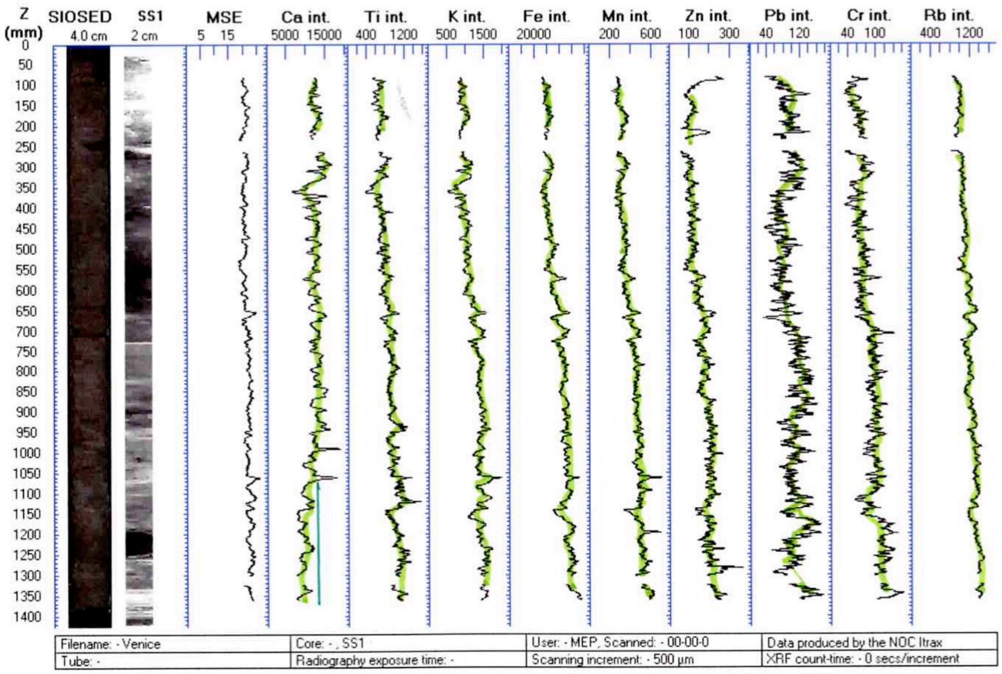
Map of Venice Lagoon with designated classifications with respect to potential contamination (see also Table 1). Stations with x are stations for the studies of benthic foraminifera.



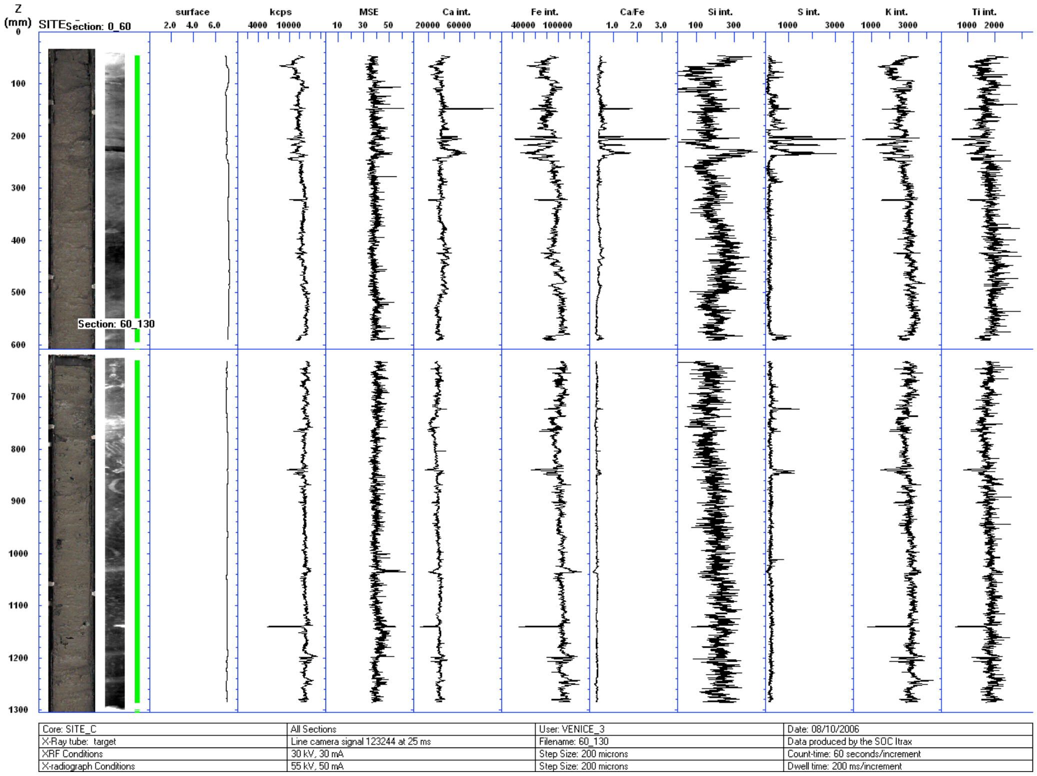
1978 **1988** **1998**

Figure 3

Surface sediment Zinc concentrations in Venice Lagoon: 1978, 1988, and 1998
Note rapid changes with time.



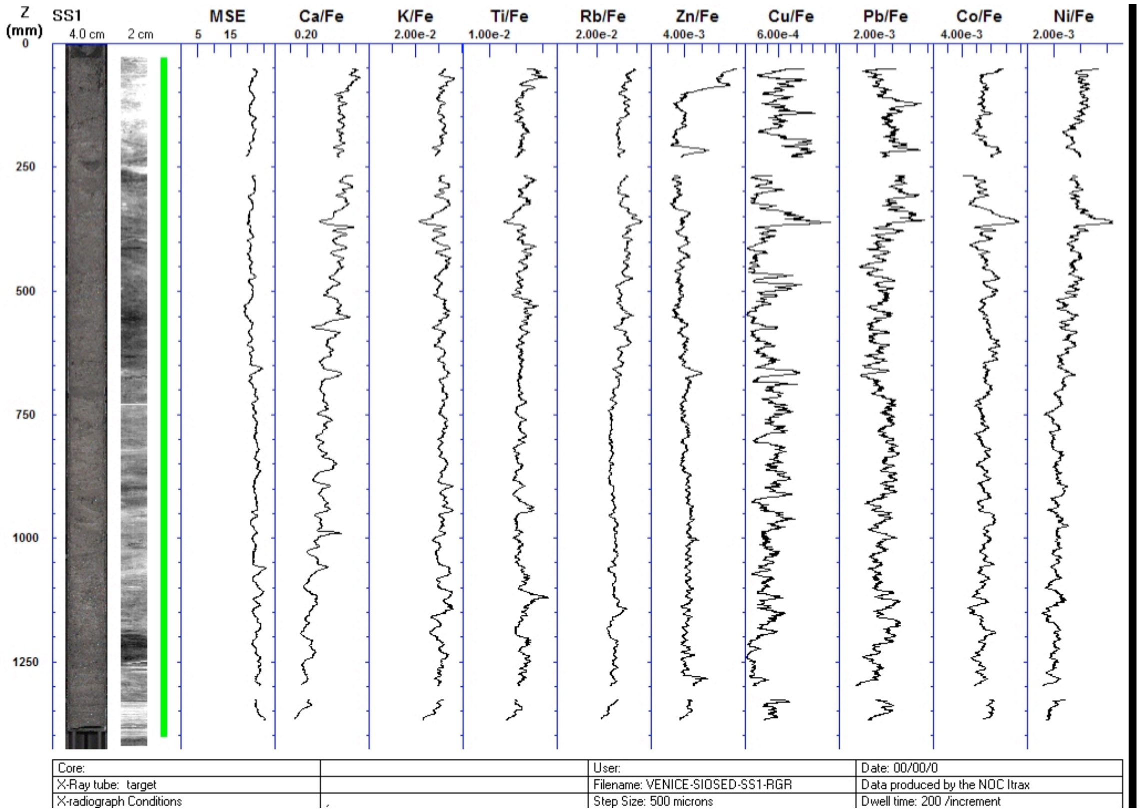
Site SS1



Site C

Figure 4

Downcore XRF intensity plots for cores SS1 and C. Note large differences in count rates, depending on instrumental settings.

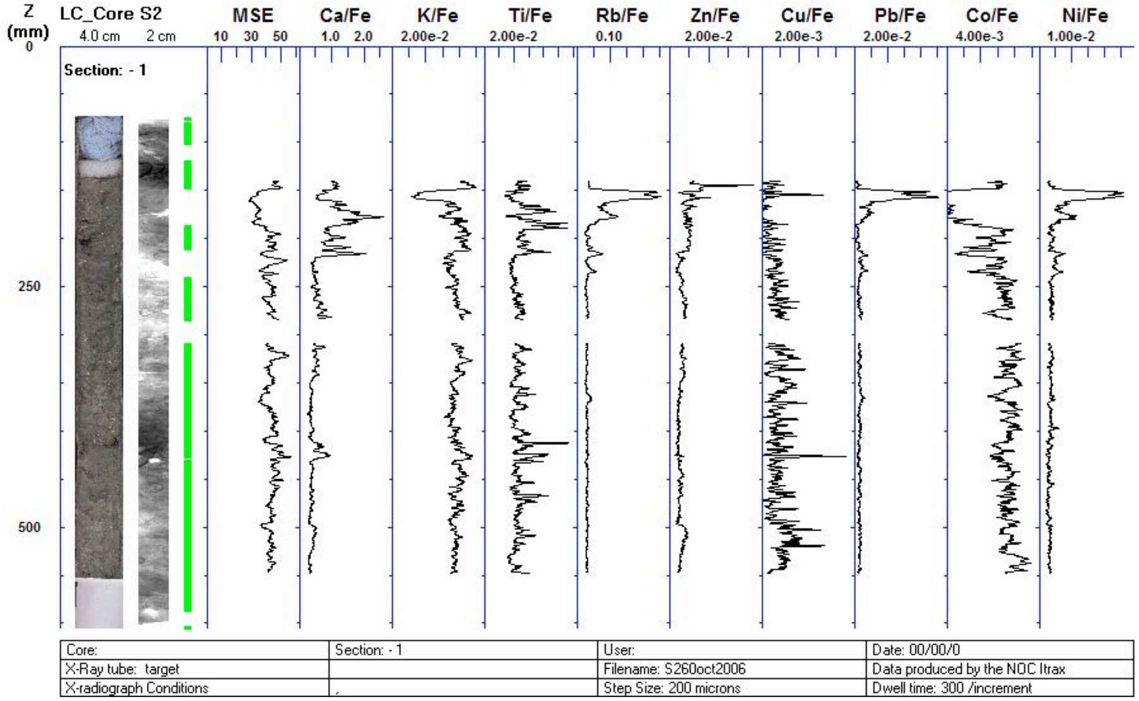


Core:
X-Ray tube: target
X-radiograph Conditions
User:
Filename: VENICE-SIOSED-SS1-RGR
Step Size: 500 microns
Date: 00/00/0
Data produced by the NOC Itrax
Dwell time: 200 /increment

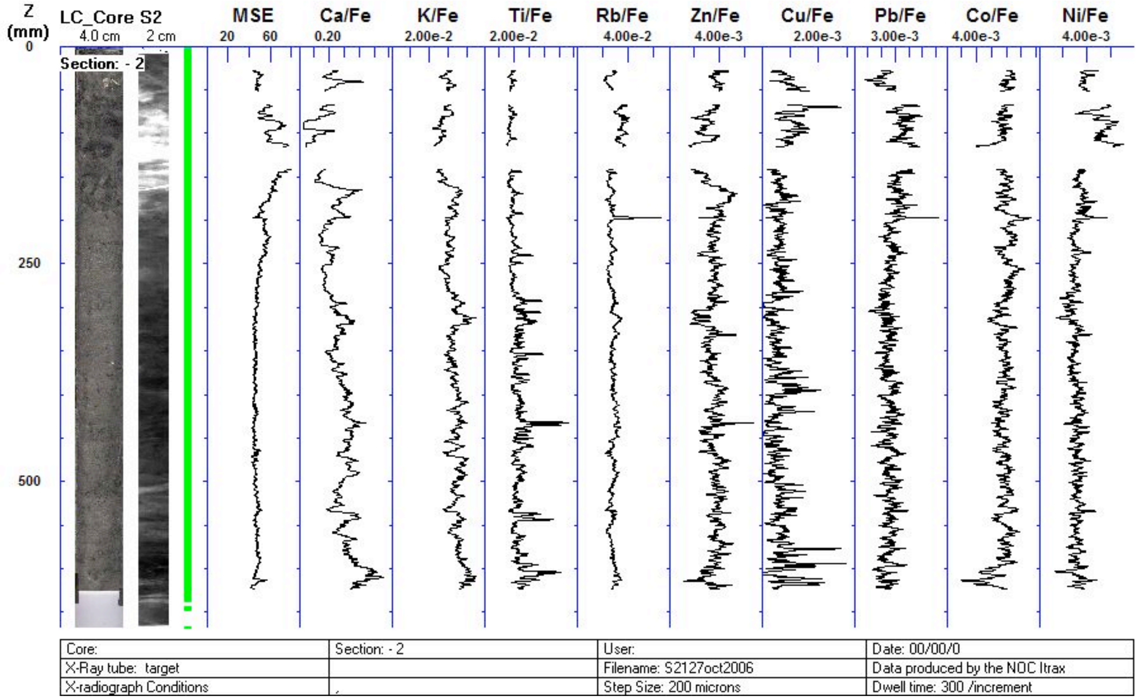
SS1

Figure 5

Downcore element over Fe intensity ratios Core SS1.



