HISTORICAL TRENDS IN SEDIMENTATION RATES AND TRACE ELEMENTS ACCUMULATION IN 'DOCE' RIVER, ESPÍRITO SANTO STATE, BRAZIL

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ABSTRACT.. The Doce River watershed presents a history of intense human occupation and variety of economic activities and consequently chemical pollution. This paper aimed to determine the concentration of trace elements in sediments (Cu, Zn, Cr, Pb, Fe, Mn and Ni) in the low course of Doce River basin. It was collected three sediments cores in different points of the basin: one upstream, one in front of, and one downstream the city of Linhares. Values between 0.12 and 2.87cm yr^{-1} of sedimentation rates were defined by ^{210}Pb dating. Several grouped peaks in trace elements were determined the sample site A (1970 and 2010). At sample point B peaks were determined for the decades of 1930, 1990 and 2000. The highest average concentrations of trace elements were determined for the point C. Trace elements contents presents accordance with historical facts recorded in the region of the Doce River watershed as a whole.
Keywords: Trace elements, Doce River, pollution, sedimentation rates.

RESUMO. Tendências históricas das taxas de sedimentação e acúmulo de elementos traço no baixo curso do rio Doce, Espírito Santo, Brasil. *A bacia hidrográfica do rio Doce apresenta uma história de intensa ocupação humana e variedade de atividades econômicas e conseqüente poluição química. Este trabalho tem como objetivo determinar a concentração de elementos traço em sedimentos (Cu, Zn, Cr, Pb, Fe, Mn e Ni) no baixo curso da bacia do Rio Doce. Foram coletados três testemunhos sedimentares em diferentes pontos da bacia: um à montante, na frente e outro à jusante da cidade de Linhares. As taxas de sedimentação entre 0,12 e 2,87 cm ano*$^{-1}$ *foram definidas pelo método baseado em* ^{210}*Pb. Picos de concentração de elementos traço foram determinados no testemunho A (1970 e 2010). No testemunho B, foram determinados para as décadas de 1930, 1990 e 2000. As maiores concentrações médias de elementos traço foram determinados no ponto C. As concentrações de elementos traço apresentam-se em conformidade com fatos históricos registrados na bacia do Rio Doce como um todo.*
Palavras chave: *Rio Doce, poluição, taxas de sedimentação, elementos traço.*

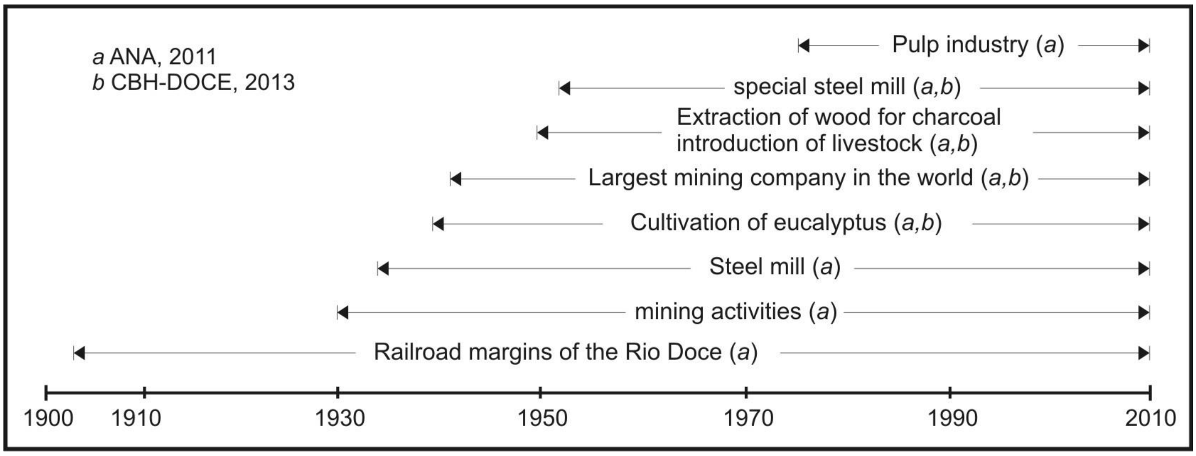
INTRODUCTION

Trace elements can be found in several chemical forms embedded in different environmental compartments, such as atmosphere, water, soil, sediments and living organisms. Among these compartments, sediments stand out in the accumulation of pollutant species from the water column due to high factors of enrichment and low rates of removal (CARVALHO; LACERDA, 1992; FÖSTNER; WITTMANN, 1981). The concentration of pollutant species in sediments can present even higher magnitudes than in the corresponding waters. Because of this, it is possible to use sediments as reliable environmental pollution indicators for both the current and the historical pollution, using reconstruction by stratification (GODOY et al., 1998), which additionally enables the knowledge of the main sources of pollution within certain aquatic system.

The main sources of these elements are the urban effluents, combustion of fossil fuels, the beneficiation industries of iron and steel, fertilizers and rainfalls in area of atmospheric pollution. In Brazil, a number of works were carried out reporting the presence of metals in sediments in locals with a historic of urban and industrial development as those in the States of Rio de Janeiro, São Paulo e Rio Grande do Sul (BARBOSA et. al., 2012; PEREIRA et al., 2007; SILVA et. al., 2011).

In this context, the Doce River watershed is a region of interest due to its history of intense human occupation e economic growth. During this period, a great variety of economic activities was installed in different areas of the watershed and one consequence of this is the increase of environmental changes observed in the region, Figure 1. It is possible to highlight the chemical pollution by different sources, the deficient wastewater treatment in the cities of the region and the intense deforestation with the replacement of original woods for agricultural crops, thus making the Doce River watershed as an environmental compartment significantly vulnerable (ANA, 2011; MARANHÃO, 2012).

Figure 1 - Timeline of historical economic activities established in the region of influence of the catchment area of the Doce River watershed



The region of Linhares, last city located on the banks of the river before its mouth, is a good example of this development process. Furthermore, due to its location on the lower course region of the watershed, which presents low energy-carrying, there is a higher rate of sediment deposition transported by the river's water. These features classify the watershed as an interesting site for studies of historic reconstruction through the geochronology of sediments of the resulting impacts of urban progress and industrial activities. Nevertheless, there are no works concerning the presence of trace elements in this region.

