TEMPORAL TRENDS OF HEAVY METALS IN SEDIMENT CORE FROM THE GULF OF PALERMO (SICILY, ITALY)

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ABSTRACT

The evaluation of long–term heavy metal concentrations in the Gulf of Palermo was carried out in this study. Measurements of Cr, Cu, Hg, Pb and Zn concentrations were performed by atomic absorption spectrophotometry (AAS) on dated fractions of a sediment core, dated by the $^{210}Pb_{ex}$ method. They are found to cover a time period from 1951 to 2004. The constant sedimentation rate model was used for dating. Specific activities of ^{137}Cs have also been measured in the sediment core sections as a check of the time scale derived by the $^{210}Pb_{ex}$ method. A time-series analysis based on temporal decomposition was used in order to investigate the presence of heavy metal pollution trend. The additive component model, widely used to estimate seasonal and long–term behavior, was chosen for the temporal analysis. Results showed the presence of a specific heavy metal concentration trend. Residual time–autocorrelation has also been taken into account in order to investigate their stochastic properties. Concentrations of some metals (Cu, Hg, and Zn) have been found increasing until the beginning of the 1970s. A peak around the beginning of the 1980s has been found for Cr and Pb. Heavy metal concentration in the sediment core show a significant decreasing after these years. Our results for the concentration time trends are in good agreement with other surveys performed in different areas of the world, and they can be explained in terms of the reduction of anthropogenic contribution to atmospheric emissions. Further investigations on time properties and spatial distributions, are also planned.

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INTRODUCTION

Valuable information on pollution condition of coastal environments can be obtained by studying the heavy metal concentrations in sediments.

Since metals are not degradated by bacterial activity, they provide an historical record of their presence in the sediment.

Many factors will influence the metal concentrations in sediments. On one hand, their origin can be related to both human activity and natural sources. On the other hand, the chemical and physical characteristics of the environment (e.g. pH, Eh, mineralogy, granulometry, red-ox state) will play a major role.

A standard investigation methodology for heavy metals in sediments requires sampling of sediment cores and their dating by reliable methods. Depths of core sections are then converted to age in order to obtain the time evolution of involved pollutants, e.g. heavy metals. Radionuclide dating is the only dating method allowing the estimation of absolute ages [1].

Recent anthropogenic heavy metal contributions exhibit time dependecies related to the enforcement of national or international laws concerning the reduction of pollutant emissions in the atmosphere. Moreover, the atmospheric pollution for heavy metals must be considered from a global point of view [2, 3].

Distribution of heavy metals in the superficial soft bottom sediments has been investigated in a previous work [4], where in-depth statistical analysis of spatial distribution through ratio-matching, hierarchical clustering, minimum spanning tree and principal component techniques have been reported.

In this work we present results on heavy metals (Cr, Cu, Hg, Pb, Zn) concentrations, and their time series analysis, in sections of a dated sediment core.

Time series analysis provides a powerful statistical tool to study the time evolution of data from many different fields (business, climate, agriculture, meteorology, and so on). It can also provide forecasting of future events. Autoregressive models can be used to fit raw data and to obtain the spectral density function. Seasonal effects and trends can be identified by time series decomposition. Periodic behaviors can be separated from noise-like background (see, for instance, [5]). Relations among datasets can be investigated by time cross-correlation analysis.

MATERIALS

One inshore sediment core (with a length and diameter of 30 and 10 cm, respectively) has been sampled in the Palermo Gulf (Sicily, Italy), within a more general investigation on the metal pollution of the area [6]. The sampling area is depicted in Fig. 1. Details on the geochemical and geographical settings, as well as on the sampling technique, can be found in [4, 7, 8].