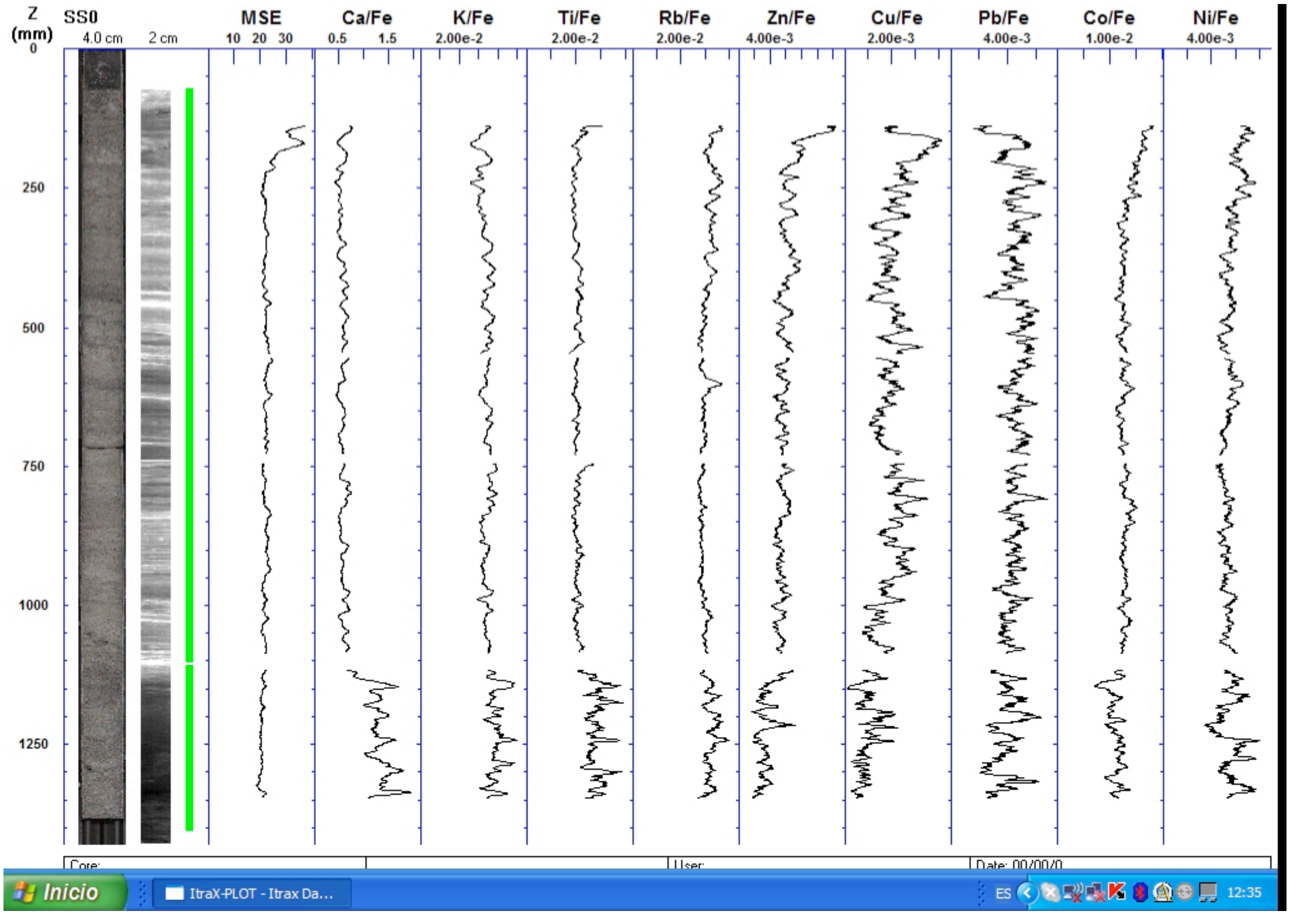
S2 Upper



S2 lower

Figure 6

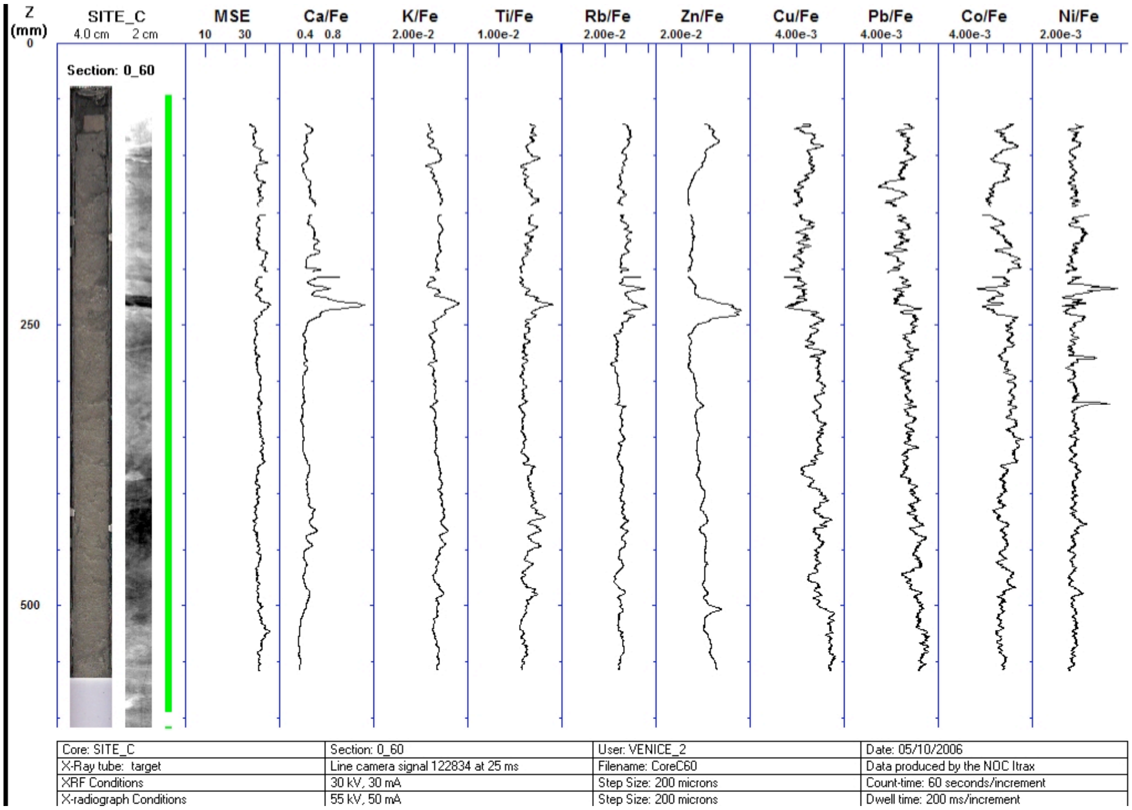
Downcore element over Fe intensity ratios Core S2



SSO

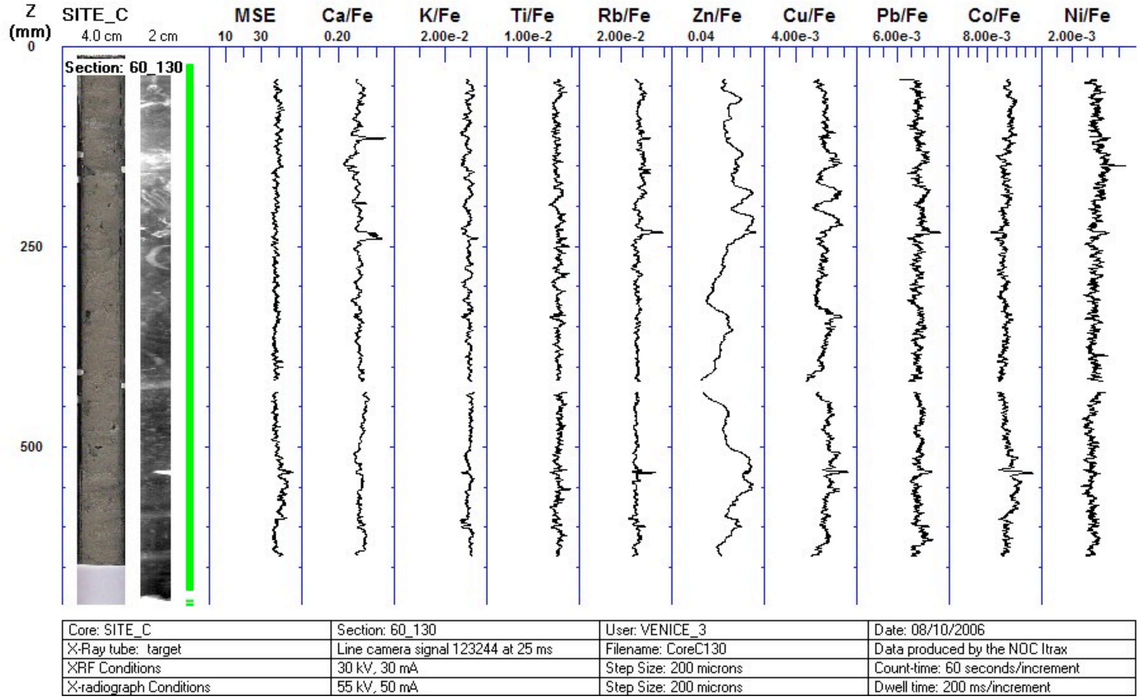
Figure 7

Downcore element over Fe intensity ratios Core SSO.



Core: SITE_C	Section: 0_60	User: VENICE_2	Date: 05/10/2006
X-Ray tube: target	Line camera signal 122834 at 25 ms	Filename: CoreC60	Data produced by the NOC Itrax
XRF Conditions	30 kV, 30 mA	Step Size: 200 microns	Count-time: 60 seconds/increment
X-radiograph Conditions	55 kV, 50 mA	Step Size: 200 microns	Dwell time: 200 ms/increment

C upper



Core: SITE_C	Section: 60_130	User: VENICE_3	Date: 08/10/2006
X-Ray tube: target	Line camera signal 123244 at 25 ms	Filename: CoreC130	Data produced by the NOC Itrax
XRF Conditions	30 kV, 30 mA	Step Size: 200 microns	Count-time: 60 seconds/increment
X-radiograph Conditions	55 kV, 50 mA	Step Size: 200 microns	Dwell time: 200 ms/increment

C lower

Figure 8

Downcore element over Fe intensity ratios Core C. Note large increases in Zn/Fe ratios.

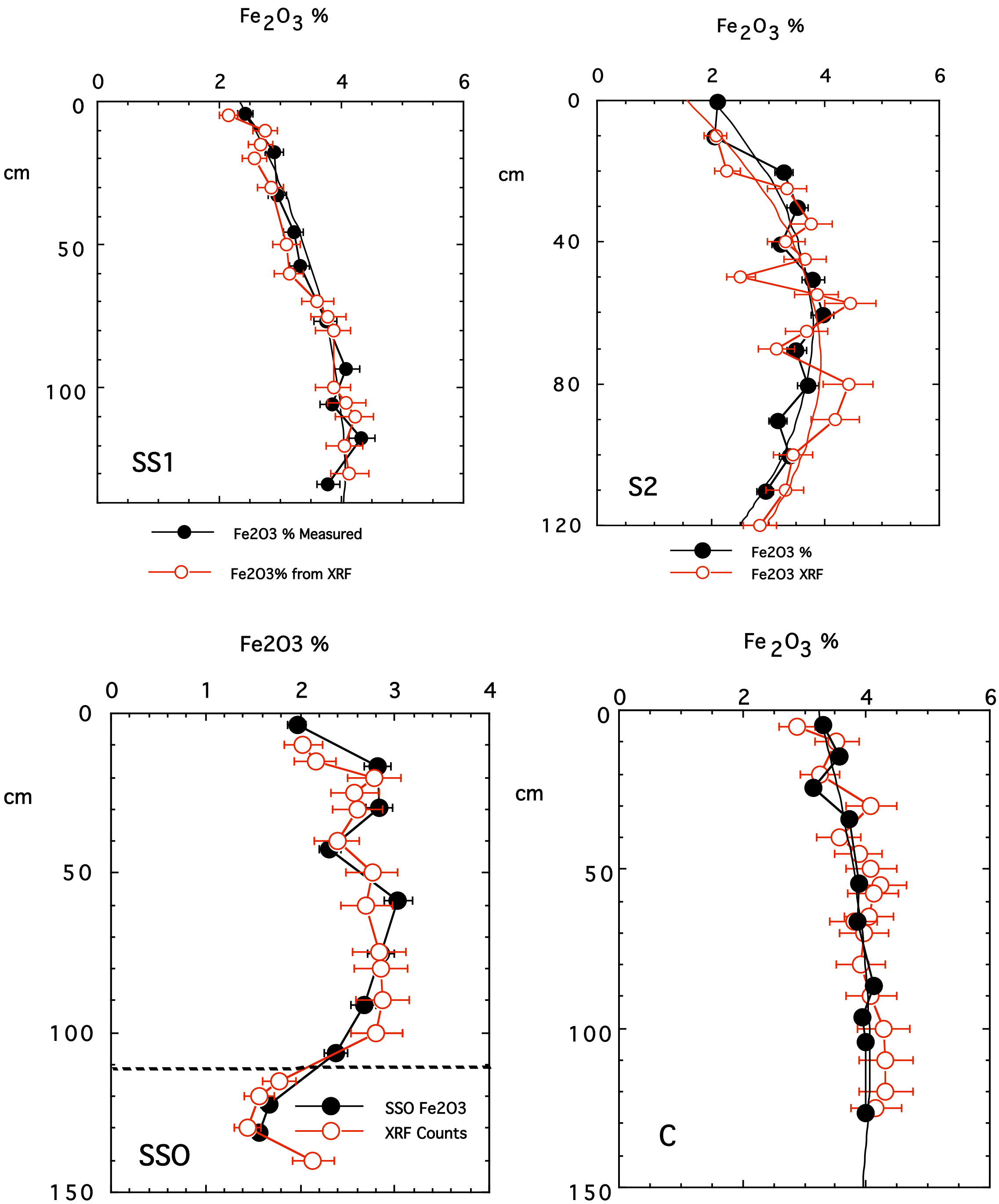


Figure 9

Concentrations of Fe_2O_3 in Cores SS1, S2, SSO, and C.
Dark circles measured by total sediment digestion; open circles Fe_2O_3 contents from adjustment of XRF intensities to fit measured values.

