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An Elemental Analysis Of Periphyton: A Natural Source Of Phosphorous In The Wetlands Of The Maya Region Of Quintana Roo, México.

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Abstract. Periphyton is a complex ecosystem composed by filamentous algal and an assemblage of heterotrophic microbes and other microorganisms that live attached to great submerged substrata in almost all aquatic ecosystems. The elemental analysis of periphyton was carried out by the IBA techniques PIXE and NRA. Pellets of periphyton were bombarded with protons at 3 MeV in vacuum and non-vacuum conditions. The NRA technique was also used in order to determine the ^{16}O and ^{12}C composition, using a deuterium beam at 1.2 MeV. The results obtained from the periphyton analysis show the presence of 25 elements and give a similar pattern in the concentration of the total macronutrients (Ca>P>S>K). Related to micronutrients, Cu and Zn were detected, but only Mn and Fe present a similar pattern of concentration According to these results, we can conclude that periphyton plays a very important role in the biogeochemical cycling, due to the fact that it acts as a natural source of nutrients in the ecosystem, as well as an important indicator of water quality. The results of this study suggest the possibility that periphyton was used as a bio-fertilizer by the Maya civilization due to its richness in phosphorus and nitrogen.

Keywords: PIXE; RBS; NRA; Periphyton; Wetlands; Ecology

INTRODUCTION

Periphyton is a complex ecosystem [1,2] that consists of a floating biomass of filamentous algal community, fungi, bacteria, protozoa and micro-crustaceans, among other microorganisms [3]. Periphyton is able to grow temporarily or permanently in the continental water bodies of the Savanna, located at the El Eden Ecological Reserve in Quintana Roo, Mexico. During the wet season, periphyton grows in the depressions of the reserve, which are rich in wetland vegetation, but is until the dry season when it appears as a periphyton crust. El Eden was one of the place020s where the antique Maya civilization was settled on. Although it is a region with seasonal dry tropical climate, as well as very shallow and poor soils, their development based on an intensive agriculture is already a mystery. The question of how could these people provide enough food to sustain a large population can only be answered with the study of the present Maya communities that still practice the agriculture using organic materials as fertilizers [4,5,6], just as the ancient Mayan communities did when they used periphyton as a bio-fertilizer [7,8,9]. Previous studies carried out on nutrient content and greenhouse experiments support the hypothesis that periphyton is a potential biofertilizer [10].

In order to verify the assumption that periphyton was used as a bio-fertilizer by the Mayan civilization due to its richness in phosphorus and nitrogen, in this work we obtained the elemental characterization of periphyton, focusing on its phosphorus concentration.

EXPERIMENTAL

Representative periphyton samples were collected at different sites in the temporal wetlands of the Savanna that covers an area of about 15 km^2 around the El Edén Ecological Reserve in Quintana Roo, México. Samples were dried at 50^o C, milled and homogenized in an agate mortar and sieved with 100 mesh. Subsecuently, pellets of 3x5 mm^2 were formed using a 5 ton pressure hydraulic press.

PIXE analyses were carried out in the 3MV 9SDH-2 Pelletron accelerator at the Instituto de Fisica, UNAM. The samples were bombarded at 3 MeV under no vacuum conditions, using simultaneously two radiation detectors: a Si (Li) and a Ge-Hyperpure detector, placed respectively at 45° and 40° normal to surface of the sample. The FWHM of the K_α Mn X-Ray lines were 250 and 155 eV respectively. A 80 μm thick Kapton filter and a 28 μm thick mylar foil were placed in front of Ge-H detector. The Si(Li) detector was used in order to detect the elements with $Z \leq 26$; meanwhile, the remaining elements were detected with a Ge-H detector.

The Instituto de Física 5.5 MV Van de Graaff accelerator was used for NRA as well as the vacuum PIXE experiments. Emitted X-rays were quantified with a Si(Li) detector with a 180 eV resolution at 5.9 keV, K_α Mn X-rays. The samples were irradiated with 2 MeV protons at an angle of 45º normal to the sample surface. A 134 µm thick Kapton funny filter with a 1.2 mm hole was set up before the Si(Li) detector to attenuate the X-rays product of the elements lighter than Fe [11]. In order to calibrate the detection system, the IAEA-SL-1 reference material was used [12].