The 1 cm thick core sections have been dated using the $^{210}\mathrm{Pb}_{\mathrm{ex}}$ method, within a constant sedimentation rate model [1]. Fitting of experimental data with a simple exponential function has allowed to calculate a sedimentation rate equal to about 5.8 ± 0.7 mm year^{-1}. This also means that a single core section contains sediment accumulated during about 1.7 ± 0.2 years. The sampled core is then an historical record of about 50 years of pollution of the area, going back to early 1950s. An independent confirmation of the obtained chronology has been provided by ^{137}Cs measurements in the same core sections [7, 8]. Radiometric measurements have been carried out

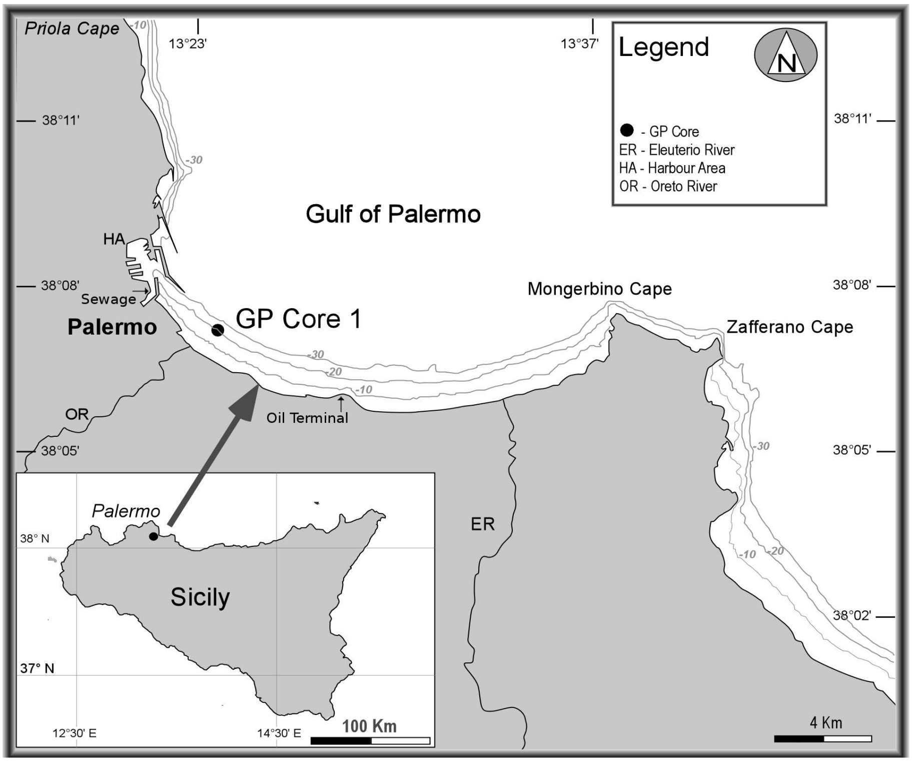

Figure 1: Palermo Bay and sampling site location.

by HPGe spectrometry. A low energy detector with a beryllium window has been used for ^{210}Pb measurements. A second germanium detector has been used for ^{137}Cs and ^{214}Bi determination.

Dating of the sediment core has allowed to correlate Pb concentrations with Pb emissions in air, due to gasoline combustion, in the last two decades [7].

Heavy metal concentrations in the < 63 μm fraction of core sections have been measured by atomic absorption spectrophotometry after wet sieving, drying and digestion procedures [4].

Time series analysis has been carried out on the obtained datasets. The *R* free software environment has been used throughout this work [9].

Heavy metal concentrations in core sections can be considered as sets of observations recorded at discrete and, in our case, equally spaced times. The concentration of metal i at time t will be denoted by x_t^i.

First of all, the auto–correlation function has been calculated for each metal. This allows to verify the presence of correlations within the univariate time series. The autocorrelation function is an useful tool to explore the mutual relation between values of a time series. It is a measure of how the values of a variable at a given time are related to the values at different times. For data x_t^i sampled at equally spaced times, the autocovariance function $C^i(k)$ is defined as:

$$C^i(k) = \frac{1}{N}\sum_{t=1}^{N-k}(x_t^i - \mu^i)(x_{t+k}^i - \mu^i) \qquad (1)$$

where k is the time lag, N is the length of the time series, and μ^i is the average value of the time series.

The autocorrelation function for time series i is the defined as:

$$\rho^i(k) = C^i(k)/C^i(0) \tag{2}$$

The significance bounds for the autocorrelation function are defined as $\pm z_{1-\alpha/2}/\sqrt{N}$, where $z_{1-\alpha/2}$ is the $(1-\alpha/2)$-quantile of the standard normal distribution.