Geochemical studies of sediments allow a historic assessment of the origin and distribution of metals in a certain region. The distribution and quantification of these elements in sediments is usually based on the concentrations obtained from the total extractions and compared to the characterization of the natural geochemical background (SALOMONS; FORSTNER, 1984).

Thus, this paper aimed to determine the concentration of trace elements in sediments (Cu, Zn, Cr, Pb, Fe, Mn and Ni) in the low course of Doce River basin, in the city of Linhares region. Then, through the geochronology technique, establish correlations between the history of local development and the concentration of such elements.

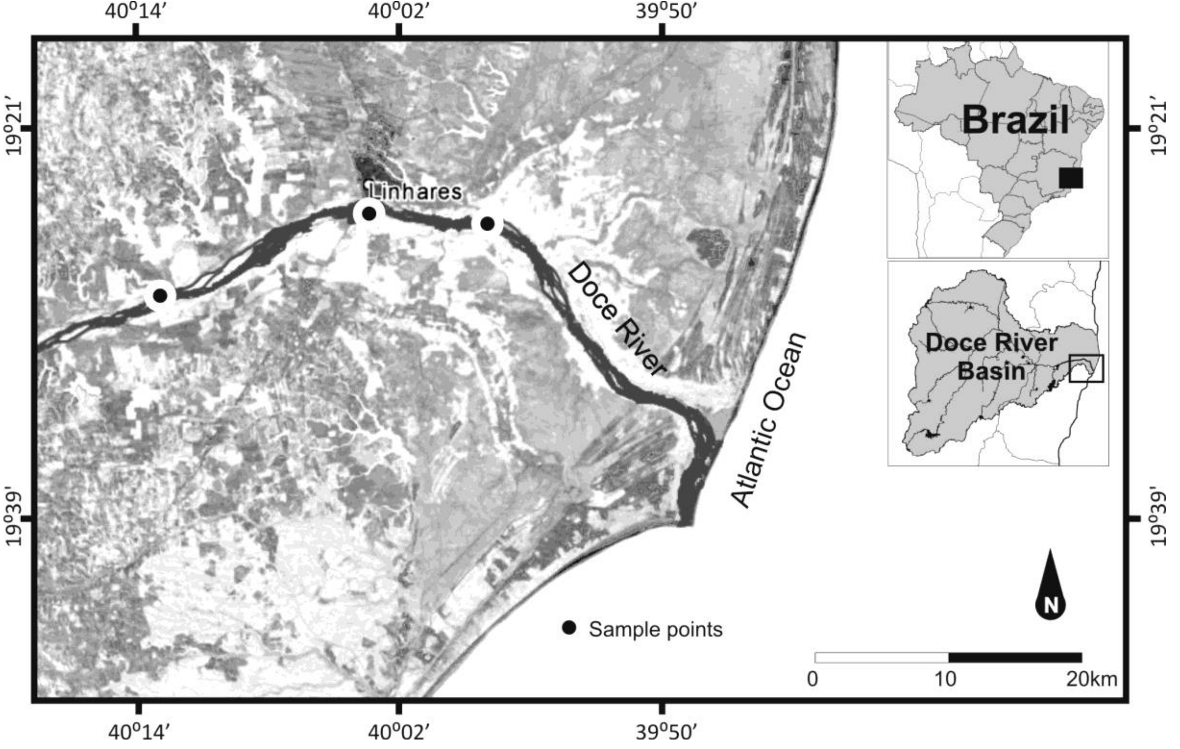
STUDY AREA

The Doce River watershed is located in the southeast region of Brazil, between the parallels 18º45' and 21º15' of south latitude and the meridians 39º55’ and 43º45’ of west longitude, as shown in Figure 2. About 86% of its area belongs to the state of Minas Gerais and the rest to the state of Espírito Santo. According to the Statistical Yearbook of Brazil (IBGE, 2004), about 3,100,000 people live in the watershed region of influence. The economy of the watershed is based mainly in agricultural activities (milk and beef cuts, coffee, sugar cane, vegetables, fruits and poultry), industrial activities (steel mill, metallurgy, mechanic, chemical, food, textile, tannery, paper and cellulose) and mining activities (iron, gold, bauxite, manganese, calcareous rocks and gems) (ANA, 2011).

Three of the biggest companies of Minas Gerais, as well as the biggest mining company of the world develop its activities in the region. Such industrial enterprises present high levels of industrial quality e productivity, being among the biggest in the world and playing a significant role in the Brazilian exports of iron ore, steel and cellulose.

The city of Linhares, situated north of the capital of Espírito Santo, Vitória, is the last one in the Doce River course and the larger one in the region of the lower course of the river. The city’s economy counts on big companies, agribusinesses, and the agriculture and livestock are extremely important for the local economy. The city is a big producer of oil and natural gas as well.

Figure 2 - Location Map of the watershed of the Rio Doce and distribution of the collection of sediment cores



MATERIALS AND METHODS

Sampling

It was collected three sediments cores in three different points of the basin: one upstream, one in front of, and one downstream the city of Linhares. The points of sampling were defined by analysing satellite images in computational environment. The Table 1 contains the geographical locations of the sampling points.

Table 1 - Geographical locations of collecting sediment cores

	Sample point local	Geographical coordinates S	 W	
A	Upstream the city of Linhares	19°29’51,50”	40°16’19,49”	35 cm
B	in front of the city of Linhares	19°24’46.24”	40°3’22.47”	50 cm
C	downstream the city of Linhares	19°25’18.55”	39°59’16.31”	35 cm

In order to collect the sediment cores, we used PVC tubes with 70 mm intern diameter previously washed with acid solution (HCl) at 10% v/v. In each sampling point, the tubes were manually introduced into the sediment and removed by vacuum with the aid of a top cover. Using a plastic spatula, each sediment core was sliced in layers of 1 cm until the depth of 15 cm, and layers of 5 cm for the rest of the core. The slices were placed in plastic pots and then dehydrated at 55 ºC for 24 hours in a stove. One aliquot of 250 mg was withdrawn from each layer in order to analyse the trace elements, while the rest of the sample was sent to the radiometric analysis.

