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### Trace Elements and Palynomorphs in the Core Sediments of a Tropical Urban Pond

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Additional information is available at the end of the chapter

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### 1. Introduction

Park Hermogenes de Freitas Leitao Filho is located in Campinas (SP), limited by the Cidade Universitaria I and Cidade Universitaria II neighbourhoods and the State University of Campinas (UNICAMP), in the Barão Geraldo district, whose population was estimated in 2011 to be around 60,000 inhabitants [1]. The park has an estimated area of 123,901.06 m² and of this total, 80,111.17 m² corresponds to the surface of a pond formed by the damming of two streams: one passes through the campus of UNICAMP, draining an area of 325.813 m². In recent decades, effluent from the University has been released into the pond. In 2004, this release was captured by the sewage system of the municipal sanitation company. Currently, the pond receives urban drainage water from the Cidade Universitária II neighbourhood and a Centro Médico Hospital, on the right bank, and the university campus and the Cidade Universitaria II neighbourhood on the left bank.

Thus, in this study we sought the presence of trace elements (As, Co, Cr, Cu, Ga, Ni, Pb, Th, V and Zn) and  $Al_2O_3$ ,  $Fe_2O_3$ , MnO and Loss on Ignition (LOI, 105  $^{\circ}$ C and 1,000  $^{\circ}$ C) in recent sediments of the pond and correlate it with the occurrence of pollen and spores derived from the surrounding vegetation. Accordingly, a 65 cm-deep core, named T-UNICAMP, forming the subject matter of this article.



### 2. Study area

Park Hermogenes de Freitas Leitão Filho is located at the coordinates 22°48'40.20" S and 47°04'11.86" W (23k, 287000 to 287700 - 7475700 to 7476000 m) and it is one of the green leisure areas surrounding the University of Campinas, Campinas (SP) in the district of Barão Geraldo.

The park and its surroundings have undergone significant changes in their vegetation cover and land use from the 1950s onwards, mainly because of the growth of the neighbourhood and the District of Barão Geraldo, as well as construction on the university campus and the urban expansion of the city of Campinas. The land use has changed from wood savannah (Brazilian Cerrado) to agricultural use (sugar cane crops and pasture), and eventually to urban use (residential and the university). The surrounding vegetation is represented by degraded fragments of wood savannah (Brazilian Cerrado) and garden vegetation.

Figure 1 shows the study area and the location of the analysed sample.

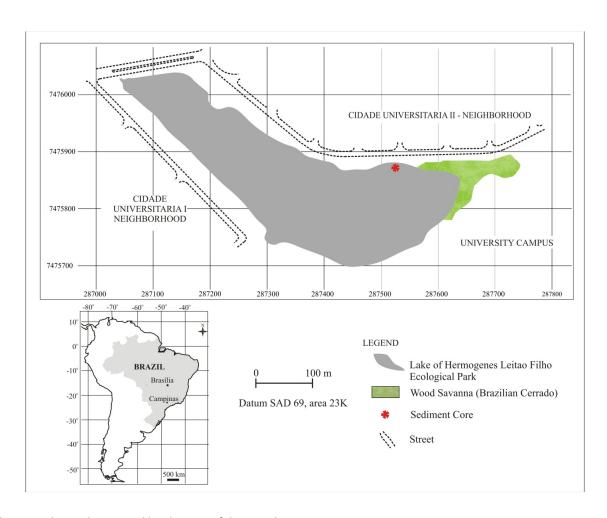


Figure 1. The study area and localization of the sample core

### 3. Material and method

The 65 cm-depth core (T-UNICAMP) was removed near the pluvial exit of the Cidade Universitaria II neighbourhood. The material collected was predominantly sandy-clay.

For the chemical analysis of the sediments, samples were taken every 10 cm, for a total of six samples. In these samples, the elements As, Co, Cr, Cu, Ga, Ni, Pb, Th, V and Zn, and  $Al_2O_3$ ,  $Fe_2O_3$ , MnO were analysed by X-ray fluorescence spectrometry (Philips PW 2404) and the Loss on Ignition (105°C and 1000°C) parameters at the Analytical Geochemistry Laboratory of the Geosciences Institute - UNICAMP. The larger elements were determined in the Uniquant program and the other elements were determined in Solo2007 – a Superq program.