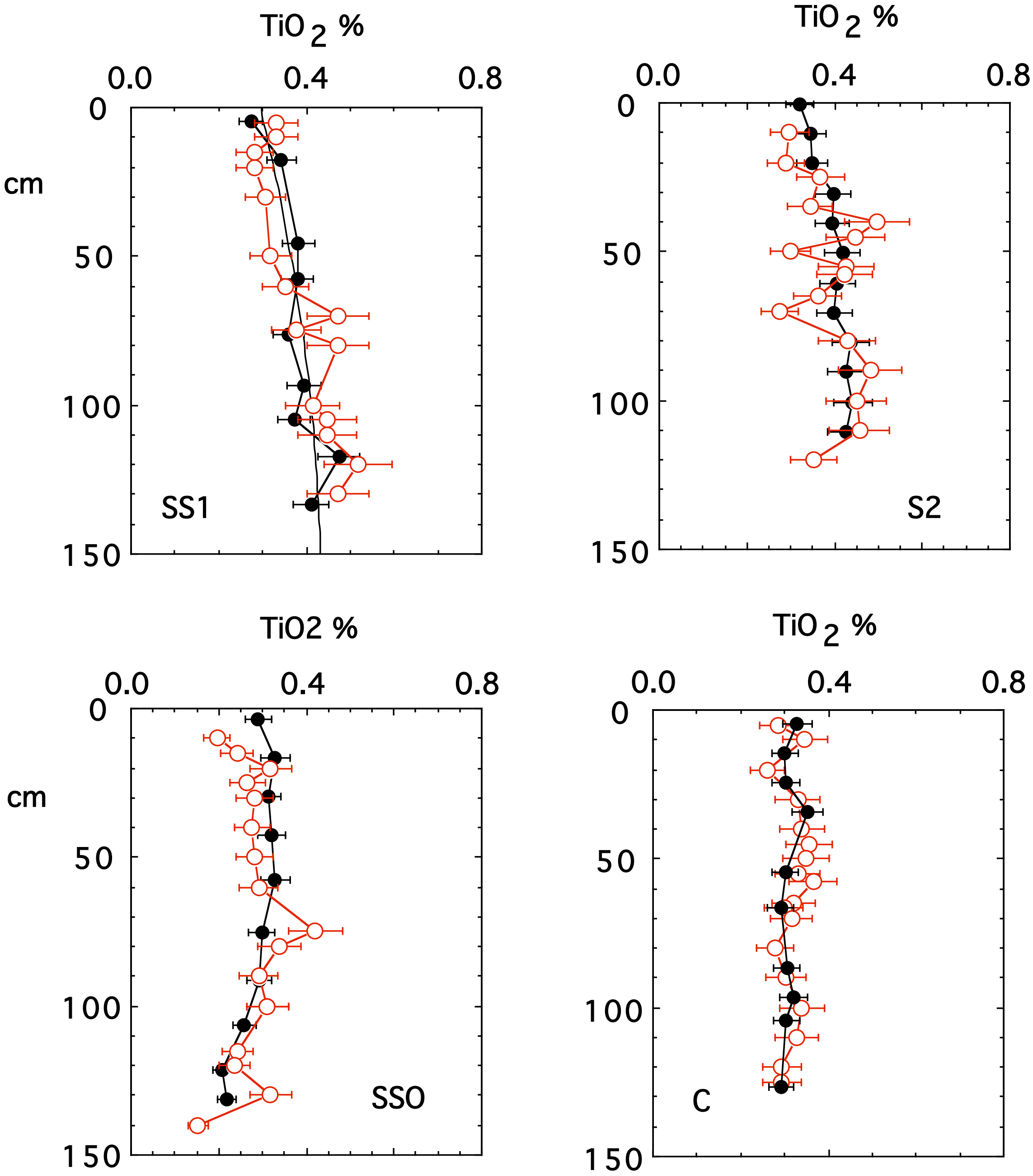


Figure 10

Concentrations of TiO_2 in Cores SS1, S2, SSO, and C.
Dark circles measured by total sediment digestion; open circles
TiO_2 contents from adjustment of XRF intensities to fit measured values.

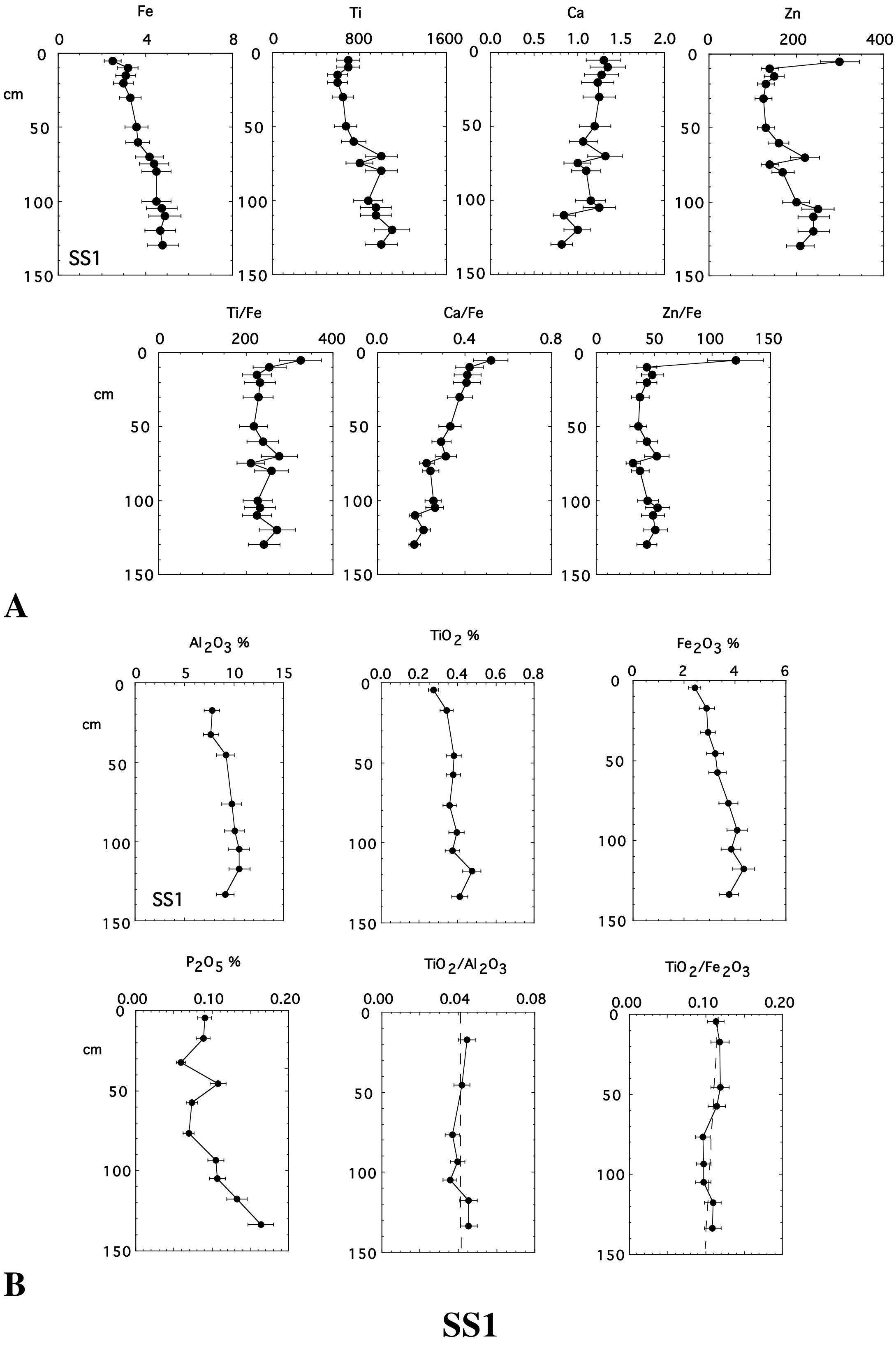
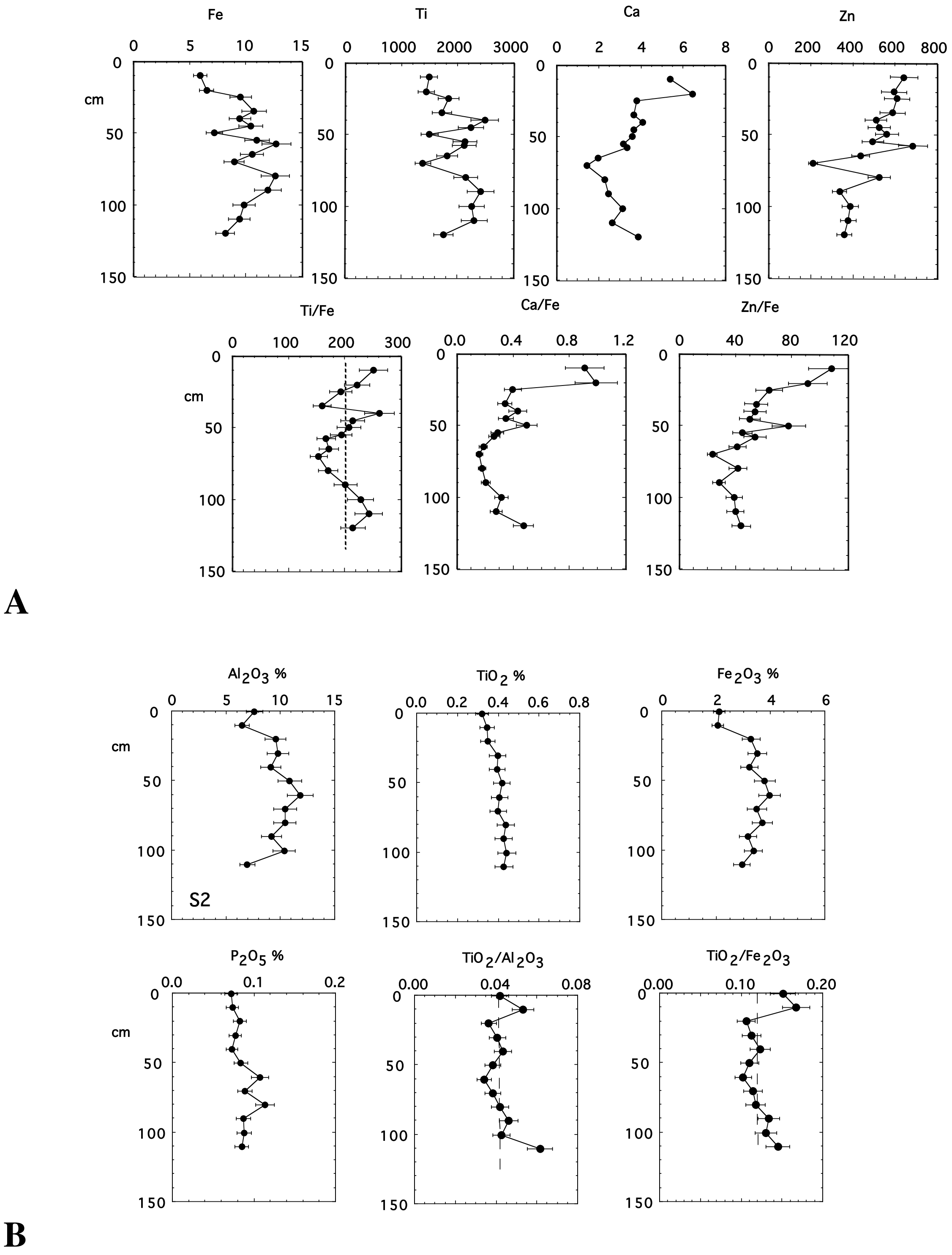