Analytical methods

In this work the aqua regia metals extraction was based on the procedure recommended by the International Organization for Standardization (ISO standard**11466**). Aliquots of 0.250 g sediment were weighed and placed in 250 ml Erlenmeyer flask, with 4 ml of HCl and HNO_3 (3:1) mixture. Then, the suspension was heated on hotplate at 130 °C for 2 h, in open system. The obtained suspension was then filtered through a 40 µm pore cellulose acetate membrane filter, diluted to 25 ml with ultrapure water (Milli-Q), and stored in polyethylene bottles at 4 °C for analyses. All the reagents used were SuprapurMerk. The blanks underwent the same procedure and it was measured along with the samples in order to assess possible contaminations.

The quantification of metals were accomplished by means of Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) installed in the Center for Competencies in Petroleum Chemistry (NCQP – UFES). In this study we used the quantitative mode of analysis and a series of patterns of calibration curves were prepared. In order to increase the sensibility, an ultrasonic nebulizer was used, reducing the size of the particles forming the aerosol taken to the plasma. The ICP OES device utilized was the Ultima II by Jobin-Yvon with an applied power of 1000 W.

Radiometry

The ^{210}Pb activity was determined through high resolution gamma spectrometry. In this technique, the radioactive emissions from the radionuclides present in the samples are detected through the interactions with a semiconductor crystal, which both identifies and quantifies such emissions. The activity of each element is determined by the energy photopeak associated with its emission, which in the case of ^{210}Pb is 46.5 keV. The measuring time for each layer is 24 hours.

This methodology presents advantages over the radiochemical one, such as the non-destruction of the sample, enabling later analysis and simplification of the technique and dispensing more complex laboratory procedures (APPLEBY; OLDFIELD, 1992). The detector used in this work was the hiperpure germanium (GeHp) type semiconductor coaxial geometry with 56 mm of diameter and 38.5 mm of length, installed in the Department of Geochemistry of the Fluminense Federal University (UFF), with relative efficiency of 50% and resolution of 1,80 keV to 1,33 MeV and 0,85 keV to 122 keV. The shielding around the detector consists of a castle of lead with a thickness of 10 cm and inner lining of copper in all the walls, which aims to reduce the contribution of external radiation.

Sediments geochronology

In order to interpret the data ^{210}Pb in the sediment cores we used a mathematical model known as Constant Rate of Supply (CRS). This model assumes that there are variations in the rates of sedimentation of a sediment core that cannot be explained by phenomena of bioturbation or physical mixing of sediments (APPLEBY; OLDFIELD, 1992). In most cases the rates of erosion and sedimentation varied over the last 150 years, so the expected profile of ^{210}Pb is non-linear.

This model is based on two assumptions: a) ^{210}Pb in excess is supplied to the surface of the sediment at a constant rate; b) The radioactive decay of ^{210}Pb is constant due to its small post-depositional mobility.

The ^{210}Pb present in the rocks comes from the chain of $^{\mathbf{238}}$U radioactive decay. At the time ^{226}Ra disintegrates and forms ^{222}Rn, a noble gas, part of it emanates from the rocks to the atmosphere, where it undergoes further disintegration until ^{210}Pb. Because this component is solid, it precipitates on the surface by gravity or "washout" and joins with ^{210}Pb formed in the crystal structure of the sediment grainsof the original rock (PREISS et al., 1996). This deposited ^{210}Pb is called excess or unsupported to distinguish it from the ^{210}Pb derived in situ from the decay of ^{226}Ra (supported).

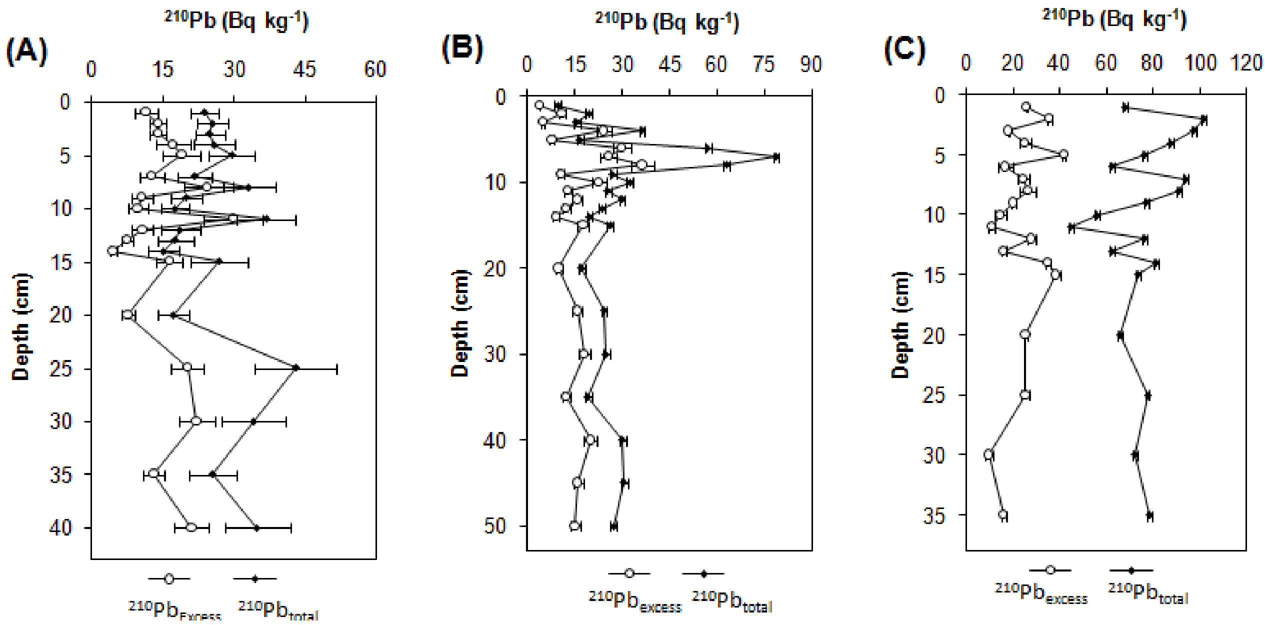
RESULTS AND DISCUSSION

^{210}Pb activity and sediment geochronology

The results determined for ^{210}Pb in the cores A, B and C are shown in Figure 3. The highest value found for $^{210}Pb_{total}$ among the cores was 101.8 Bq kg^{-1} (core C), whilst the lowest value was 9.4 bq kg^{-1} (core B). For the $^{210}Pb_{excess}$, the highest value determined was 41.9 Bq kg^{-1} and the lowest was 1.15 Bq kg^{-1} (both in core C).