For pollen analysis, six samples were collected at the same intervals of depth for the analysis mentioned above. The palynology samples were processed according to the classical method of [2] for Quaternary sediments, which comprises the following steps: dissolution of silicates by HF; removal of silica colloidal with diluted HCl (hot); destruction of humic acids by 10% KOH solution; centrifugation and washing the sample with distilled water; blade mounting, with 50 microlitres of the sample, and observation under a Axioimager Zeiss microscope at the Palaeo Hydrogeology Laboratory of the Institute of Geosciences - UNICAMP.

### 4. Results

### 4.1. Description of sediments

The sediments are predominantly sandy clay, for the interval 0 to 40 cm deep. The sediments then become silty clay, up to 51.5 cm. From this depth, fine sandy sediments occur. Note that the sediments are oxidized to a depth of 30 cm.

Figure 2 presents a description of the sediments, the distribution of the palynomorphs and the chemical elements along the sampled profile.

### 4.2. Chemical analysis

The results of sediment analysis are presented in Table 1.

Depth	10 cm	20 cm	30 cm	40 cm	50 cm	65 cm
Al <sub>2</sub> O <sub>3</sub> (%)	21.1	22.8	25.4	26.2	23.7	2.1
Fe <sub>2</sub> O <sub>3</sub> (%)	2.4	2.5	1.3	1.2	15.3	0.3
MnO (%)	0.02	0.01	0.01	0.01	0.09	0.01
LOI (105°C) (%)	4.7	4.4	5.4	4.6	2.7	0.2
LOI (1000°C) (%)	20.2	17.2	17.0	14.0	12.9	0.9

Depth	10 cm	20 cm	30 cm	40 cm	50 cm	65 cm
As (ppm)	2.7	3.3	1.0	1.0	5.1	1.0
Co (ppm)	8.8	10.6	6.4	7.9	20.0	8.0
Cr (ppm)	77	78	202	204	77	18
Cu (ppm)	82	8	11	152	166	6
Ga (ppm)	26.0	27.0	33.0	32.0	30.0	4.5
Ni (ppm)	25.0	27.0	34.0	36.0	42.0	3.2
Pb (ppm)	29.0	24.0	34.0	41.0	26.0	6.1
Th (ppm)	11.6	12.3	16.0	15.7	10.5	2.9
V (ppm)	227	223	103	94	359	23
Zn (ppm)	118	380	57	40	171	6

**Table 1.** Results of the chemical analysis of sediments.

The  $Al_2O_3$  concentrations varied from 21.1 to 26.2% to a depth of 40 cm and a minimum value of 2.1 % on the basis of the core. The  $Fe_2O_3$  concentration was found between 0.3 and 15.3 % at depths of 65 and 50 cm respectively. In the other depths, the concentration ranged from 1.2 to 2.5 %.

The MnO has concentrations ranging from 0.01 to 0.09%, which is highest in the sample at 50 cm deep.

The LOI values ranged from 0.2 to 5.4% (LOI 105°C) and 0.90 to 20.20 % (LOI 1000°C). The lowest values were found at the base of the core.

Regarding the trace elements, the concentrations of As ranged from 1.0 to 5.1 ppm, Co from 6.4 to 20.0 ppm, Cr from 18 to 204 ppm. The concentrations of Cu, Ga and Ni ranged from 6 to 166 ppm, 4.5 to 33.0 ppm and 3.2 to 42.0 ppm, respectively. The elements Pb, Th, V and Zn presented concentrations ranging from 6.1 to 41.0 ppm, 2.9 to 16.0 ppm, 23 to 359 ppm and 6 to 380 ppm, respectively.

On the basis of the core (interval from 65 to 50 cm), the lowest concentrations of the trace elements analysed are found in the most sandy portion.

In the 51.5 - 40 cm and 40 - 30 cm intervals, there is a higher proportion of clay in the reduced environment with organic matter, which favours the retention of trace elements such as Cr, Cu, Ga, Ni, Pb and V. The depth interval from 50 to 40 cm has higher concentrations of the chemical elements As, Co, Cu, Ni, V and Zn. The 20 - 0 cm interval presented a high concentration of Zn and significant concentrations of other elements.