If the time series has a long memory, the autocorrelation function goes to zero very slowly.

The spectral density function, or power spectrum, is the square of the magnitude of the Fourier transform of the autocorrelation function, and allows to switch from the time to the frequency domain, identifying the periodic components.

The small size of our datasets ($N = 30$), would produce a very noisy spectrum. Our series have then been differenced in order to make them stationary, and then an auto-regressive model $AR(p)$ [5] has been used to fit the obtained data, from which the spectrum has been calculated.

Detrending is the operation of removing trend from time serie and, generally, is used as a preprocessing step in time series analysis in order to achieve stationarity condition.

In order to determine the trend and the seasonal variations, we assumed that our time series are described by a three component additive model:

$$x_t^i = T_t^i + S_t^i + \varepsilon_t^i \tag{3}$$

where T_t^i, S_t^i and ε_t^i are the deterministic trend, the seasonal component and the residuals, respectively. The seasonal component was modeled by a Loess locally weighted polynomial regression [10].

Next, cross–correlations have been considered. The cross correlation gives information on the relationship between pairs of variables. It is defined as:

$$\rho^{ij}(k) = \frac{C^{ij}(k)}{\sigma_i \sigma_j} \tag{4}$$

where

$$C^{ij}(k) = \frac{1}{N} \sum_{t=1}^{N-k} (x_t^i - \mu^i)(x_{t+k}^j - \mu^j) \tag{5}$$

and σ_i is the standard deviation for the series i. The above formula is for $k \geq 0$. For $k < 0$, we have $C^{ij}(k) = C^{ji}(-k)$.

RESULTS AND DISCUSSION

Heavy metals raw data vs. core section depth are shown in Figs. 2 and 3 Top horizontal axis shows the estimated chronology as obtained by $^{210}\mathrm{Pb}_{\mathrm{ex}}$ method.

Fig. 4 shows the autocorrelation function for the five metals. Horizontal dashed lines are the significance bounds at a 95% confidence level. Since each lag corresponds to ≈ 1.7 years (see above), we can see that all the autocorrelation function go to zero in ≈ 12 years. Values outside the significance bounds suggest that a trend must be present. A Box-Ljung test [11] was performed in