Core A had values between 4.4 and 29.9 Bq kg^{-1} for $^{210}Pb_{excess}$, reached in the layer of 11 cm in depth, after a behaviour of increase in values from the more superficial layers. Between the layers of 20 and 30 cm depth it is observed another trend of increase, reaching 22.1 Bq kg^{-1}. For the core B, values between 1.15 and 36.6 Bq kg^{-1} were found. The trend of rising values starting from the surface layers was observed until a peak in the 8 cm layer. Then the values showed a decline to 8.9 Bq kg^{-1}. In core C values oscillate between the layers until 15 cm deep. From there, a reduction in the values until the deeper layers of the core occurs. The mean values observed in this work bear resemblance to those found in studies conducted in other regions of Brazil (LIMA et al., 2011; SABARIS; BONOTTO, 2010).

Figure 3 - Profile of $^{210}Pb_{total}$ and $^{210}Pb_{excess}$ in cores A, B and C. Activity (Bq kg^{-1}) versus depth (cm). The horizontal error bars indicate 1σ counting errors



Once determined the activity of ^{210}Pb over the strata of sediment, the dating of the testimonies was possible, Table 2.

The dating was possible until the year 1928 (core A), 1911 (core B) and 1905 (core C). Identifying the age of sedimentary strata is the first step for the historical analysis of the sedimentation processes and behaviour pattern of metals intake in the river course.

The determination of sedimentation rates in the three profiles can be seen in Figure 04.

A more detailed analysis highlights behaviours that are repeated in the three profiles (shaded bands identified by codes 2, 4 and 6). A behaviour of increased rates of sedimentation began in the early 1940s, reaching a peak between 1960 and 1963 and declining until the early 1970s (code 2). Historical context: from 1930, mining activities startin the higher altitude regions of the watershedunti 1940, when the introduction of eucalyptus cultivation occurs. In 1950, the process of deforestation in the region intensifies due to the growing demand of coal for the steel industry (CBH-DOCE, 2013). The sum of these events of modification in the landscape and vegetation cover of the drainage region of the basin may be associated with a greater amount of available sediment and consequently higher deposition in the lower course of the river.

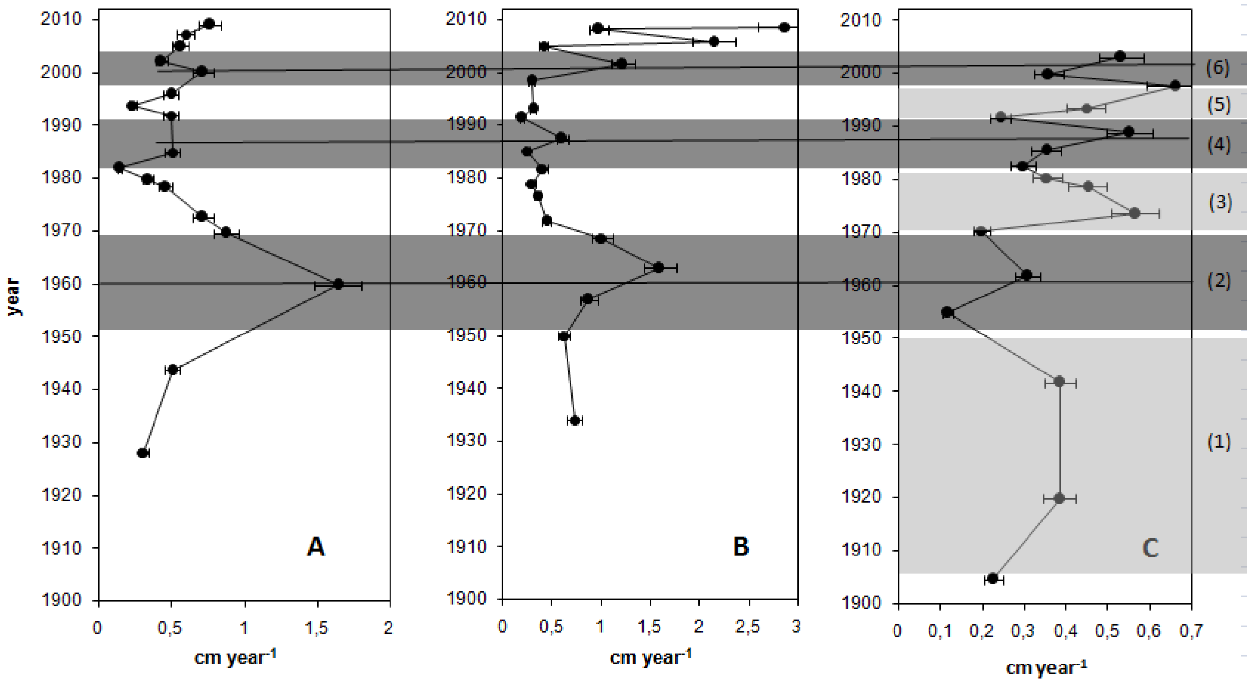
Another event (code 4) reaches the maximum value between the years 1985 and 1989, declining in the early 1990s. Historical context: in 1986, the construction of a bridge across the Doce River started in the town of Colatina, approximately 30 kilometres away from the sampling point A. This type of construction is related to a complex of changes in land use which usually generates impacts on erosion at the site and deposition along the river bed, a fact already reported in several studies (TAYLOR et. al., 2008).