Figure 11

Site SS1: A: Depth profiles derived from XRF data Fe, Ti, Ca, and Zn; in addition element over Fe ratios. B: Total digestion chemistry of major element



S2

Figure 12

Site S2: A: Depth profiles derived from XRF data Fe, Ti, Ca,
and Zn, in addition element over Fe ratios. B: Total digestion chemistry of major elements

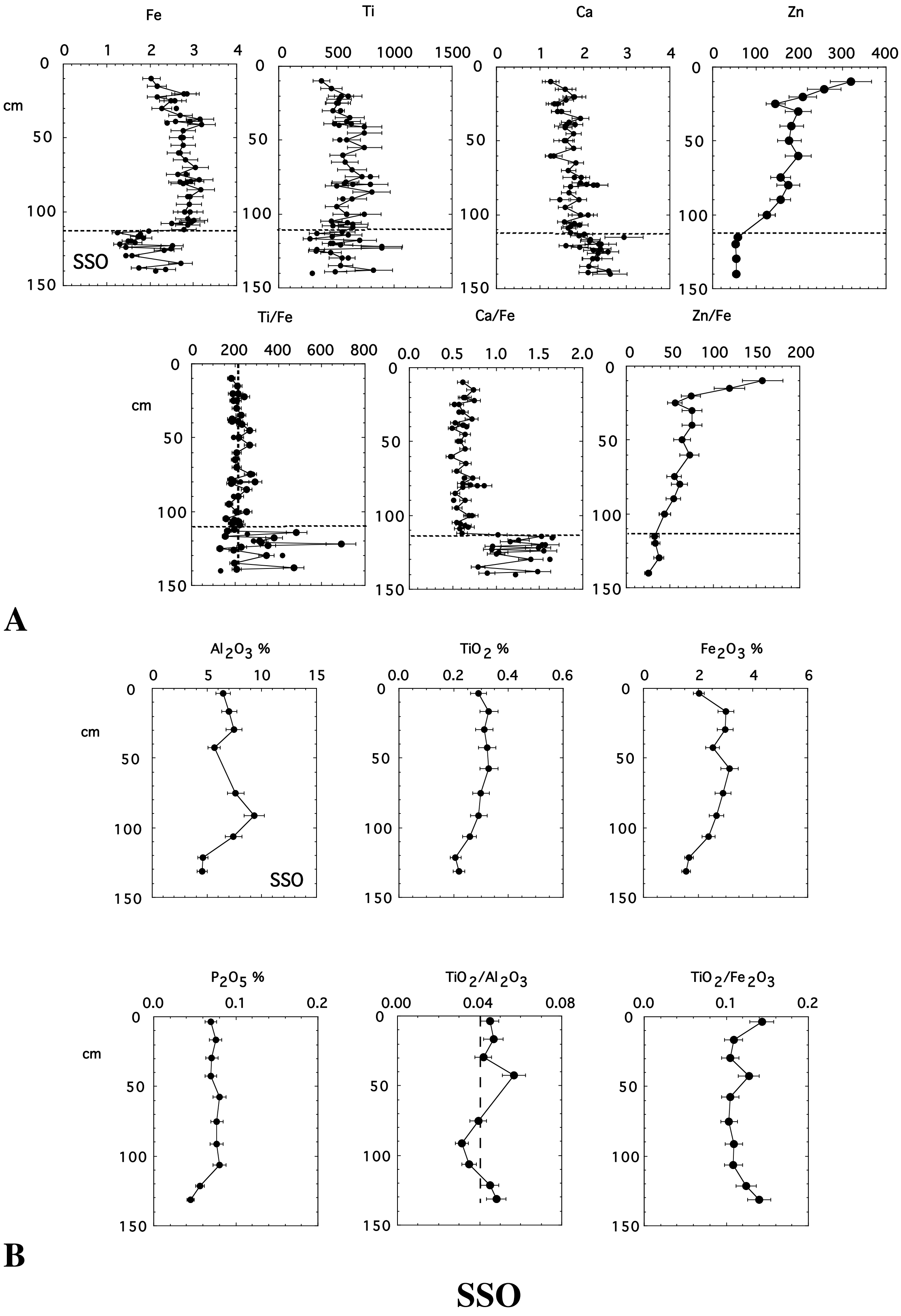


Figure 13

Site SSO: A: Depth profiles derived from XRF data Fe, Ti, Ca, and Zn, in addition element over Fe ratios. B: Total digestion chemistry of major elements

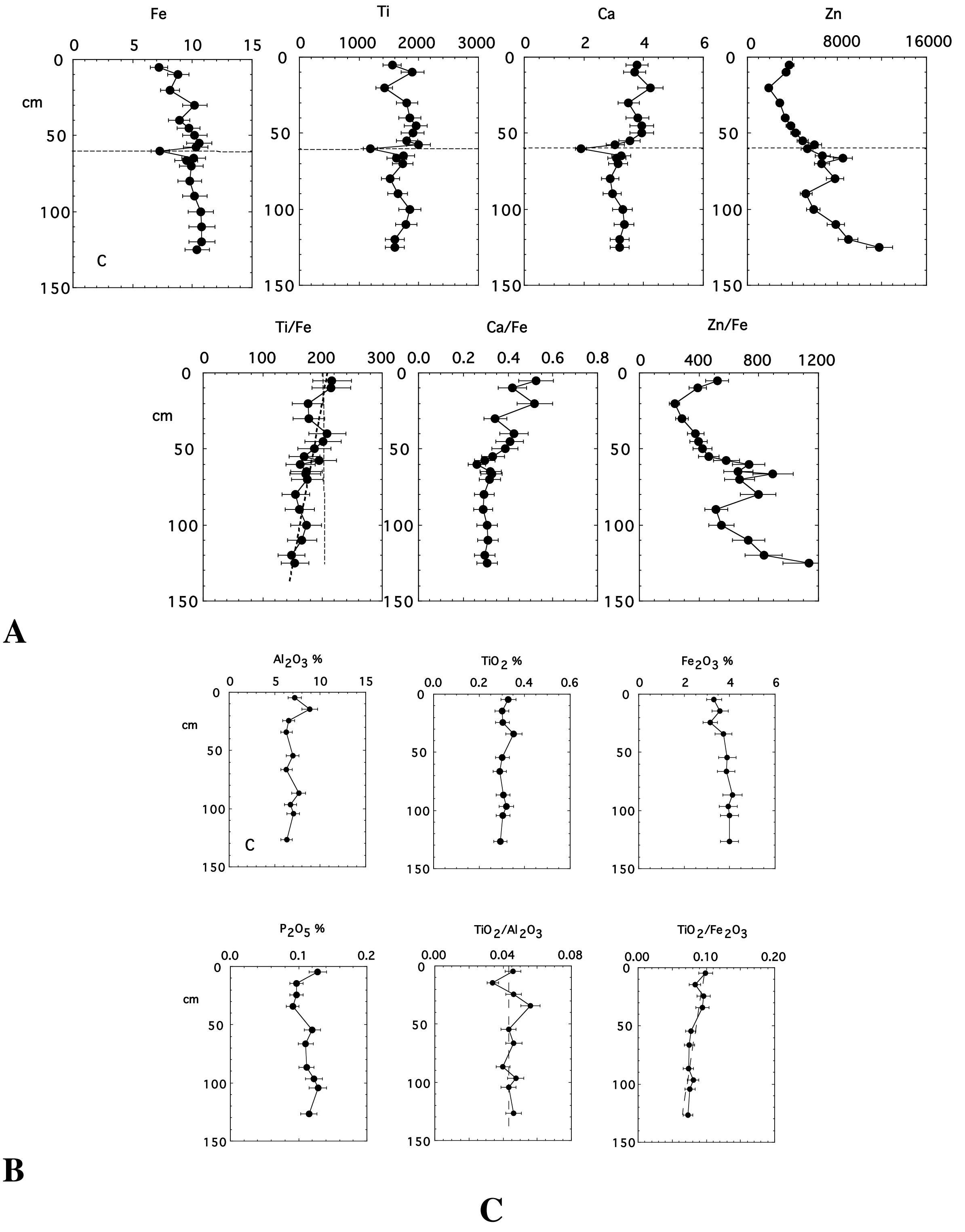
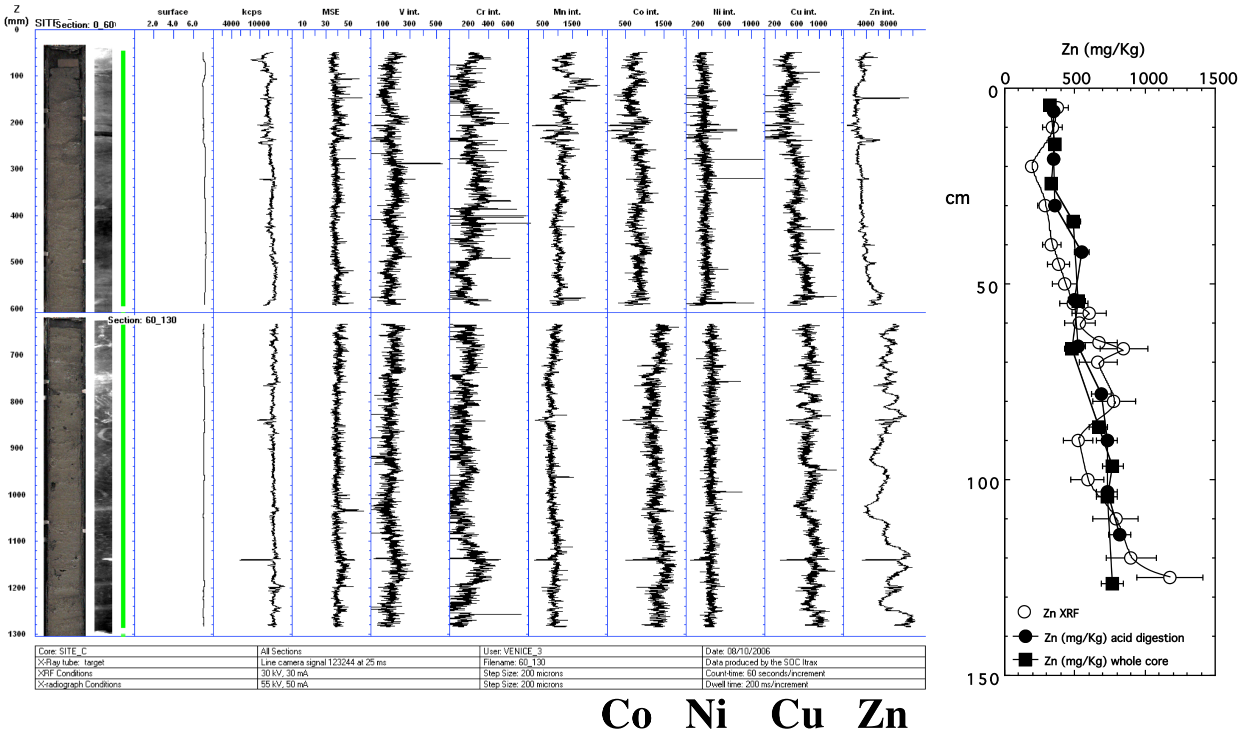


Figure 14

Site C: A: Depth profiles derived from XRF data Fe, Ti, Ca, and Zn, in addition element over Fe ratios. B: Total digestion chemistry of major elements



Core: SITE_C	All Sections	User: VENICE_3	Date: 08/10/2006
X-Ray tube: target	Line camera signal 123244 at 25 ms	Filename: 60_130	Data produced by the SOC Itrax
XRF Conditions	30 kV, 30 mA	Step Size: 200 microns	Count-time: 60 seconds/increment
X-radiograph Conditions	55 kV, 50 mA	Step Size: 200 microns	Dwell time: 200 ms/increment

<u>Open symbols</u>: XRF Trace derived

<u>Closed symbols</u>: Analytical Concentrations

Site C

Figure 15

XRF traces of trace metals in Core C; to the right actual Zn concentrations and XRF adjusted Zn concentrations. Note greater detail of the XRF trace.