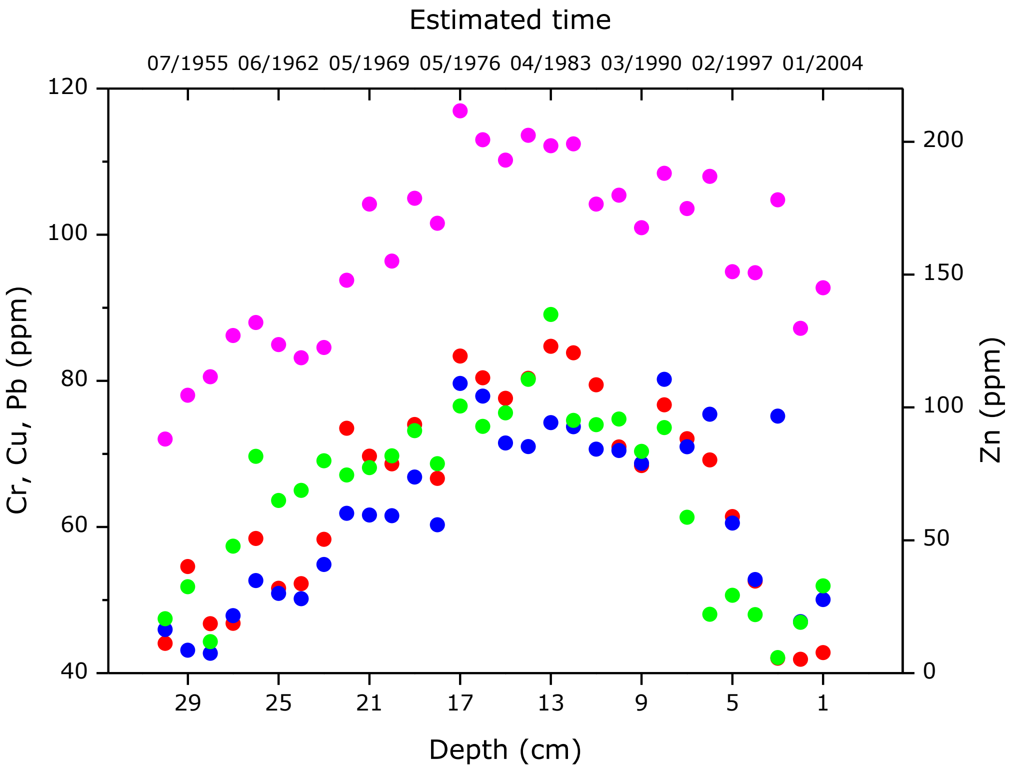

Figure 2: Cu, Cr, Pb (left scale, blue, red and green symbols, respectively) and Zn (right scale, magenta symbols) concentration vs. core section depth. Top axis is the estimated age of the section.

order to asses the autocorrelation values significance. All time series come out to be significantly autocorrelated. This allows to say that a trend behavior is present in each series.

Spectral density functions have been calculated for all metals, after data fitting by an autoregressive model. Only Hg shows a well defined sharp peak. Its spectrum is shown in Fig.5. The first peak in the frequency domain corresponds to a period of ≈ 11.5 years, very close to the average sun spot cycle. The other peaks are not meaningful, and can be considered as a fitting procedure artefact, since they correspond to a range for which too few data are available.

We can now remove trend and seasonal component from the time series. A Box-Ljung test, performed on the residuals, shows that they are not significantly correlated. Raw data, seasonal component, trend and residuals for Hg are shown in Fig. 6. Its periodic seasonal component is clearly evident.

In order to examinate the mutual relation among the metal series, in Fig. 7 we show all the series trends, as obtained by decomposition, normalized to their maximum value. It can be seen that Hg trend reaches its maximum earlier than all the other metals. This behavior has been further investigated calculating the cross-correlation function of Hg with respect all the other metals. They are shown in Fig. 8. All curves are shifted towards positive lags. This confirms the different time behavior of Hg.

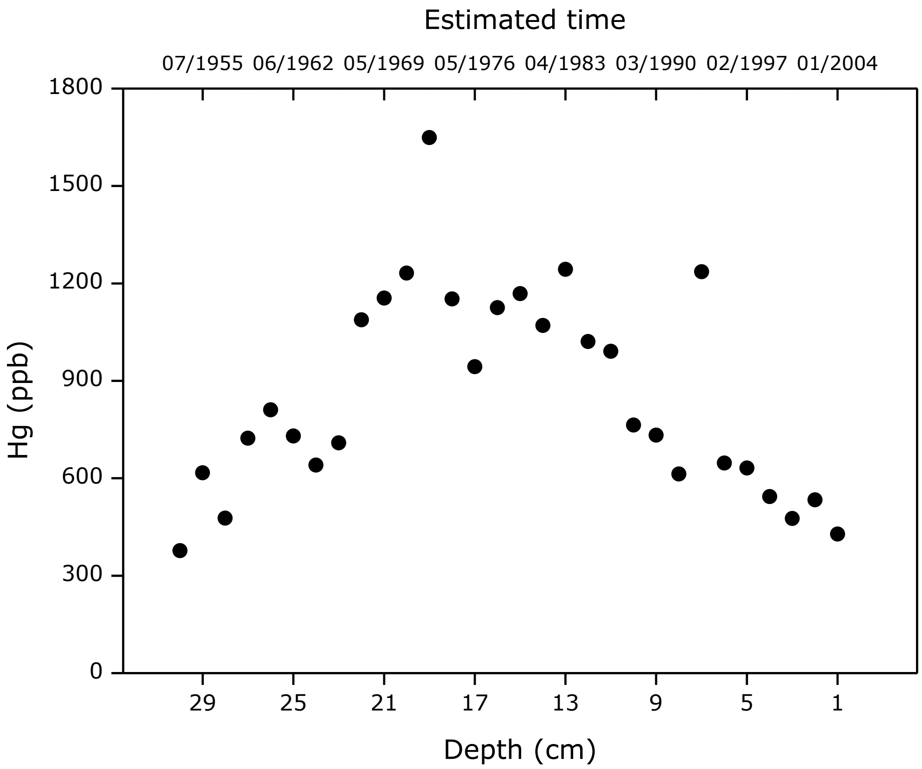

Figure 3: Hg concentration vs. core section depth. Top axis is the estimated age of the section. Please note that *y*-axis units are now ppb.