The NRA analysis was carried out by irradiating the samples with a normal incidence 1.3 MeV $^2H^{++}$ beam. The backscattered particles and the products of the nuclear reactions were detected with a surface barrier detector, at a scattering angle of 165º.

The PIXE spectra were analyzed using the GUPIX 2000 code [13]; meanwhile the NRA spectra simulation was performed with the SIMNRA code [14].

RESULTS AND DISCUSSION

The comparative PIXE analyses, applied to samples 1-5 at vacuum conditions and to samples 6-11 at no vacuum conditions, demonstrated no significant differences. It is important to remark the outstanding of the simultaneous use of both X-ray detectors, the Si(Li) and Ge-H. Table 1 shows the mean concentration of the elements detected in the periphyton samples, in which for N it only includes the mean value of those samples where this element was detected. A 6% uncertainty was estimated in all the PIXE analyses.

TABLE 1. Mean elemental concentration obtained from periphyton samples.

ELEMENT	Mean * ($mg\ kg^{-1}$)	N	TECHNIQUE	
Si	10948 ± 1543	11	Si(Li) detector	PIXE
P	66494 ± 13585	11		
S	18598 ± 5874	11		
Cl	4948 ± 2442	11		
K	5459 ± 328	11		
Ca	419801 ± 73329	11		
Ti	658 ± 39	6		
V	102 ± 6	7		
Cr	157 ± 9	7		
Mn	688 ± 41	11		
Fe	5639 ± 338	11	Germanium detector	
Co	93 ± 6	3		
Ni	200 ± 12	8		
Cu	18 ± 1	5		
Zn	28 ± 2	8		
Ga	54 ± 3	4		
As	30 ± 12	2		
Br	69 ± 4	5		
Rb	106 ± 6	5		
Sr	230 ± 14	4		
Y	850 ± 338	2		
Zr	287 ± 152	3		
Ba	108 ± 51	5		
Pb	162 ± 72	2		
O	308679 ± 42140	11	particle detector	RBS-NRA
C	135802 ± 16858	11		
N	21712 ± 2992	11		

* Mean measured ± Typical uncertainty combinated

Figure 1 shows the results obtained from measuring three important elements: carbon, nitrogen and phosphorus, the last ones were the main goal of the investigation as it is known that they constitute the organic part of the biofertilizers. It can be observed that nitrogen is almost constant for all the samples, but its increment comes with an increase in the carbon signal, as well as a decrease in the phosphorus amount. This result proves that these three elements are correlated as they constitute the organic part of the periphyton. The ternary P-C-N diagram in Figure 2 shows that the samples collected in different places are grouped in two very close areas, what makes us think about the richness of the earth at the El Eden Ecological Reserve.

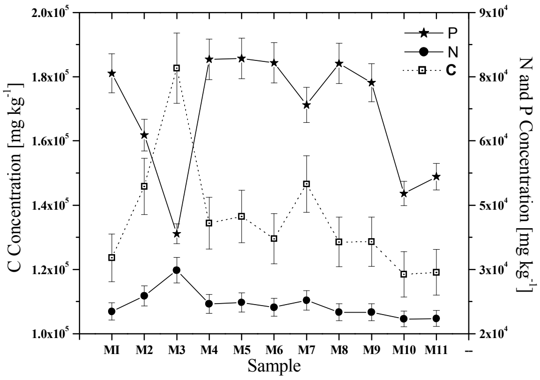

FIGURE 1. Nitrogen, carbon and phosphorous concentration of periphyton samples.