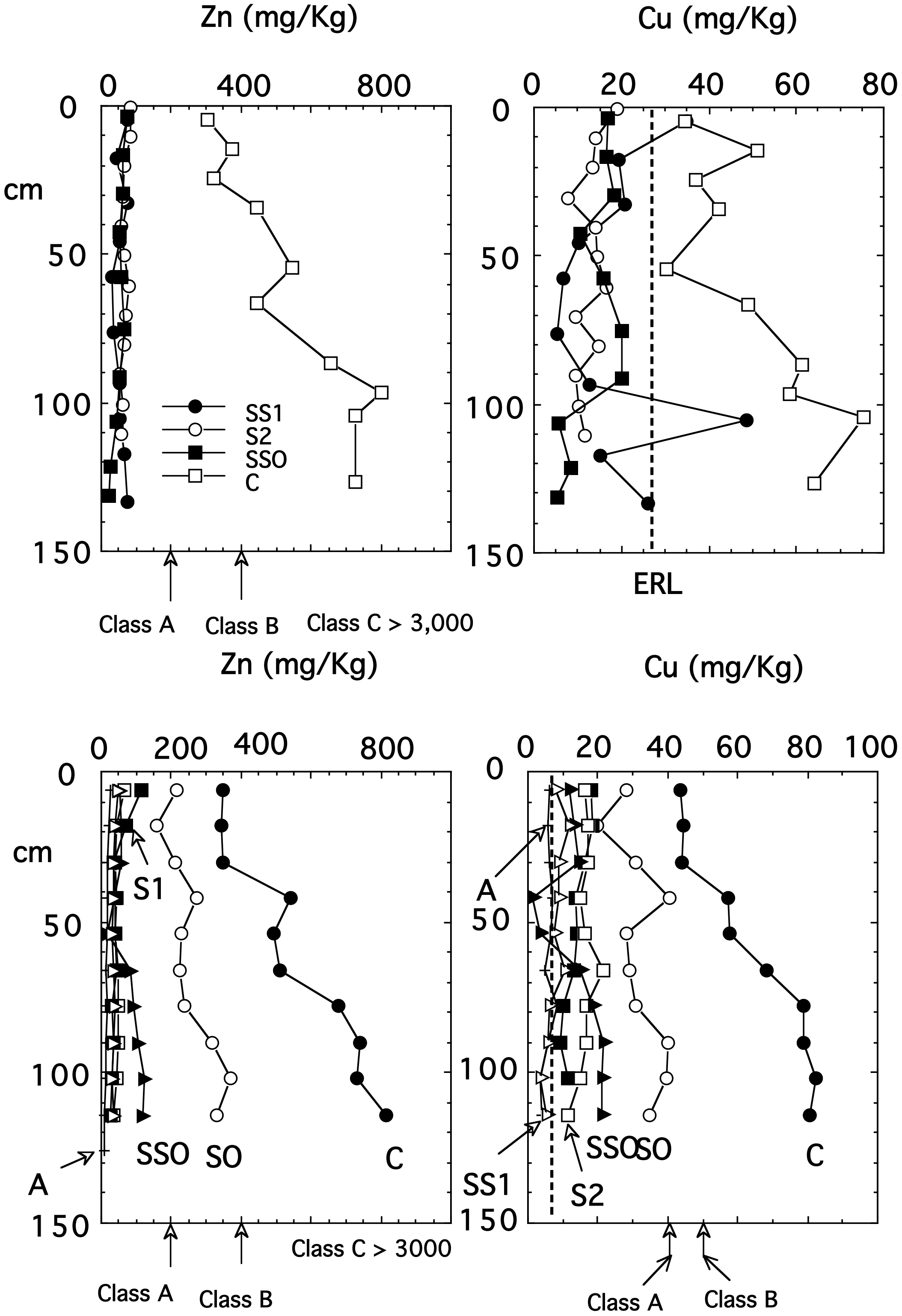


Figure 16

Zinc and Copper concentrations in sediments of SIOSED long cores. Upper section: from whole sediment digestion; lower section: data from nitric acid sediment digestion. Whole sediment core is diiferent from the core used for the nitric acid digestion samples.

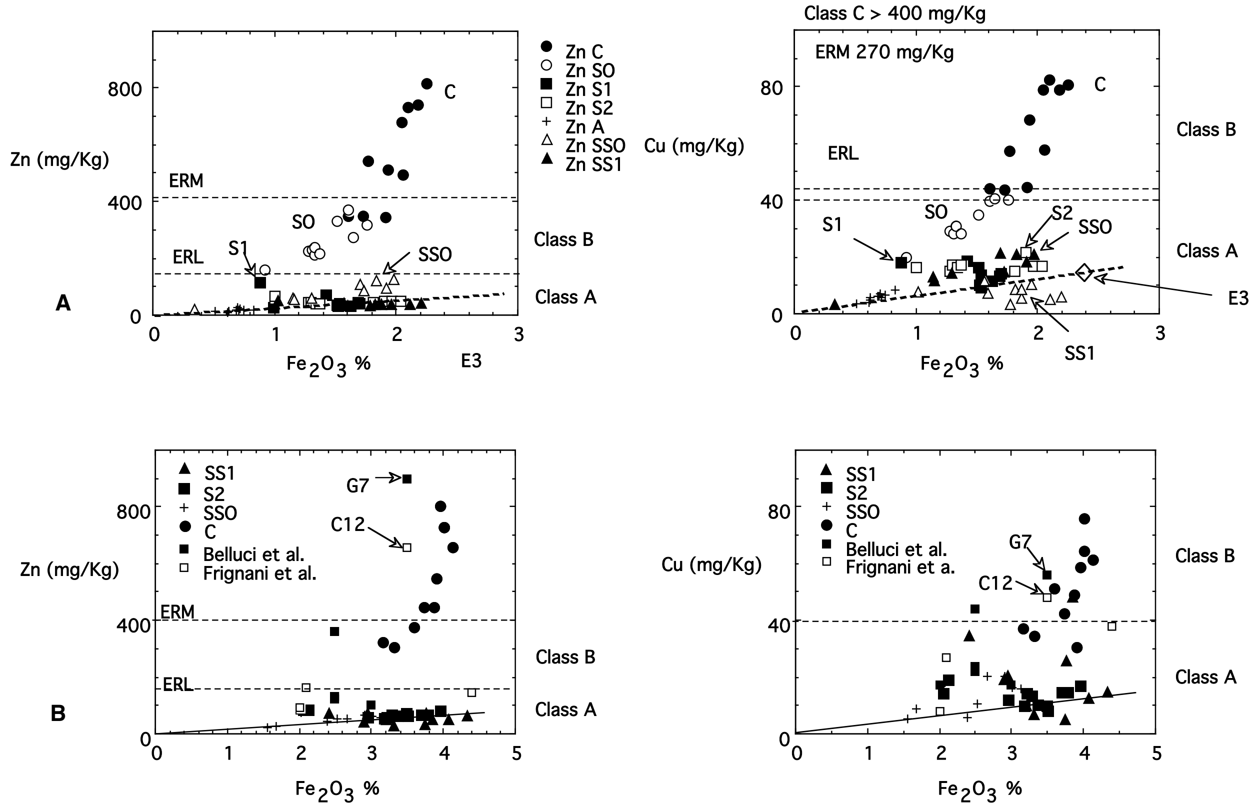


Figure 17

Zn and Cu *versus* Fe_2O_3 in sediments of SIOSED long cores.
Note similarities in trace metals (upper figure from HNO_3 dissolution; lower figure total sediment dissolution), but lower Fe_2O_3 values. Note zonation limits: Zn ERL = 40 mg/Kg, ERM = 400 mg/Kg; Cu ERL = 40 mg/Kg, ERM = 270 mg/Kg

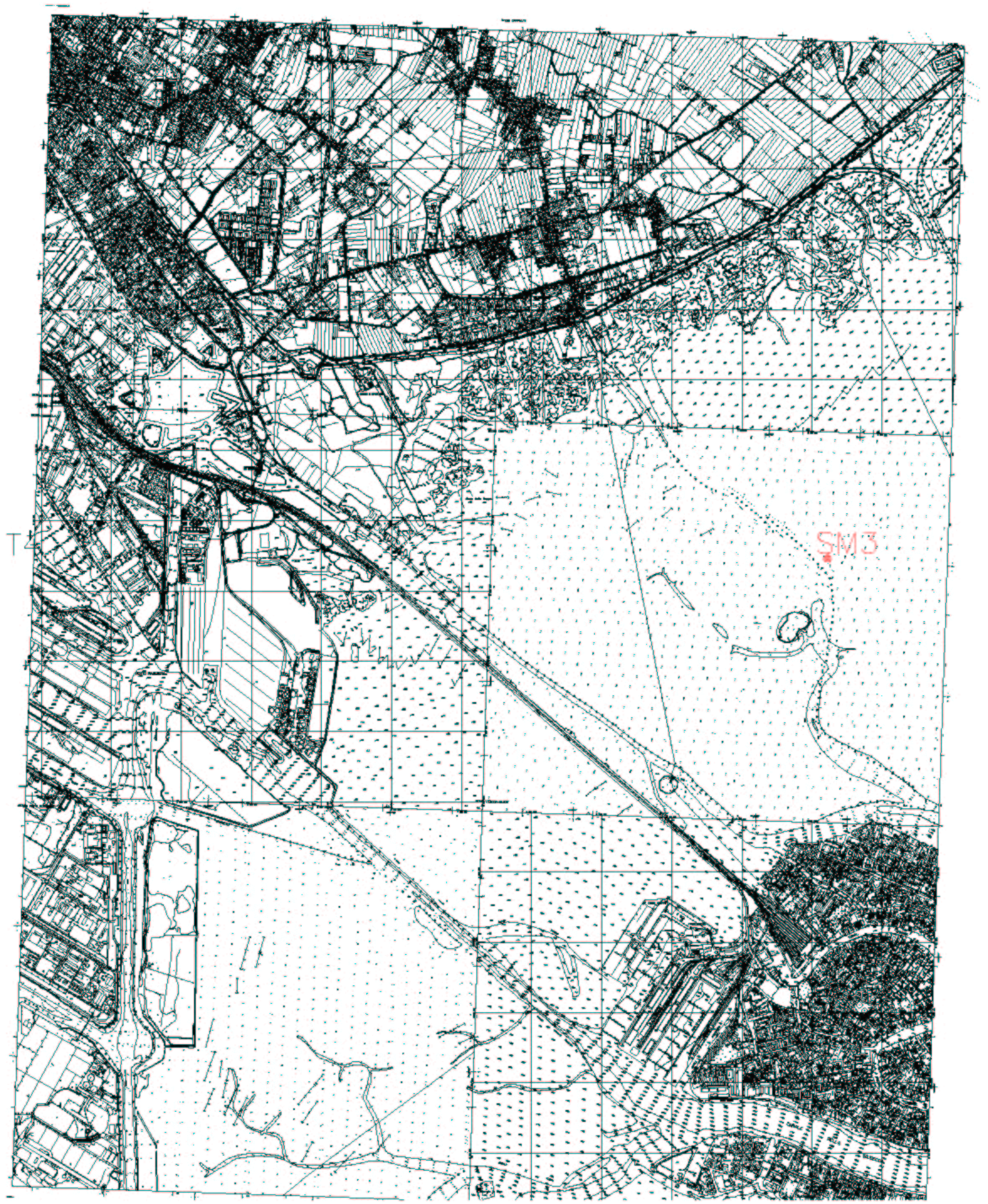


Figure 18

Drill Hole SM3 located to the northwest of Venice.

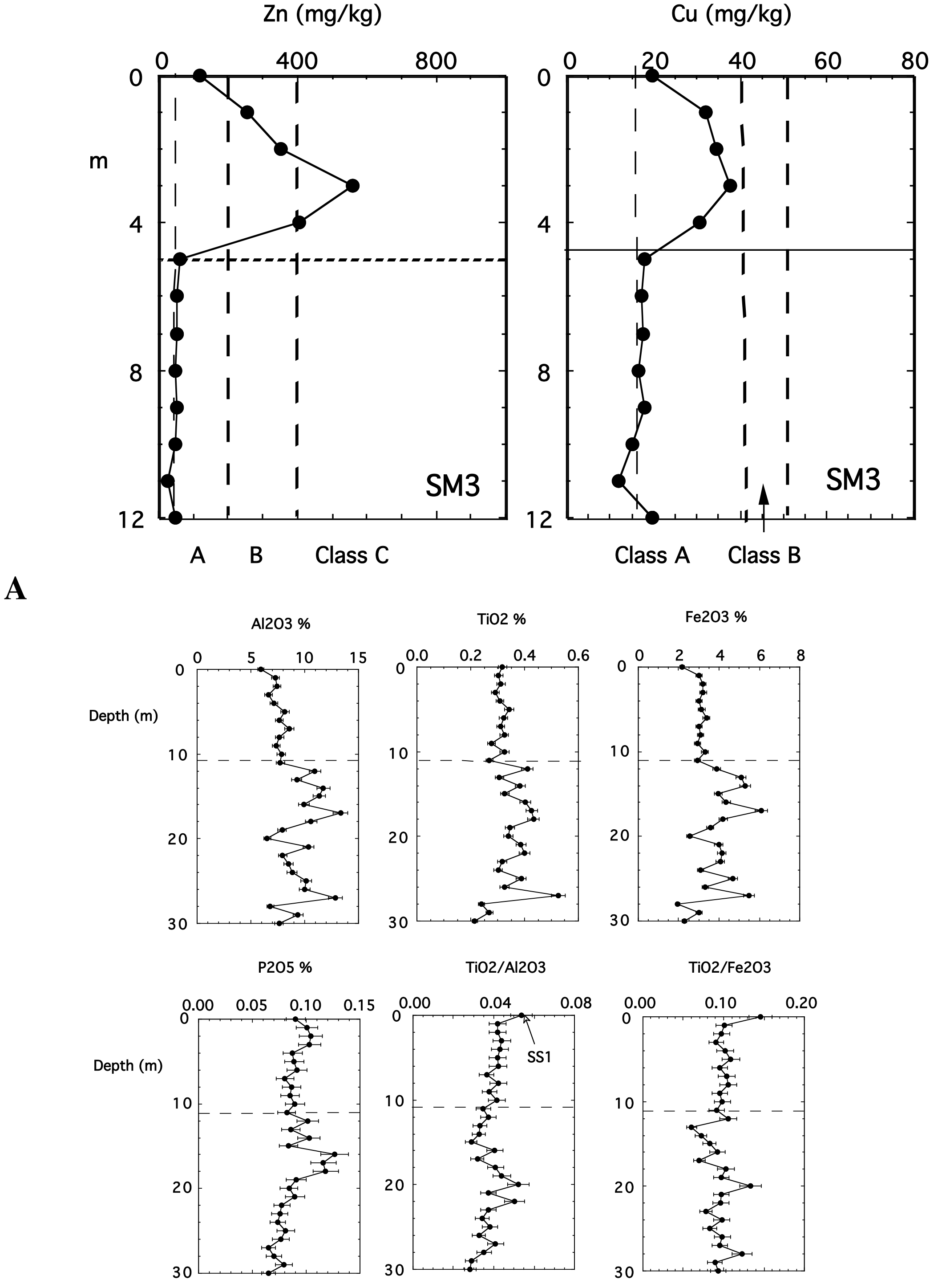


Figure 19

Chemistry of sediments of Drill Hole SM3.