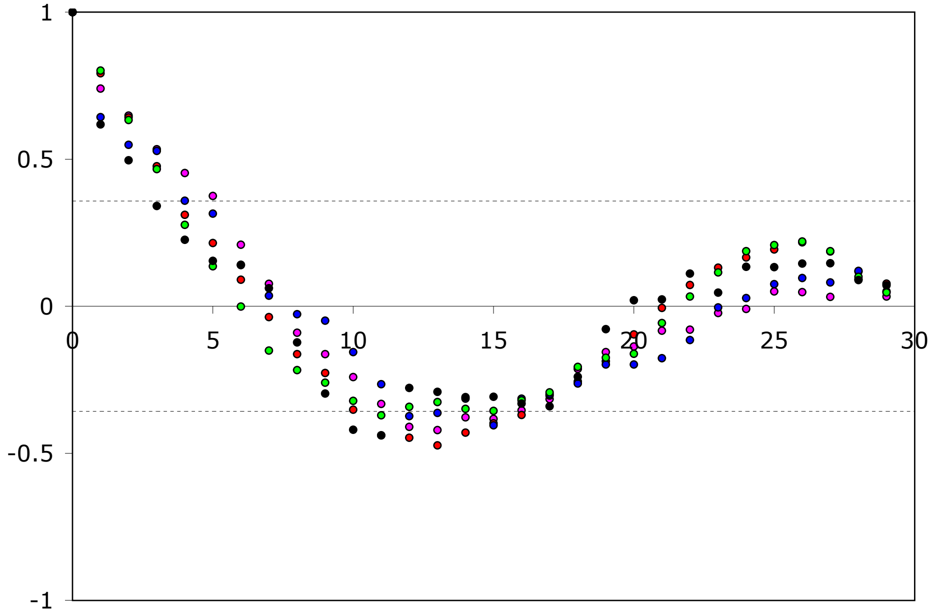

Figure 4: Autocorrelation function for the five metals. Colors as in Figs. 2 and 3. Horizontal dashed lines indicate the significance bounds at a 95% confidence level.