The  $Al_2O_3$  concentration due to the presence of clay has little variation (between 21.1 to 26.2 %) up to the 65 cm interval, which has the lowest value (2.1%) in the sandy portion. The  $Fe_2O_3$  concentration is found in highest percentage in the interval of 50 cm, along with MnO.

The Loss on Ignition parameter (105°C and 1000°C) occurs in all the intervals, ranging from 0.2 to 5.4% and 0.9 to 20.2%, respectively. Thus, organic matter is present in the more superficial portions of the core to a depth of 50 cm, with a strong decrease in the sandy portion (65 cm interval).

### 4.3. Pollen analysis

As it can be seen in Figure 2, pollen grains were identified in two intervals: T-UNICAMP/32-35 cm and T-UNICAMP/42-46 cm. Figure 2 shows, in alphabetical order, the main pollen types distribution found, of which 19 were Angiosperms and 3 were Pteridophytes (Figure 3). We observed the existence of 446 pollen grains distributed in 19 pollen types and 36 spores. Among the different taxonomic categories we considered as indeterminate those that could not be identified to family level, which amounted to 41 grains of pollen.

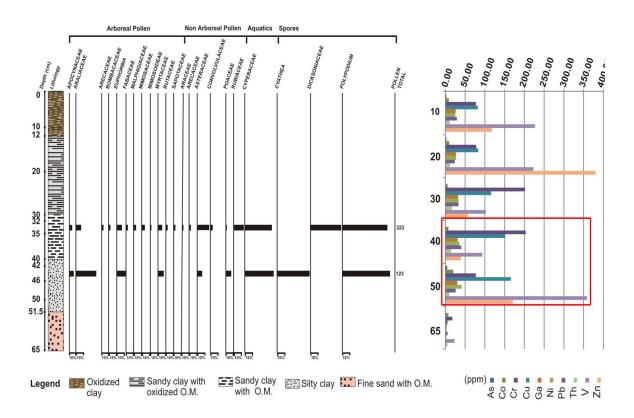
The 42-46 cm interval is mainly characterized by a low concentration of pollen grains and the presence of spores. In this interval, we mainly observed the presence of Cyperaceae, Araliaceae, Poaceae and Myrtaceae. As for the spores, these were of the families Polypodiaceae (*Polypodium*) and Cyatheaceae (*Cyathea*).

The 32-35 cm interval is characterized by a higher concentration and amount of pollen grains and the presence of rate indicators of wood savannah (Brazilian Cerrado). However, we did not observe a significant number of Pteridophytes spores. The predominant families in this interval were: Araliaceae, Asteraceae, Rubiaceae, Malpighiaceae, Myrtaceae, Fabaceae and Cyperaceae - featuring wood savannah (Brazilian Cerrado) - present in the remaining fragments of the vegetation surrounding the pond. As for the spores, we saw the presence of Cyatheaceae, Polypodiaceae and Dicksoniaceae.

### 5. Discussion

Urban lakes suffer pollution problems arising primarily from the activities of their urban surroundings, which may contribute to the greater amount of trace elements, which are concentrated in the pond fine sediments. Trace elements such as Cd, Cu, Pb and Zn are toxic and present adversity to aquatic organisms and humans [3].

The elements As, Cr, Cu, Ni and Zn (T.E.) were analysed taking as sediment toxicity screening values for aquatic life the TEL and PEL - according to [4] - indices adopted by the Sao Paulo state environmental agency. The acronym TEL means "Threshold Effect Level" and PEL means "Probable Effect Level". These values are guidelines for sediment quality, and differ in values for each parameter analysed, although both aim to protect life in aquatic environments. The proposed values of these bands are divided into three parts: below the minimum value suggested, where an adverse effect is rarely expected (<TEL); between the minimum and the maximum value, where the possibility of an adverse effect might be expected (>TEL and <PEL); and the higher than the maximum value suggested (> PEL), where an adverse effect is often expected. Thus, Table 2 presents the patterns of TEL and PEL for each element (As, Cr, Cu, Ni and Zn), the depths of their occurrence and their classification as to the quality of the sediments.