The most recent set of events can be observed in the three cores and extends to the present days (code 6). It can be summarized by the presence of some peaks and a general trend of increase in rates in the three profiles. Historical context: from the year 2000, many dams for hydroelectric power plants were constructed along the Doce River watershed. This type of construction can be associated with these peaks of sedimentation and the global trend of increase of the current rates (ASEADA et. al., 2012; DAI et. al. 2013; MAGILLIGAN; NISLOW, 2005).

Table 2 - Ages calculated with ^{210}Pb (CRS model) for sedimentary profiles A, B and C

Depth (cm)	Core A		Core B		Core C	
	Year	Time period	Year	Time period	Year	Time period
0 - 1	2012	2009 - 2012	2010	2007 - 2013	2006	2003 - 2009
1 - 2	2011	2008 - 2014	2010	2007 - 2013	2004	2001 - 2007
2 - 3	2009	2006 - 2012	2009	2006 - 2012	2003	2000 - 2006
3 - 4	2007	2004 - 2010	2008	2005 - 2011	2000	1997 - 2003
4 - 5	2005	2002 - 2008	2006	2003 - 2009	1998	1994 - 2002
5 - 6	*	-	2005	2002 - 2008	1993	1990 - 1996
6 - 7	2002	1999 - 2005	2002	1999 - 2005	1992	1989 - 1995
7 - 8	2000	1997 - 2003	1998	1995 - 2001	1989	1986 - 1992
8 - 9	1996	1992 - 1999	1993	1990 - 1996	1985	1983 - 1987
9 - 10	1994	1991 - 1997	1991	1987 - 1993	1983	1980 - 1986
10 - 11	1992	1989 - 1995	1987	1984 - 1990	1980	1977 - 1983
11 - 12	1985	1982 - 1988	1985	1982 - 1988	1979	1974 - 1984
12 - 13	1982	1979 - 1985	1982	1980 - 1984	1974	1971 - 1977
13 - 14	1980	1978 - 1983	1979	1976 - 1982	1970	1967 - 1973
14 - 15	1978	1975 - 1981	1977	1972 - 1982	1962	1959 - 1965
15 - 20	1973	1970 - 1976	1972	1969 - 1975	1955	1951 - 1959
20 - 25	1970	1965 - 1973	1969	1966 - 1972	1942	1939 - 1945
25 - 30	1960	1957 - 1963	1963	1960 - 1966	1920	1917 - 1923
30 - 35	1944	1941 - 1947	1957	1953 - 1961	1905	1902 - 1908
35 - 40	1928	1925 - 1931	1950	1947 - 1953	--	--
40 - 45	--	--	1934	1931 - 1937	--	--
45 - 50	--	--	1911	1908 - 1914	--	--

Figure 4 - Sedimentation rates determined for the three sedimentary profiles (A, B, and C)



In addition to the events described above, the core C shows three other unique events. In the first one (code 1), there is an increase in the values of sedimentation rates between the years 1905 and 1950, with a maximum value in 1920 which is maintained until 1940. Historical correlation: between the years 1903 and 1910, the construction of a major railway which was intended to drain the production of mining companies installed in the state of Minas Gerais occurs. In 1910 a first miner gets active in the city of Itabira. In 1937, the first steel plant installed on the banks of the Doce River is inaugurated (CBH-DOCE, 2013).

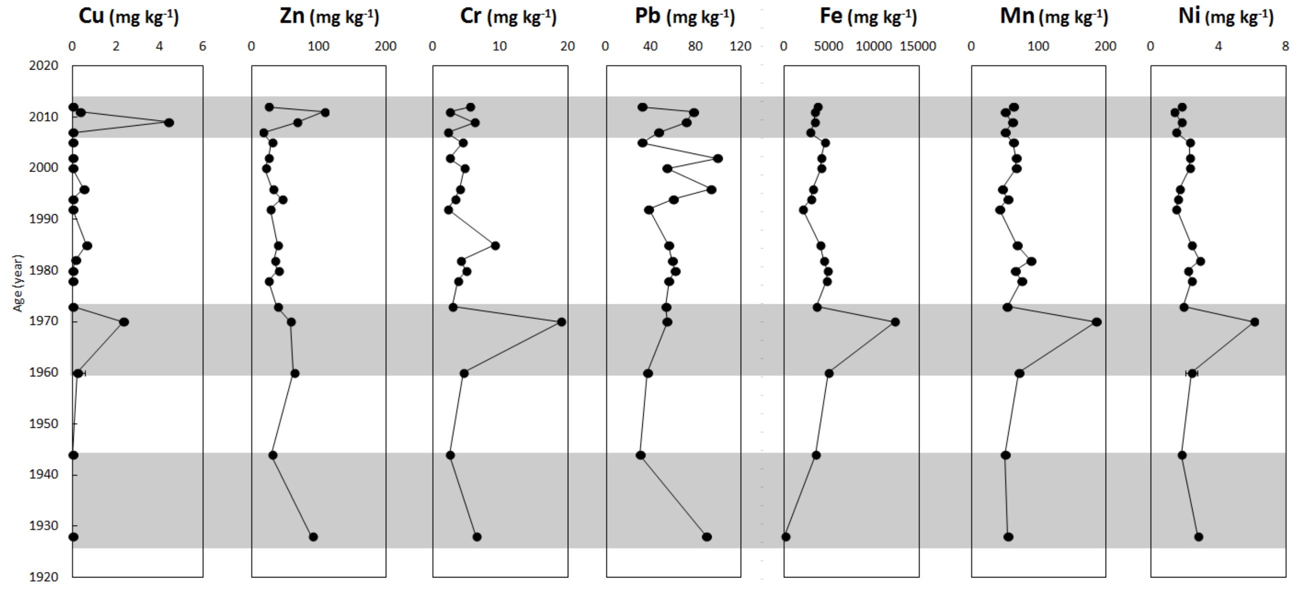
During the 1970s it is possible to identify in the core C another process of increase in sedimentation rates (code 3), reaching a peak in 1974, with a gradual reduction until 1983. Historical context: throughout this decade the city of Linhares, closer upstream of that point, had a population growth of approximately 30% and a major industrial and urban development, accompanied by an intense change in the occupation of the region. This development process is typically associated with a higher amount of sedimentary material for the rivers of the region (LINHARES, 2014).