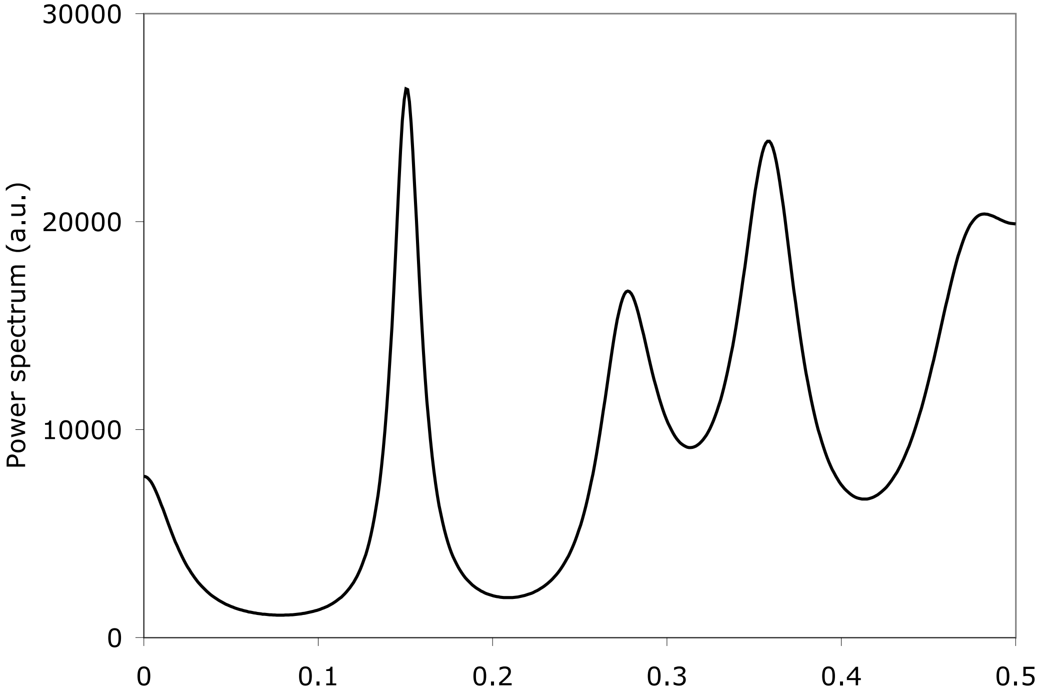

Figure 5: Power spectrum for Hg. Data have been detrended and fitted by an autoregressive model.

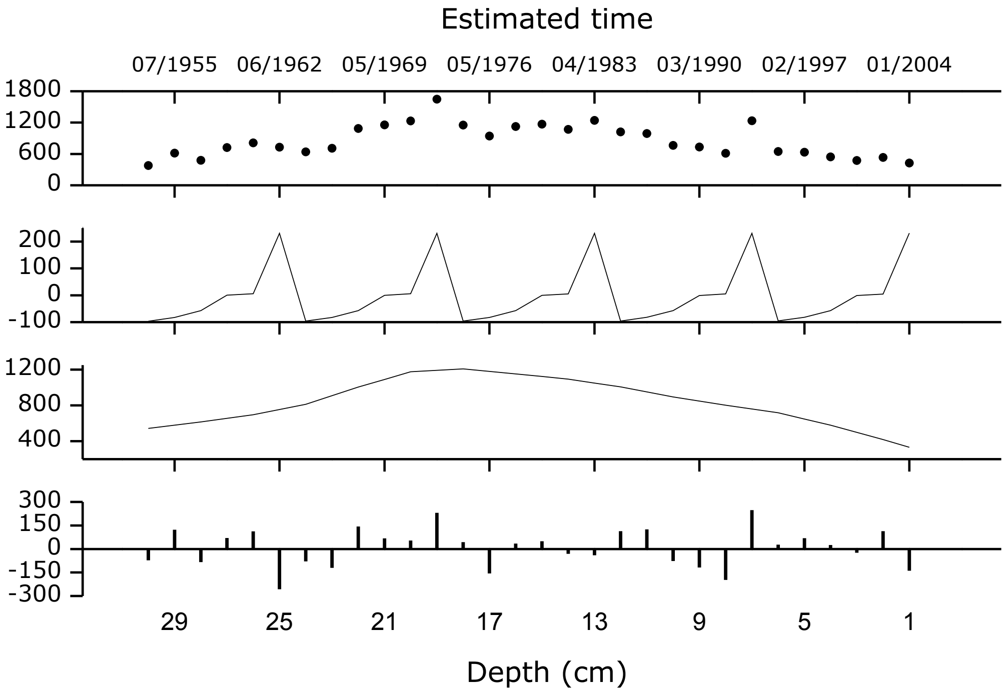

Figure 6: From top to bottom: raw data, seasonal component, trend and residuals for Hg. Axes as in Fig. 3.

