Limnetica, 37(2): 297-309 (2018). DOI: 10.23818/limn.37.24
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Influence of dominant environmental processes in the tropical Cuban basin Hanabanilla and reservoir on sediment composition

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Received: 04/04/16 Accepted: 30/04/18

ABSTRACT

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The Hanabanilla reservoir was built in 1960 in the center-south of Cuba and is used for human supply and power generation. This research was aimed at identifying the important processes affecting sediment composition, through the analysis of particle size, and organic carbon (OC), nutrients, and major trace elements concentrations in sediment samples taken at the outlet point of the reservoir. The documentary review allowed us to identify how the nature and management of the basin and the operation of the reservoir affected sediment quality. The application of principal components analysis (PCA), and the determination of ionic relationships and correlations between the sediment quality variables, allowed for the identification of influential processes on sediment quality. Anthropic activities in the period 1960-2012 produced residues rich in OC, total phosphorus (TP) and total nitrogen (TN) that were stored in reservoir sediments. During the first years of the reservoir (1964-1976) the highest concentrations of sediment TP were recorded and the sediments functioned as a sink. The OC and TN mean concentrations were higher in the last stage of the study (2006-2012). The main influential processes on sediment composition were the operation of the reservoir, the geochemical cycle of P, the mineralization of the substances in the water column, and the weathering of silicates and the contribution of organic matter from the basin. Sediment quality data indicate that OC and TN were of allochthonous origin and TP was of autochthonous origin. Levels of sediment OC and TN also corresponded with an increase in anthropic activities in the basin.

Key words: reservoir operation, ionic ratios, anthropic activities

RESUMEN

Influencia de los procesos ambientales predominantes en la cuenca y el embalse Hanabanilla sobre la composición de su sedimento

El embalse Hanabanilla fue construido en 1960 en el centro-sur de Cuba y sus usos principales son el abastecimiento humano y la generación de energía eléctrica. Esta investigación tuvo como objetivo identificar los procesos fundamentales que afectan la composición del sedimento, mediante el análisis del tamaño de las partículas, y el contenido de carbono orgánico (OC), nutrientes y elementos traza mayoritarios en muestras de sedimento tomadas en la obra de toma del embalse. La revisión documental permitió identificar cómo afectan la naturaleza y el manejo de la cuenca, y la operación del embalse a la calidad del sedimento. El análisis de componentes principales (PCA), las relaciones iónicas, y las correlaciones entre las variables de calidad del sedimento, permitieron identificar los procesos influyentes en la calidad del sedimento. Las actividades antrópicas en el período 1960-2012 produjeron residuos ricos en OC, fósforo total (TP) y nitrógeno total (TN) que se almacenaron en los sedimentos del embalse. Durante los primeros años del embalse (1964-1976), se registraron las más altas concentraciones de TP en el sedimento que actuó como sumidero. Las concentraciones medias de OC y TN fueron más altas en la última etapa del *estudio (2006-2012). Los principales procesos que influyeron en la composición del sedimento fueron: la operación del embalse, el ciclo geoquímico del P, la mineralización de las sustancias en la columna de agua, y el lavado de los silicatos, unido a la contribución de la materia orgánica de la cuenca. Los datos indicaron un origen alóctono para el OC y el TN, y autóctono para el TP. Los niveles de OC y TN en el sedimento también se correspondieron con un incremento en la actividad antrópica en la cuenca.*

Palabras clave: *operación del embalse, relaciones iónicas, actividades antrópicas*

INTRODUCTION

Sediment may constitute the main source of pollutants to lakes from their basins (nutrients, organic matter, metals among others) (Liu *et al.*, 2013). During heavy rain events, high flows can discharge abundant quantities of sediments from the basin and pollutant levels in water can increase from the erosion of superficial and sub superficial sediment layers (Gourdin *et al.*, 2014). Lakes can consequently become sinks or sources of pollution depending on environmental conditions (Betancourt *et al.*, 2010a, Betancourt *et al.*, 2010b). Changes that occur in the sediments can be studied by geographical region (Lamba *et al.*, 2015). In temperate regions, the main processes determining the variation of sediment composition are the degree of alteration/weathering of materials and the association of some metals with organic/clay aggregates (López *et al.*, 2012). Climatic change can alter patterns of temperature, rain and soil use (Kim *et al.*, 2013). This in turn can provoke changes in erosion and sedimentation processes that can be evaluated by the study of lake sediment.