**Figure 2.** Descriptive profile of the T-UNICAMP core featuring a pollen diagram and the distribution of trace elements (T.E.) in depth.

T.E.	TEL (ppm)	PEL (ppm)	<tel (depth)</tel 	"/>TEL and <pel (depth)</pel 	"/>PEL (depth)
As	5.9	17	10, 20, 30, 40, 50 and 65 cm	0 -	F
Cr	37.3	90	65 cm	10, 20, 50 cm	30 and 40 cm
Cu	35.7	197	65 cm	10, 20, 30, 40 and 50 c	m-
Ni	18	36	65 cm	10, 20, 30 and 40 cm	50 cm
Zn	123	315	10, 30, 40 and 6	5 cm 50 cm	20 cm

Table 2. TEL and PEL results from a comparative analysis of the trace elements' (T.E.) distribution in depth.

The most adverse concentrations of Cr (> PEL) are found in depths of 30 and 40 cm. At the depth of 50 cm, Ni concentrations exceed the PEL index and at the depth of 20 cm, the element Zn is greater than the PEL index. Above the TEL index, but below the PEL, samples from depths of 10, 20, 30 and 40 cm present Cu and Ni elements within this range of values. Nonetheless, within this PEL / TEL interval, at the depth of 50 cm, there are Ni and Zn elements.

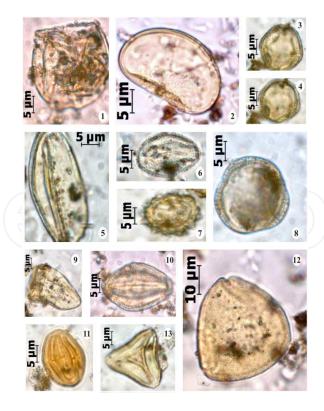
In the sand fraction at the greater sampled depth (65 cm), we found lower concentrations of the elements studied (<TEL).

The element As was found in concentrations below the TEL, where an adverse effect is rarely expected. Figure 2 shows the pollen diagram compared with the results of chemical analysis of the sediments. Thus, in the intervals 42 - 46 cm and 32 - 35 cm, the occurrence and preservation of palynomorphs is related to high levels of trace elements like As, Co, Cr, Cu, Ni, Pb, V and Zn. This association may be related to an environment of reduced deposition [5, 6] where high concentrations above environmental standards - especially of Cr, Ni and Zn - present toxicity to those microorganisms and invertebrates that feed on organic matter.

The presence of fine sediments (clay and silt) and organic matter which may come from biomass killed by this toxicity favours the concentration of trace elements found in the depths [3, 7].

In the intervals sampled above 30 cm, the trace elements had concentrations above the environmental standards. However, oxidized sediments are presented by varying the water level of the pond, which would explain the non-preservation (absence) of palynomorphs in the upper levels of the core.

At intervals below 50 cm, the absence of palynomorphs and the low concentration of trace elements is a consequence of the occurrence of sandy sediments, indicating an environment of higher energy; as such, it is more abrasive for palynomorphs and has a lower capacity to absorb the elements studied [5, 6].



**Figure 3.** Palynomorphs: 1) Apocynaceae; 2) Araceae; 3) Araliaceae; 4) Araliaceae; 5) Arecaceae; 6) Bombacaceae; 7) Asteraceae; 8) Convolvulaceae; 9) Cyperaceae; 10) Euphorbiaceae; 11) Fabaceae; 12) Mimosoideae; and 13) Myrtaceae.

### 6. Conclusion

The urban lake of Park Hermogenes Leitão Filho has sediments with adverse registers for the elements Cr, Ni and Zn, possibly due to sewage discharge from urban occupation and services surrounding the pond. The presence of clay and organic matter contributed to a higher retention of these elements and palynomorphs in the sediments.

The study showed that in those areas strongly impacted by human activities the concentration of toxic elements in fine and anoxic sediments, the preservation of the assemblages of palynomorphs may occur, since this polluted environment does not allow for the survival of microorganisms and invertebrates that feed on organic matter.

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