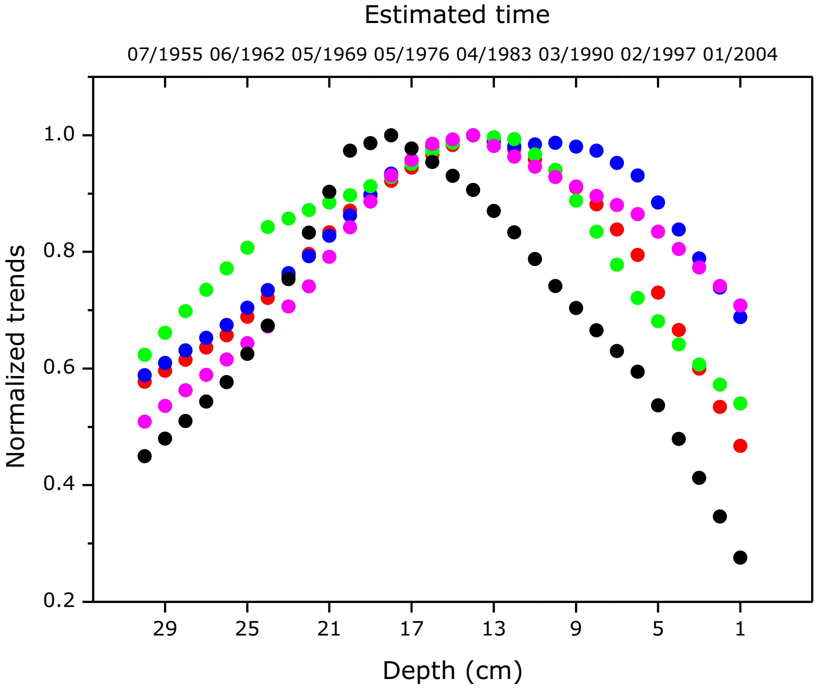

Figure 7: Cu, Cr, Hg, Pb and Zn trends. Each series has been normalized to its maximum value. Horizontal axes and colors as in Figs. 2 and 3.

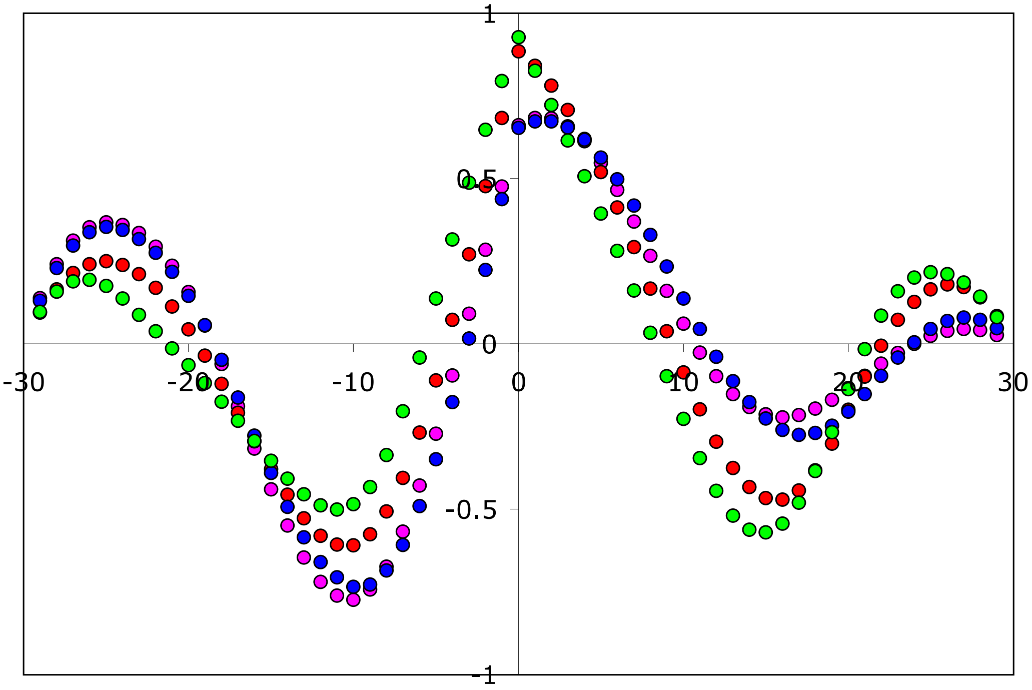

Figure 8: Cross-correlation function of Hg with respect to all the other metals. Colors as in Fig. 2.

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CONCLUSIONS

In this work we have studied the time behavior of heavy metals in sediment core sections sampled in the Palermo Gulf, and dated by radiometric $^{210}Pb_{ex}$ method. Time series statistical tools have been used to investigate autocorrelations, seasonal components, trends and cross-correlations. A very well defined cycle has been found for Hg time series, with a value corresponding to the sun spot cycle. Metal time trends, as resulting from decomposition, have qualitatively shown the different behavior of Hg. it reaches its maximum value in the beginning of the 1970's, while all the others reach their maximum later. This has been confirmed by cross-correlation functions of this metal with respect to all the others.

All metal show a well marked decreasing in the last years. Further investigations are planned for a better and deeper understanding of time trends and seasonal effects.

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