The evaluation of physical-chemical variables in sediment can contribute to scientific support for making decisions on controlling diffuse sources of contamination (Wellen *et al.*, 2015). The principal physical-chemical variables studied in sediment include: nitrogen (N), phosphorus (P), organic carbon (OC), organic matter, C/N/P ratios, metals and particle size (Ahiablame *et al.*, 2010). The C/N ratio has been used as a representative proxy to reconstruct the depositional environment of freshwater lake sediments (Duan *et al.*, 2017). Major (Na, K, Ca, Mg, and Si) and trace (Al, Fe, Mn, Zn, Cu, and Cr) element concentrations in reservoir sediment can help inform the aquatic ecosystem history and the process and impacts of human activities that occur at the watershed scale (Mora *et al.*, 2017).

In spite of the significance of lake sediment studies, there is limited research on this topic in Cuba. There are ten basins of maximum priority in the country, ranked on the basis of economic, social and environmental complexity, the degree of impact on natural resources, and general basin characteristics. One of these maximum priority basins is the Hanabanilla basin.

The beneficial uses of Hanabanilla reservoir include public water supply for the cities of Cienfuegos, Santa Clara and surrounding population in the area and power generation. In spite of these uses and the importance of understanding sediment quality to inform management strategies

Table 1. Characteristics of Hanabanilla reservoir. *Características del embalse Hanabanilla.*

Characteristic	Value	Characteristic	Value
Volume LNW (hm^3)	286.0	Maximum width(km)	1
Volume LMW(hm^3)	340.7	Dead Volume (hm^3)	14.00
Area (km^2)	18.8	Maximum depth (m)	43.0
Maximum length (km)	17.8	Average depth (m)	15.5
Border line (km)	75.0	Closing coordinates	N: 282.3, E: 596.3

LNW: Level of normal waters; LMW: Level of maximum waters.

to protect water quality, to date there have been few sediment-related studies in the reservoir.

The objectives of this research were: (1) to characterize the accumulated sediments in the outlet zone of the reservoir, and (2) to identify how processes related to management and use of the basin and the operation of the reservoir affect the composition of sediments.

MATERIAL AND METHODS

Description of Hanabanilla reservoir and basin

The Hanabanilla reservoir (Table 1) started operation in 1960. It is one of the deepest reservoirs in Cuba. Water used for power generation is sent to Paso Bonito dam and used as the water source for the cities of Cienfuegos and Santa Clara and other settlements (Betancourt *et al.*, 2009). The Hanabanilla basin is located within the Arimao River basin and spreads from the extreme southwest of Santa Clara up to the northwest of the Cienfuegos province (Fig. 1). The basin includes the Escambray Mountains and has an average elevation of 635 m above sea level and an area of 191.6 km^2. The maximum elevations and slopes of the center of Cuba are located in the basin, which is also dominated by geology with low permeability that favors drainage over infiltration.

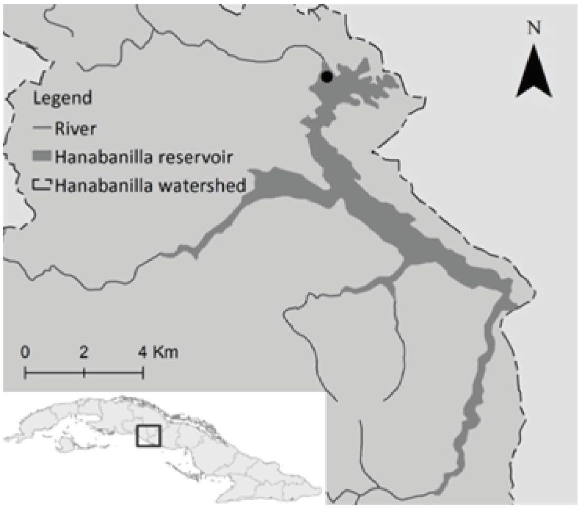

Figure 1. Map showing the outlet point in Hanabanilla reservoir (central Cuba). Geographical location of the Hanabanilla basin and reservoir. *Mapa de la obra de toma del embalse Hanabanilla (Cuba central). Localización geográfica de la cuenca y el embalse. Hanabanilla.*

Annual precipitation in the Hanabanilla basin varies between 1500 and 1900 mm. The period of maximum precipitation is typical from May to October, and the dry period is typically from November to April. The predominant wind direction in the Hanabanilla basin is southwest to southeast. Summer average air temperature is 23.5 ºC and air temperature seldom exceeds 26.0 ºC. Highest temperatures have been registered in May and April, when the reservoir exhibits thermal stratification (Sánchez, 2000).