A: Zinc and Copper;

B: Major element chemistry based on total sediment dissolution. Note: sediments below 11m are pre-lagoonal in nature.

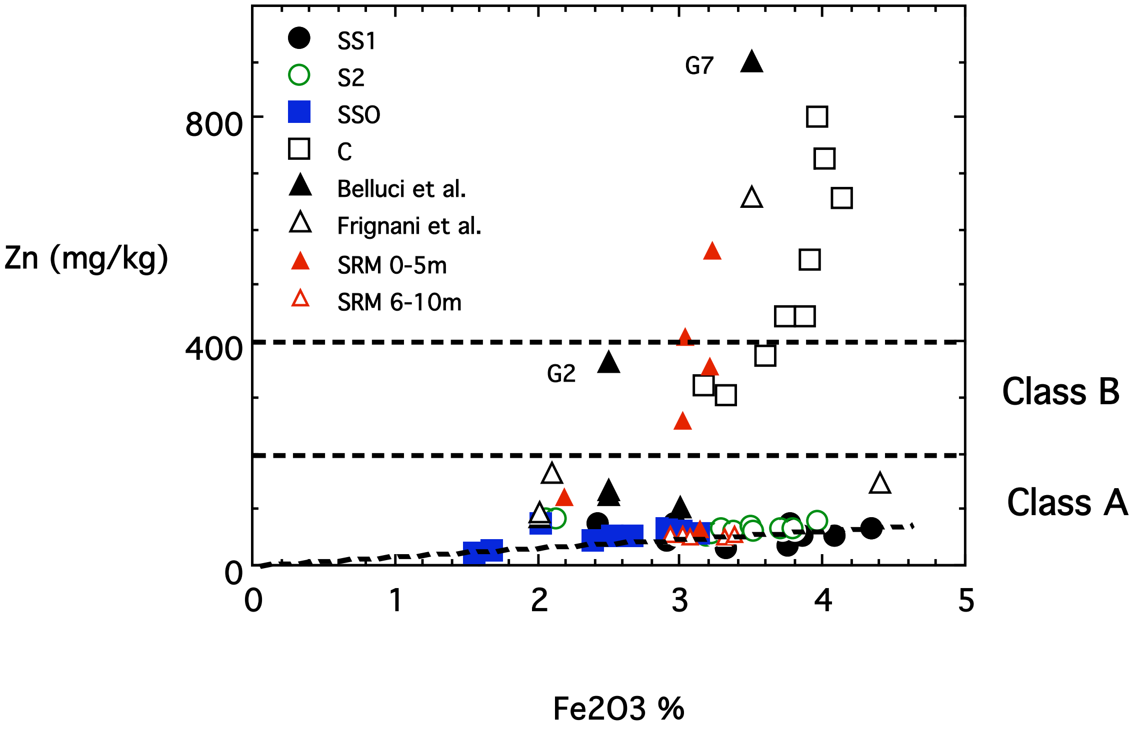
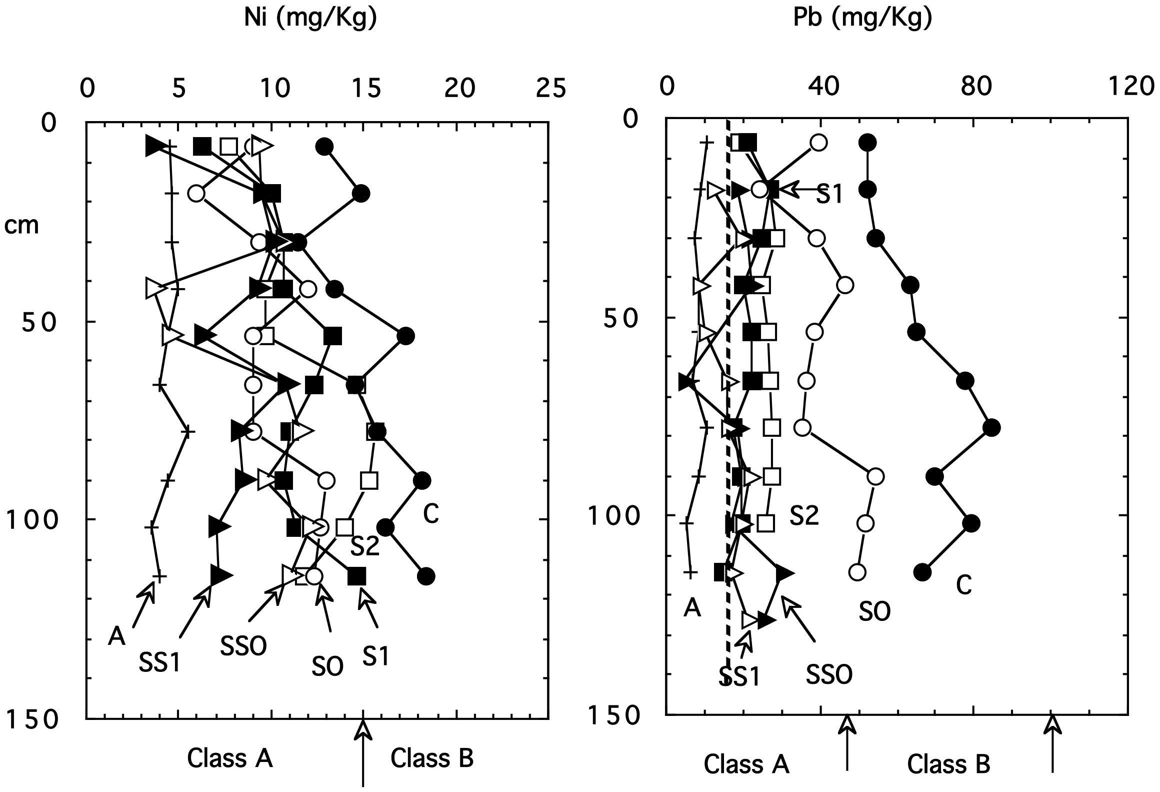


Figure 20

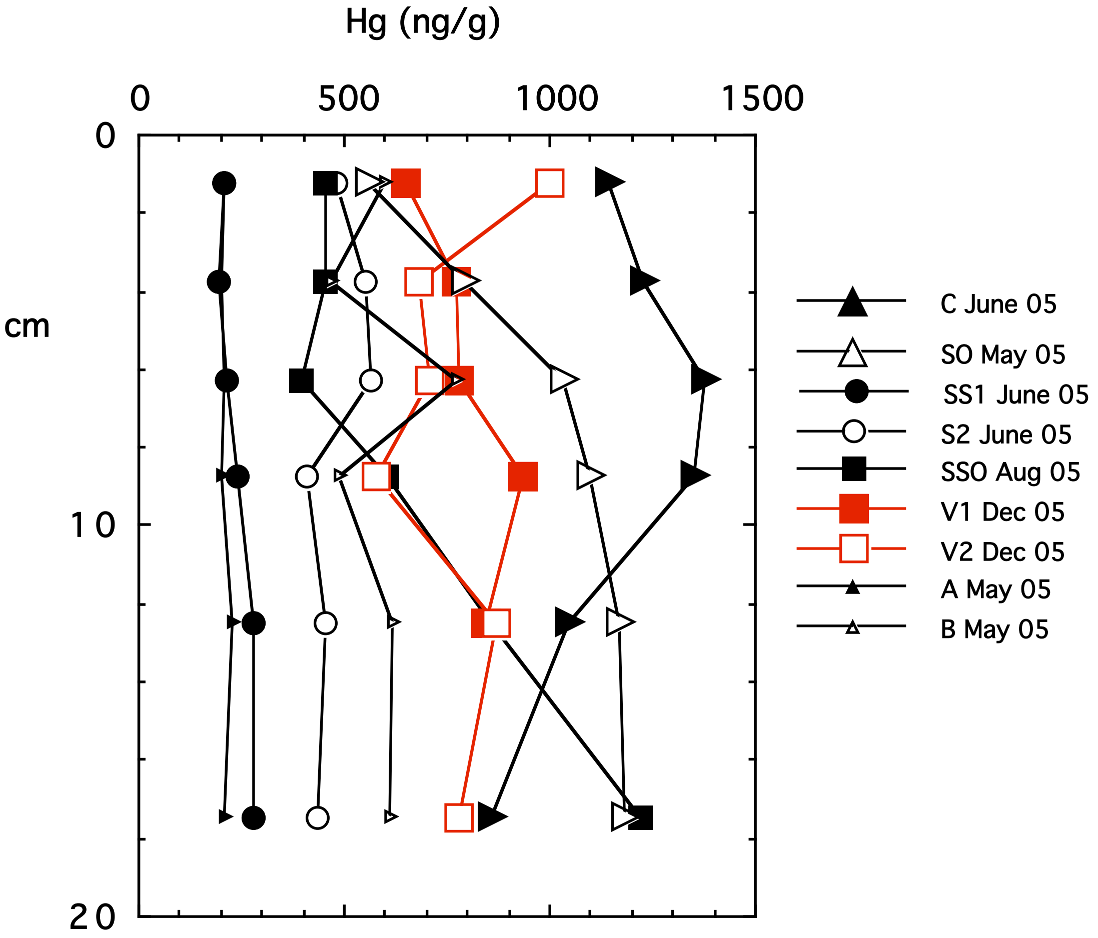
Zinc *versus* Fe_2O_3 in sediments of lagoonal section of Venice Lagoon.



ERL = 20.9 mg/Kg **ERL = 46.7 mg/Kg**

Figure 21

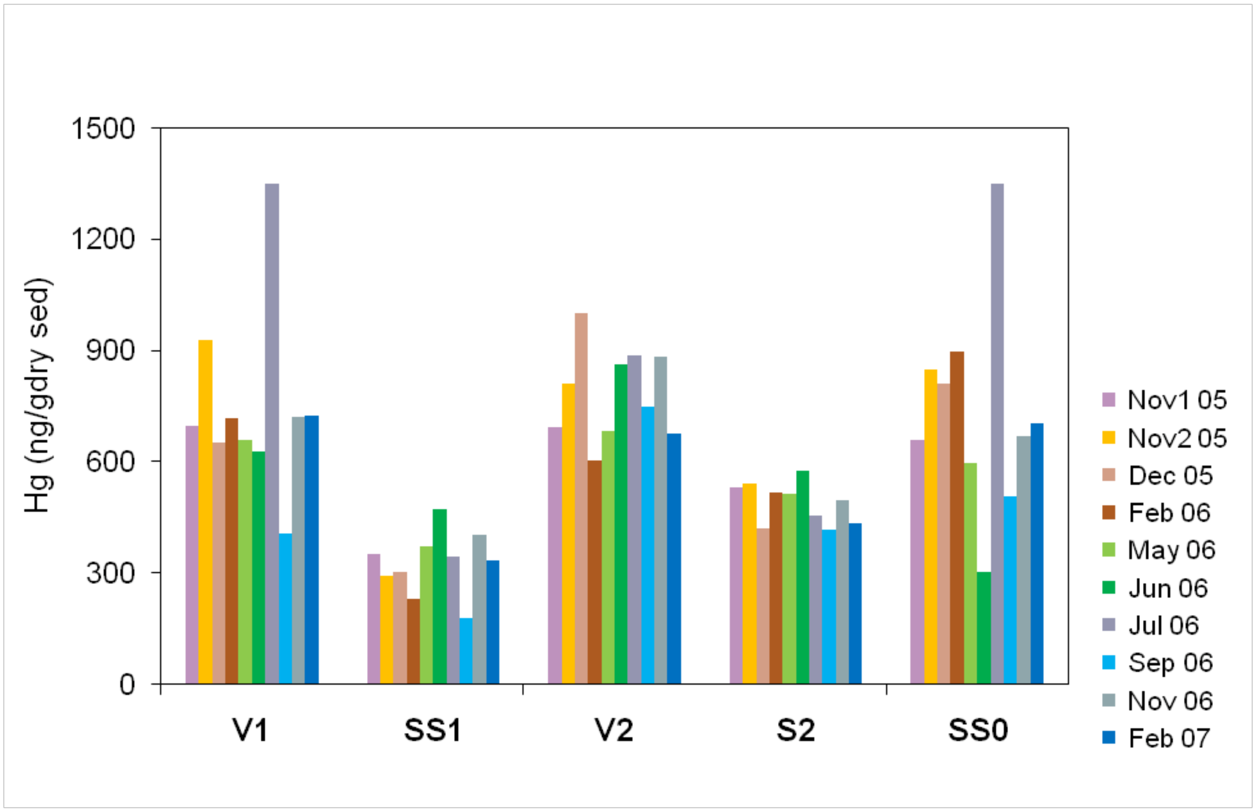
Nickel and Lead concentrations of SIOSED sediments of VeniceLagoon. Data based on HNO_3 dissolutions.