Still in the profile C, there is an increase beginning in 1992 and maximum in 1998 (code 5). Historical context: in the city of Linhares, between 1992 and 1995, it takes place the construction of a new bridge to replace the old one, opened in 1954. As previously described, the impact of this type of construction can be verified by changes in deposition of sediments throughout the riverbed (TAYLOR et. al., 2008).

Historical reconstruction of contamination by metals

The historical behaviour of trace elements over the analysed sedimentary cores can be correlated with historical events in the development process of the region of influence of the watershed, Figure 5.

Figure 5 - Stratigraphic variations of trace metals concentrations in sediment core (A) (mg kg^{-1})



In the greatest depth reached by the core, dated in 1930, there is a higher concentration of the metals Cr, Pb and Zn, which can be related to the start of mining activities in the watershed. The maximum values for Cr, Cu, Fe, Mn and Niwere verified between 1960 and 1970, period wherea pulp industry was installed at the banks of the Piracicaba River (CBH-DOCE, 2013). Such economic activity is normally related to the occurrence of these metals in environmental compartments (DEAN et. al., 1972; JESUS et. al., 2004). Between the years 2008 and 2013, there is another addition in the concentration of heavy metals Cr, Cu, Pb and Zn, which coincides with the construction of a large hydroelectric dam on the Doce River course, with the flooded area involving six cities of the watershed (CBH-DOCE, 2013; CHEN et al., 2011).

Between 1910 and 1960 it is possible to observe an important increase for Zn, Pb, Fe, Mn and Ni in core B, Figure 6, possibly referring to the start of mining activities in the region, as discussed in the core A.

Between the years 1980 and 2000 it can be noticed an increase in metals Zn, Cr, Pb, Fe, Mn and Ni. As this collection point is located in front of the city of Linhares, it can be influenced by sewage discharge.At that time, there was a turnaround in the city's economy, which came out from the predominance of agricultural activities to apronounced industrial and urban development (IBGE, 2011). This may be related to the elevation of the metal values in question. Finally, since 2000, the growth in all analysed metals can be associated to the various industrial activities initiated in the city of Linhares, as well as the construction of the dam for the hydroelectric plant, already discussed in the data of core (A).

In general, core C (Figure 7) did not show well defined peaks, presenting predominantly fluctuations around an average value.

Figure 06 - Stratigraphic variations of trace metals concentrations in sediment core (B) (mg kg^{-1})

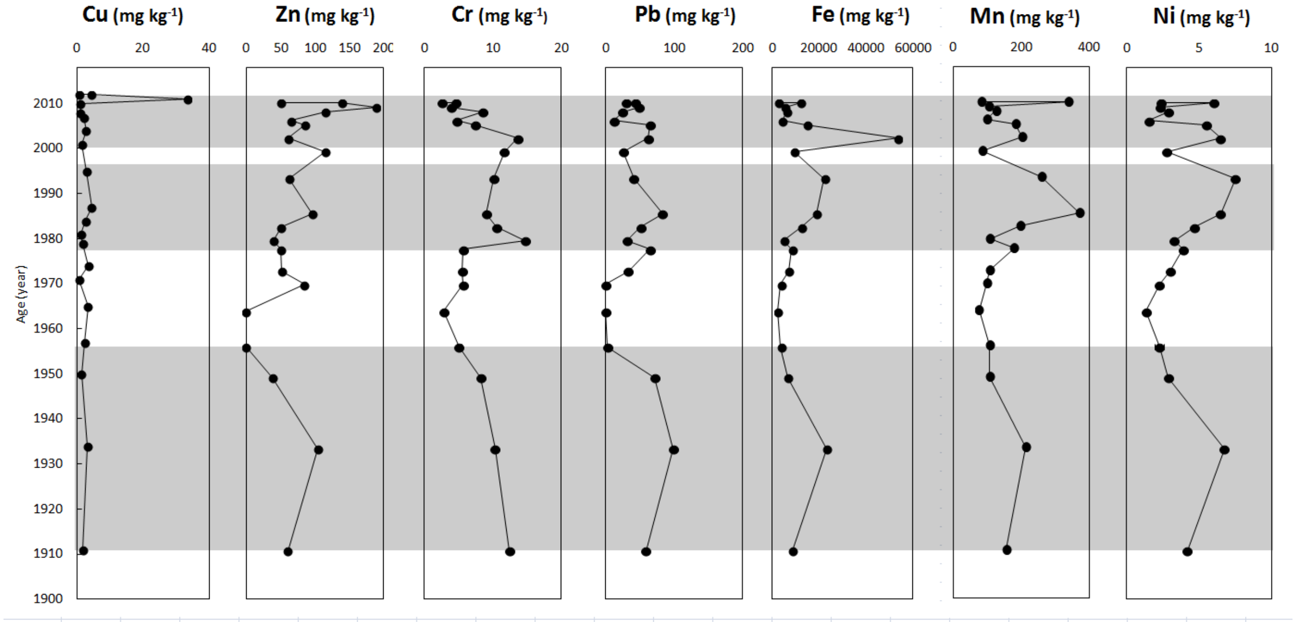
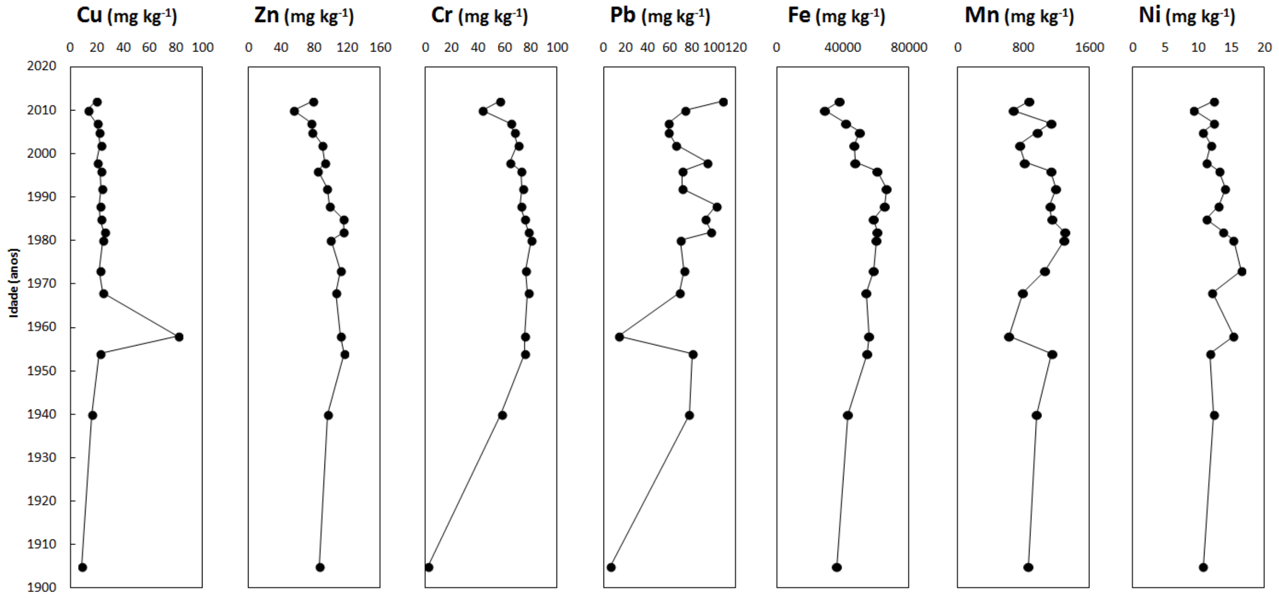