The north part of the Hanabanilla basin presents an extensive zone of igneous granodiorite intrusion, while the south presents a zone of micaceous, amphibolic, deoritic and graffitic schists with a less intense intermediate zone of crystalline limestone (Sánchez, 2000). Basin soils are predominantly located on slopes with high erosion potential (5-60 %), are low in nutrients and organic matter, and have a predominating sand fraction (< 0.2 mm).

Sánchez (2000) reports monthly water quality data for the outlet point of Hanabanilla reservoir for 1990 to 1999. Total nitrogen ranged from 0.27-0.60 mg-N/L and was dominated by organic N. Total P (TP) ranged from 0.025-0.040 mg-P/L. The ratio N/P of 2.5-8.9 suggests limitations by N. Hypolimnetic anoxia occurred from May to November, however, the reservoir was classified as oligotrophic/mesotrophic.

Sediments sampling

The sampling of sediments was done on April 12, 2012, in the outlet point of the reservoir located at the geographical coordinates N 22005' 35" W 080004' 00" at 29 m deep (Fig. 1). The election of this point was done considering the mentioned direction of wind, added to horizontal flow of water in reservoirs, which maintain some characteristics of rivers (Margalef, 1983). This causes the mass of water of the three inflowing rivers to move towards the outlet point of Hanabanilla reservoir. In a previous study in this reservoir (Sánchez, 2000), the outlet point was found to capture average water quality characteristics (nutrients, oxygen, metals, pH) of the overall reservoir. In addition, Chapman (1996) recommend the use of outlet points for sampling in reservoirs used for human consumption.

An UWITEC corer with PVC liner (90 cm length, 8.6 cm inner diameter) was used for collecting the sediment sample. The system possesses a closing device which seals the bottom of the sediment column after penetration in the sediment. For extrusion of the sediment, we used a mechanism that pushes sediment on the lower part of the core, and sediment was cut in sections of 2 cm as it was extruded upwards from the sampling tube. The cut was done with a plate of rustproof steel. Homogenized sections were stored in clean containers, closed hermetically and labeled. Samples were preserved at 4 ºC to inhibit microbiological activity during the transportation to the laboratory.

Sediment quality analysis

To determine the age of each core stratum used for sediment quality analyses, dating was done by means of gamma spectrometry (^{210}Pb and corroboration with ^{137}Cs) (Díaz-Asencio *et al.*, 2017). N in sediment was quantified by the Kjeldahl method and was reported as TN. The sample of sediment was heated in the presence of concentrated sulfuric acid and catalysts. As a result, organic N turned into ammonia, and then into ammonium sulfate. The formed ammonic salt was decomposed in a caustic alkali and the liberated ammonia was distilled to an excess of boric acid. The collected ammonium was then measured by a volumetric method. Sediment TP was determined by the formation of a chromogenic compound of vanadium-molybdenum-phosphoric system, which comprised all the phosphoresced contents present in the sediments, by means of the spectrophotometric method according to the Cuban Standard NC 34:1999. The determination of OC was based mainly on loss of weight by ignition, which happens by sediment incineration at 550 ºC for 4 hours. The granulometry of sediment samples was analyzed by means of mechanic agitation sifters of 63 and 2 µm and separated into three size fractions (reported in percent mass): ≥ 63 µm; between 63 and 2 µm; < 2 µm.

Analysis of data

The Spearman correlation analysis was applied, and the differences of variables by years were analyzed by Mann-Whitney test for independent variables. To identify the main processes related with the quality and composition of sediments, Principal Components Analysis (PCA) was applied with the rotation method with equamax Kaiser normalization (statistic package SSPS, version 15).