A and SS1	**Class A – about 200 ng.g**
S2 and B	**Class B 400-650 ng/g**
C, SO, deeper part SSO	**Class C > 700 ng/g**
30 m Core	**Class C 0-5 m 900-1400 ng/g**

Figure 22

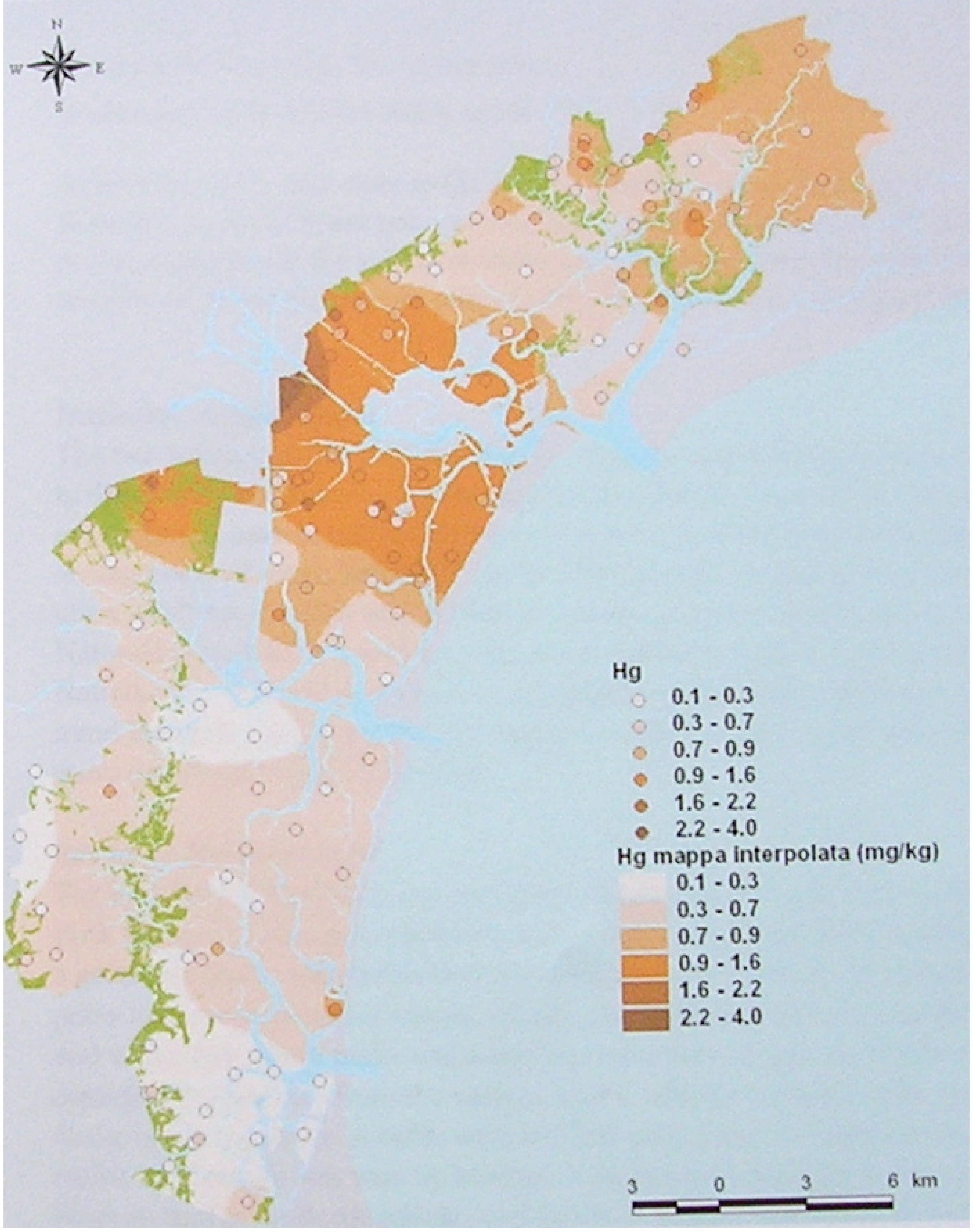
Depth distribution of total Mercury concentrations of Venice Lagoon sediments.



Class B: > 500 ng/g

Figure 23

Time variation in total Mercury concentrations in surface sediments of Sites V1, V2, SSO, and reference Sites SS1 and S2.



Reference:

"MAV-CVN, 2004. ICSEL A.1. Valutazione integrata dello stato qualitativo attuale dei sedimenti lagunari superficiali. Technical Report

Figure 24

Distribution of Mercury in surface sediments of Venice Lagoon (MAV-CVN, 2004b).

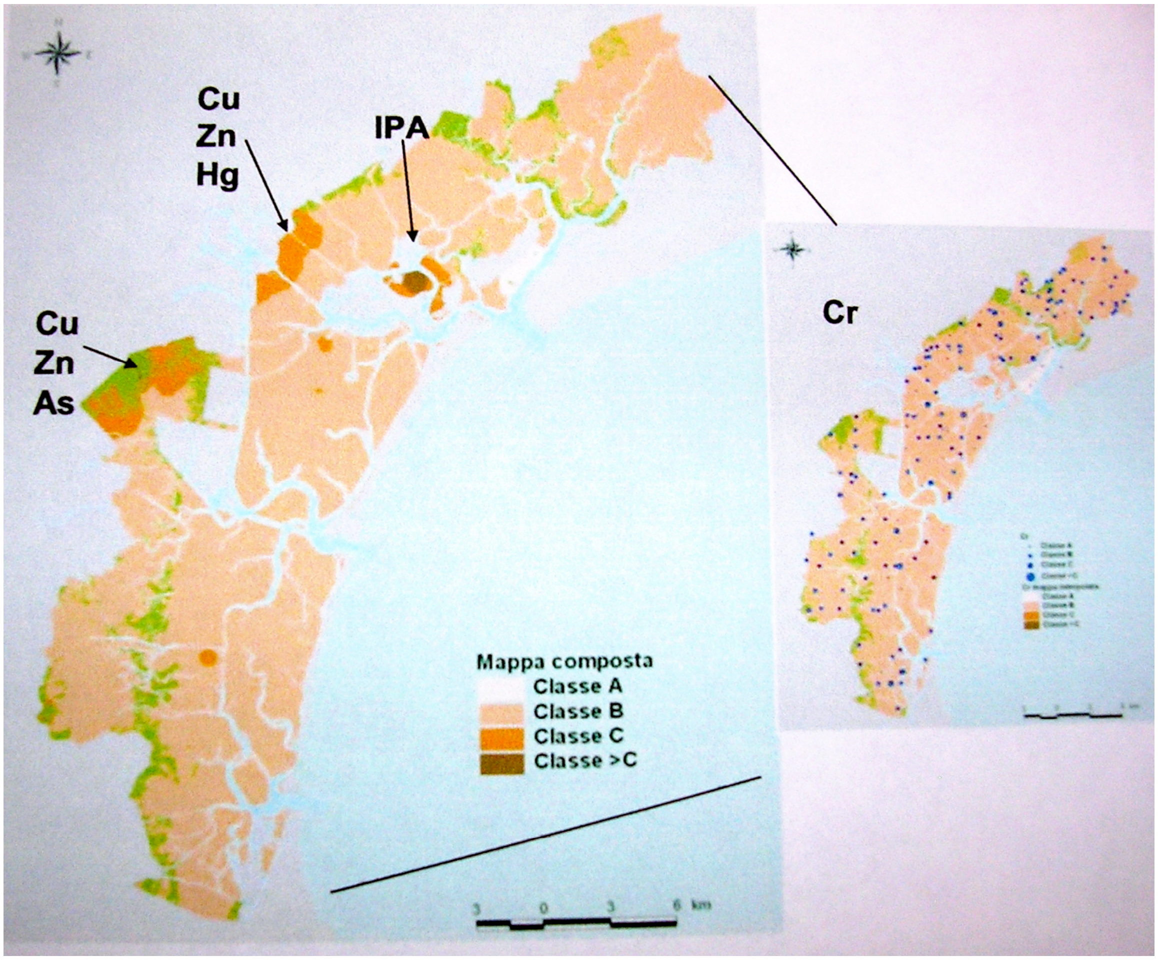


Figure 25

Overview Map of trace metals in Venice Lagoon (MAVCVN, 2004a,b). Note the high trace metal concentrations near the industrial areas of the lagoon, as well as in the city of Venice canals.

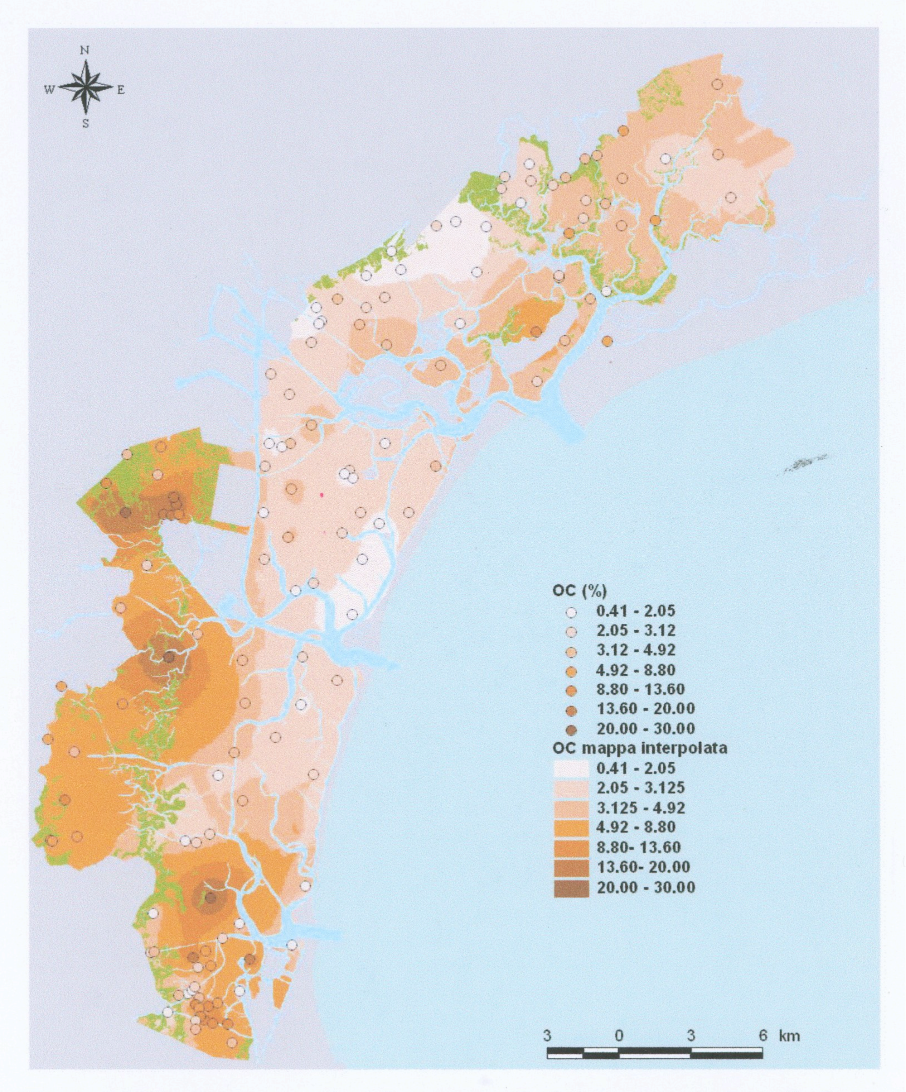
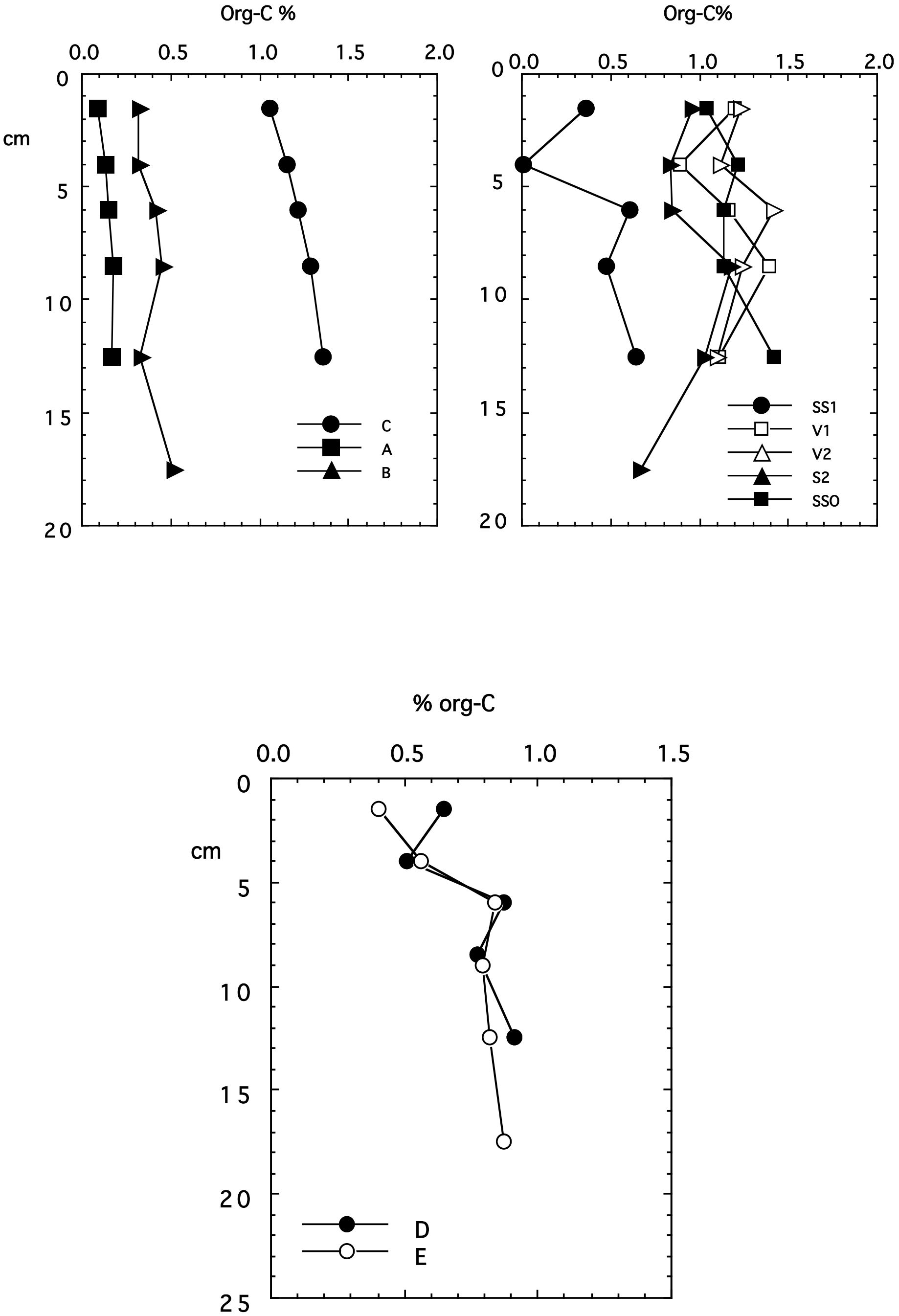