It is important to emphasize the high level of homogeneity in the macro elemental composition compared with the micro elemental content found in the periphyton samples, independently of their spatial and temporal origin. Furthermore, even the PIXE spectra of two samples with different phosphorus concentrations show a similar "finger print" as can be observed in Fig 3. Previous chemical analyses done on periphyton by Palacios et al. [10] are in good agreement with the phosphorus concentrations presented in this work, as well as the organic matter concentrations (C, N, O) that are not far from the levels that were found by RBS-RNA. A Cluster analysis was done to the samples in order to identify the different sources of the elements. We identified two different sources: the soil and the contaminants traces. The contaminant-trace group is formed by Y, Cr, Sr, Zr, Ba, Pb, Rb, Ga, As, Cu, Br, Co, V and Ti, which form a block of elements with the lower concentration and/or the less frequency.

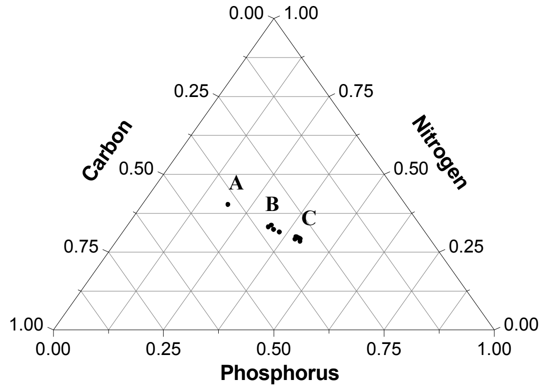

FIGURE 2. Ternary P, N and C diagram. Most of periphyton samples are grouped in blocks B and C and only one appears in block A.

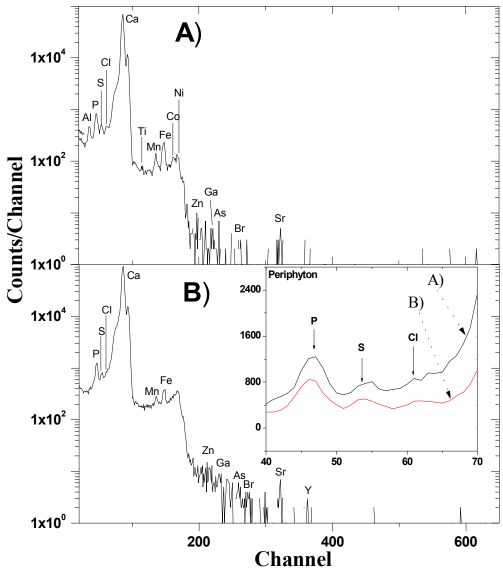

FIGURE 3. Comparitive PIXE spectra of two periphyton samples. It can be noticed a higher P content in spectrum B. Nevertheless a finger print was observed.

The group that was identified as the soil group was split into four subgroups, the first one corresponds to Mn and Si; the second group includes elements (K and Cl) with low concentrations that appear in all the sites where periphyton was collected. The third group is formed by Fe that is present as the most abundant oligoelement (5639 μg kg^{-1}). The fourth group contains the most abundant elements: S (18598 μg /kg^{-}1), P (66494 μg kg^{-1}), C (135802 μg kg^{-1}), N

(21712 μg kg-[1]) and Ca, the most abundant element of all with a concentration of 419801 μg kg^{-1}.

CONCLUSIONS

The results obtained in this work, suggest the possibility that periphyton was used by the Mayan civilization as a biofertilizer, due to its richness in phosphorus and nitrogen. This statement is supported by the results of experimental studies that show the positive effect of periphyton on plant growth, which is equivalent and sometimes superior to the effect of chemical fertilizers [8]. Simultaneous PIXE-RBS analyses were a suitable method to characterize periphyton, particularly in phosphorus content. RBS-RNA could also be a suitable method to obtain C:N ratios in biomaterials as periphyton. Despite periphyton is a very complex biomaterial, the elemental analysis indicates a high level of homogeneity in the macro elemental composition, independently of spatial and temporal origin. Periphyton analysis indicates a similar pattern of concentration of the total macronutrients (Ca>P>S>K); in the case of the micronutrients, only Mn and Fe show a similar pattern of concentration (Fe>Mn). Cu and Zn (Zn>Cu) were detected only in 5 and 8 sites respectively. According to the results, it can be concluded that periphyton plays a very important role as a natural source of nutrients in this ecosystem.

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