Figure 7 - Stratigraphic variations of trace metals concentrations in sediment core (C) (mg kg^{-1})

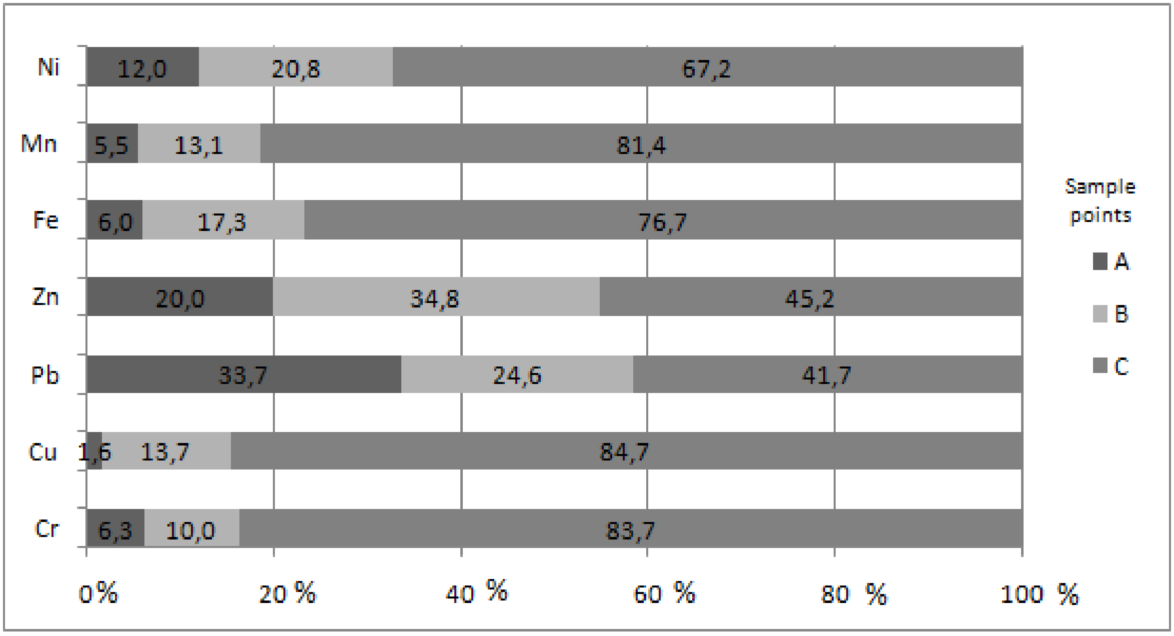


It can be noticed for the metals Cr and Pb a comportment of continuous increase in concentrations since 1910 to 1980 and from there an also continued reduction until today. For Cu metal, we can observe a peak in the years 1960, behaviour already reported in cores.

In Figure 8, there is a predominance of higher mean values in profile C, downstream of the city of Linhares. This municipality has shown rapid demographic and urban development in recent decades, reaching 141,306 inhabitants in 2010 (IBGE, 2011).With the significant discharge of raw sewage directly into the river (only 16% of it is treated), a highly anoxic environment is formed, occurring reduction of sulfates to sulfides, thus favoring the precipitation of metals in sediments.

Similar event has been reported for the estuarine system of Vitória Island, also in Espírito Santo (LINHARES, 2014; JESUS, et al., 2004).

Figure 8 - Relative distribution of metals in three points analyzed



Another explanation for this lies in energy reduction in river flow due to the characteristic of slope on its bed. This can be confirmed in Figure 9 (next page), on which we note that next to points A and B the slope region shows significant reduction in comparison with the rest of the basin, and the point C lies at an altitude close to zero. The angular coefficients confirm this difference. The consequence is the increased residence time in these regions and a higher rate of precipitation of metals from water to sediment.

The comparison of the values of metals determined in this work with others reported in several regions of Brazil and the world is presented in Table 3.