Figure 26

Map of organic carbon contents of sediments of Venice Lagoon (MAV-CVN, 2004a,b).



Near Sites SO and S1

Figure 27

Organic carbon contents in near surface sediments of sediments obtained by SIOSED. Note stations D and E are located near Sites SO and S1 (Figure 1).

Appendix 1

Sediment Age Information

Sediments were dated by means of ^{14}C dating of sedimentary organic matter booth by us (DeHeyn and Perez), as well as by Serandrei Barbero, et al. (2006) and Zoppi et al. (2001).

Prior to commenting on the ages is appropriate to refer to the Frignani et al. (1997) paper, because it presents the time series of recent metal pollution in the Venice Lagoon, based on good data from ^{210}Pb excess and ^{137}Cs dating techniques. In that paper it is shown that the years 1920 – 1930 were the principal starting dates of metal pollution associated with Porto Marghera industrial activity. Lately this pollution has started to become somewhat diminished as a result of environmental measures. Note that the cores studied for this purpose were located away from canals and thus were associated with more common slow sedimentation rates. Frignani et al. (2005) also give some more relevant ages, near the industrial zone.

The ages of the 30-meter drill hole SM3, located northeast of Venice, are presented in Figure 1. Note that immediately below the lagoonal sediment section (deeper than ~ 11m) there is a rapid increase in age in the underlying pre-lagoon sediments. Figure 2 summarizes the data obtained in the Venice Lagoon proper, with most of the ^{14}C data available (Serandrei-Barbero et al., 2006; Dimitri DeHeyn and Elena Perez, personal communication). With the exception of Core 39C (near Porto Marghera) there appears to be a trend in the data, from Sites C to SS1 and S2, to B, and then to SSO. Nonetheless, all dates appear to be 1000 years or older then the present. No corrections were made for the potential "reservoir age" (Zoppi et al., 2001; Serandrei-Barbero et al, 2005).

This correction can be as high as 1,200-1,300 years. I have drawn the post 1920 age limit set for the sediments by the Zn enrichments in the sediments (see also Frignani et al., 1997). In addition, there is good evidence that many of the long cores are to some extent enriched in trace metals (at least in the cores C, S2, etc), as are the cores from the upper 10 m of the drill hole (to ~ 5 m subsurface). Thus most ^{14}C age dates in the drill hole are close to zero AD, but a Zinc-Age of less than 75 years. Applying reservoir age corrections for such polluted cores may be tenuous at best.

In summary, the estimated ^{14}C ages of the sediments are somewhat controversial in the upper sediments of the Lagoon, but below the lagoonal section, the presence of much older sediments is evident.

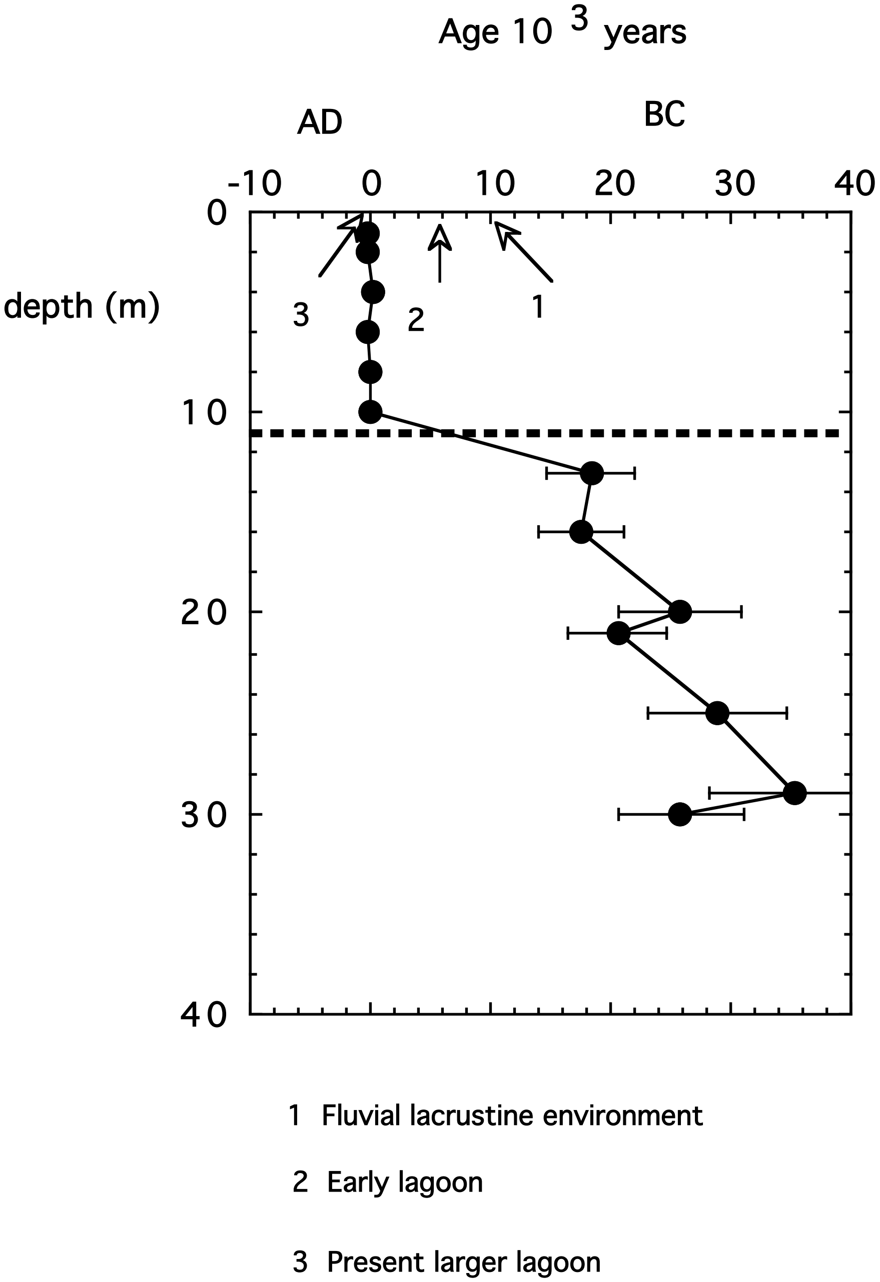
References

Frignani et al. (1997). Metal fluxes to the sediments of the northern Venice Lagoon. Marine Chemistry, 58: 275-292

Frignani et al. (2005). Pollution historical trends as recorded by sediments at selected sites of the Venice Lagoon. Environment International, 31: 1011-1022

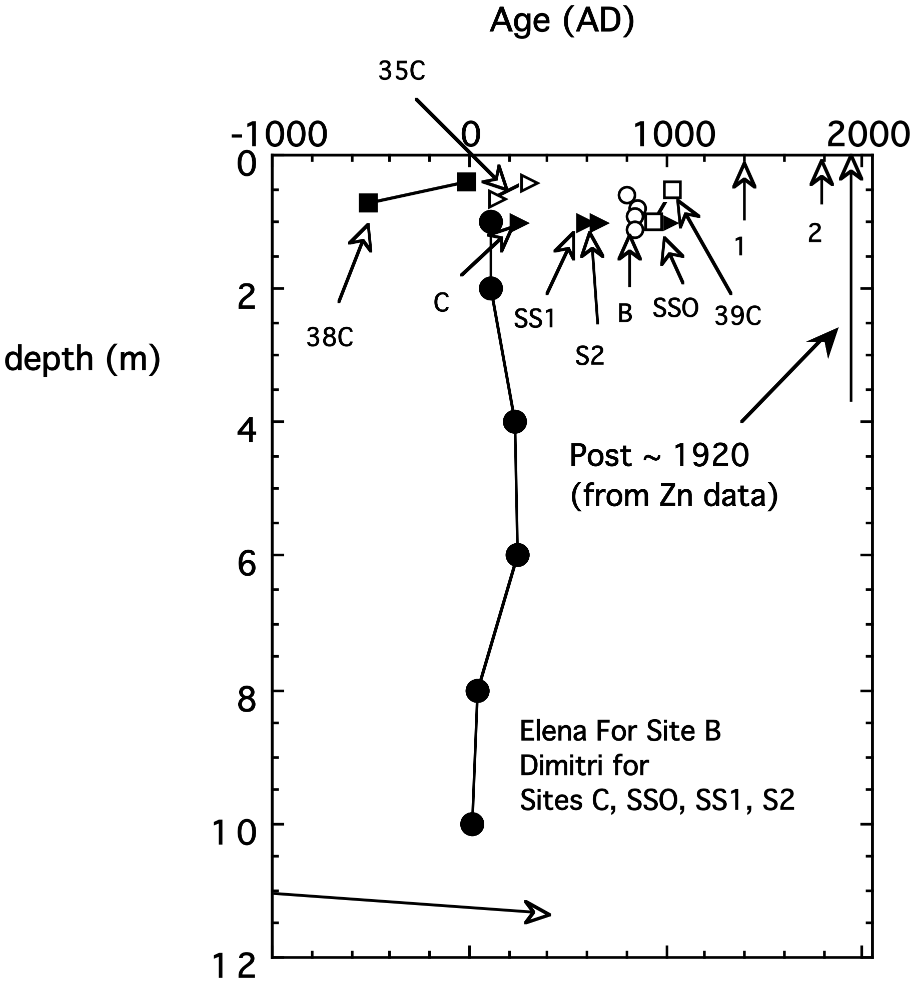
Serandrei-Barbero et al. (2006). Past and recent sedimentation rates in the Lagoon of Venice (Northern Italy). Estuarine and Coastal and Shelf Science, 69: 255-269

Zoppi, U., Albani, A., Ammerman, A., Hua, Q., Lawson, E. and Serandrei Barbero, R. (2001) - Preliminary estimate of the reservoir age in the lagoon of Venice, Radiocarbon, 43, 489-494



Age 10 3 years
AD
BC
-10
0
10
20
30
40
depth (m)
0
10
20
30
40
3
2
1
1 Fluvial lacrustine environment
2 Early lagoon
3 Present larger lagoon

Figure 1



1 Lagoon initiated 6000 y BP
Before 1400 BP natural trends
1400 - 1800 River diversions started

2 Reduction of surface initiated

Core 31C: Half way coast of Lido, similar to B

Cores 31C, 35C, 39C from Serandrei et al.
(see reference)

Figure 2