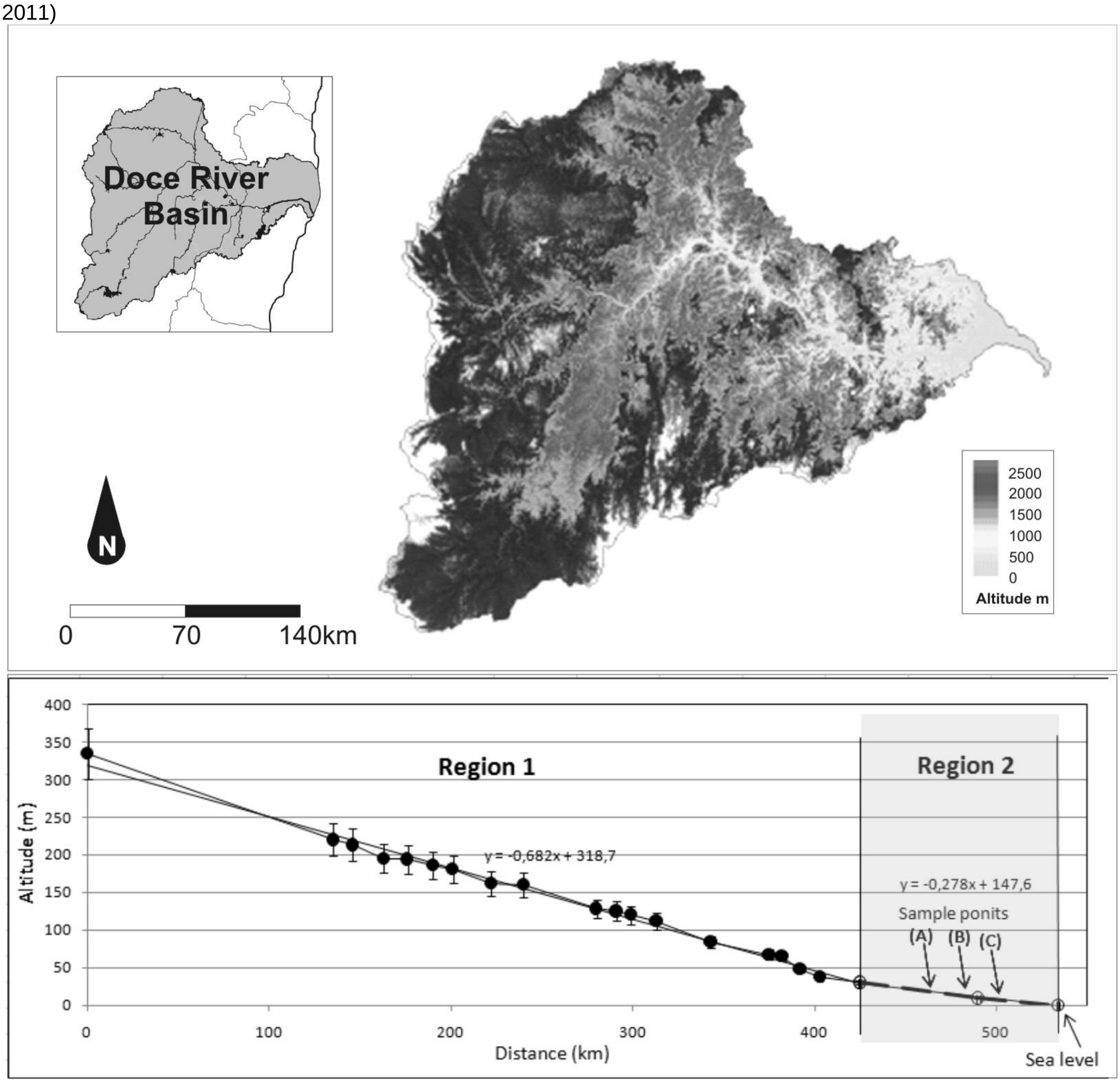
In this study we verify that the values of the metals Fe and Mn found in the region of the lower Doce River is the highest among the studies analyzed. Only the Betari River (SP) and the Elizabeth River (USA) have higher concentrations of Pb. Similar behaviour also occurs in the rivers Lacang (China) and Elizabeth (USA), for the Ni. Values of Cu and Zn are only higher than those found in Betari River (SP) and the estuary of the Patos Lagoon (RS). As for Cr, the concentration determined in this work was the smallest of all.

Table 3 –Values of metal concentration in other regions of Brazil and the world

Local	Cu	Zn	Cr	Pb	Fe	Mn	Ni
Lower Doce River [a]	0,5-23,8	41,9-94,9	4,9-65,5	42,2-71,4	0,4-5,2	66,5-989,9	2,3-12,6
Estuarine lagoon dos Patos, RS [b]	18,9 -39	6,4-41,9	---	0,4 – 8,8	---	---	---
Beaches on Itaipú lagoon, PR [c]	21 - 90	19- 108	6,4-71,9	12-38,1	1,3-1,8	182-529	1,9-3,6
Guanabara bay, RJ [d]	5 -26,7	20 – 53,3	---	16,7-70	---	11 – 45,3	5 – 6,7
Betari River, SP [e]	3,5 – 17,5	14,9-5247,3	---	21,7-5280,6	0,048-0,26	178,3-623,9	1,8-4,4
Lacang River, China [f]	2,5-95,5	28,5-110,7	5,5-167,1	10,4-27,3	---	---	1,61-80,5
Elizabeth River, Virgínia, EUA [g]	54,8-248,7	156,3-1049,9	31,6-236,4	72,9-256,3	---	---	21,7-90,5

([a] Present study; [b] Barbosa et. al., 2012; [c] Belo et al., 2010; [d] Machado et al., 2002; [e] Cotta et al., 2006; [f] Bai et al., 2009; [g] Conrad et al., 2007)

Figure 9 - altimetry profile of Doce River. Region 1) altimetry profile between the cities of Rio Doce and Colatina, Region 2) altimetry profile between the city of Colatina and the mouth of the Doce River at sea (source: MARCUZZO et al., 2011)



CONCLUSIONS

Through the technique of geochronology of sediments we could perform the historical reconstruction of the sedimentary profile of the lower Doce River region. The historical trend of the sedimentation rate in the analysed cores presented events in common, which are related to the intense processes of urbanization and economic growth in the region. The analysis of metal contents in accordance with the dating performed to the strata make it possible to associate the behaviour of the observed values along the profiles with historical facts recorded in the region of the Doce River watershed as a whole. It was possible to locate and identify the signs of the growth process in a large geographical area that is interconnected through the rivers present in the second largest watershed in Brazil.

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