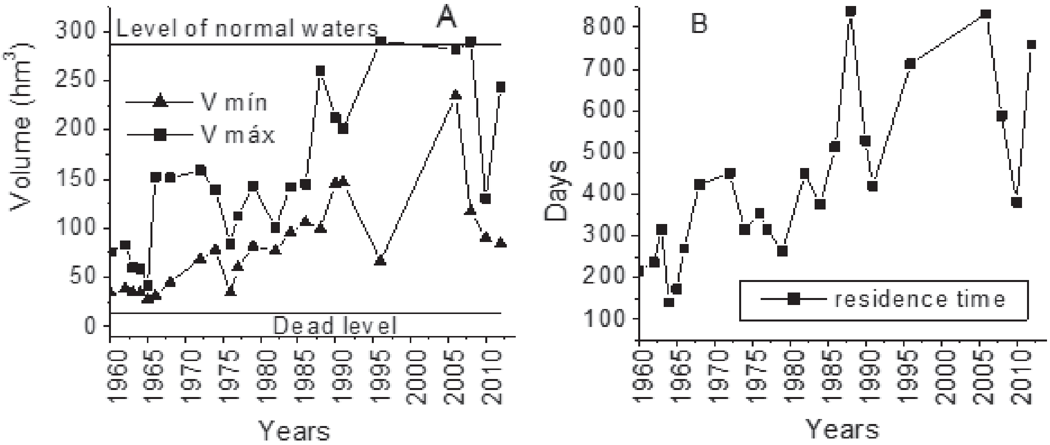

Figure 2. Maximum and minimum volumes (A) and residence time of the water (B) in the reservoir. *Volúmenes máximos y mínimos (A) y tiempo de residencia del agua (B) en el embalse.*

RESULTS

Basin use and management

Predominant land uses in the basin include coffee cultivation, grasslands, forest, scrublands and various farming activities. The basin includes a total population of around 7000 inhabitants who discharge much of their sewage into tributaries to the reservoir. Other basin activities include a coffee depulpating plant, areas of tourist interest, cattle grazing, hydroelectric facilities, and a factory that builds plastic boats.

In the 1960-70s there was an exodus of population from the mountains caused by a number of factors (García-Suárez, 1973), with the consequent disappearance of some communities within the Hanabanilla basin. In the 1980s there was a repopulation of the mountains and a number of small human settlements reappeared. In parallel with repopulation, activities related to intensive cultivation of coffee began, including the general use of agricultural fertilizers and chemicals, and activities related to a military institution formed to promote agricultural work by youngsters. These activities increased the generation of waste and erosive processes in the basin. Unlike other areas of the province, human activity in the Hanabanilla basin continued during the 1990s, and permanent cultivation was largely replaced by annual crop agricultural that resulted in an increase in agricultural activity in the basin.

Reservoir management

The use of the dammed water for power production has generated an over-exploitation, which has resulted in extreme fluctuations in stored water volume and reservoir water quality. During the study period (1960-2012), especially during the first two decades of operation, high volumes of water were extracted and the reservoir's minimum annual volume was commonly near the dead volume of reservoir (Fig. 2). In the last three decades it was possible to observe an increase both in the maximum volume and in the minimum, as well as a general increase in the annual residence time of the reservoir (Fig. 2). The changes of volume facilitated the growth of vascular plants in areas where sediment was not covered with water. Some of these plants with short growth cycles have been cultivated by nearby residents. These plants were often submerged by water when the level of the reservoir raised, and the products of biomass decomposition were deposited on to reservoir sediment.

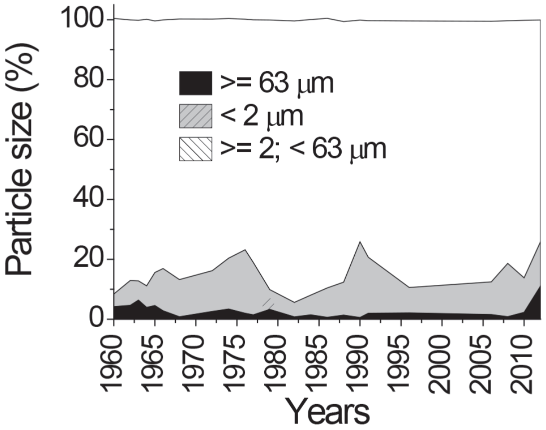

Figure 3. Vertical distribution of particle size in the sediments of the reservoir. *Distribución vertical del tamaño de partícula en el sedimento.*

Sediment quality

The composition of the sediment was dominated by particles < 63 µm, which revealed the high proportion of clay and slime and their potential for the storage and transport of nutrients and pollutants (Fig. 3). The percentage of particles ≥ 63 µm was low and averaged 3 %. The percentage of particles ≥ 63 µm for the period 1960-1977 were higher than 1978-2010 ($p < 0.001$). The percentage of particles < 2 µm were generally less than 20 %, and this percentage correlated positively with Si/Al ratio.

OC concentrations in Hanabanilla reservoir sediment ranged from 70-110 mg/g (dw: dry weight). OC levels showed dramatic shifts with time and peak concentrations were observed around the mid-1960s, 1980 and after 2005 (Fig. 4a). OC correlated positively with Ca/Al, Ca/Mg, Mn/Fe, OC/TN ratios and Ca, and negatively

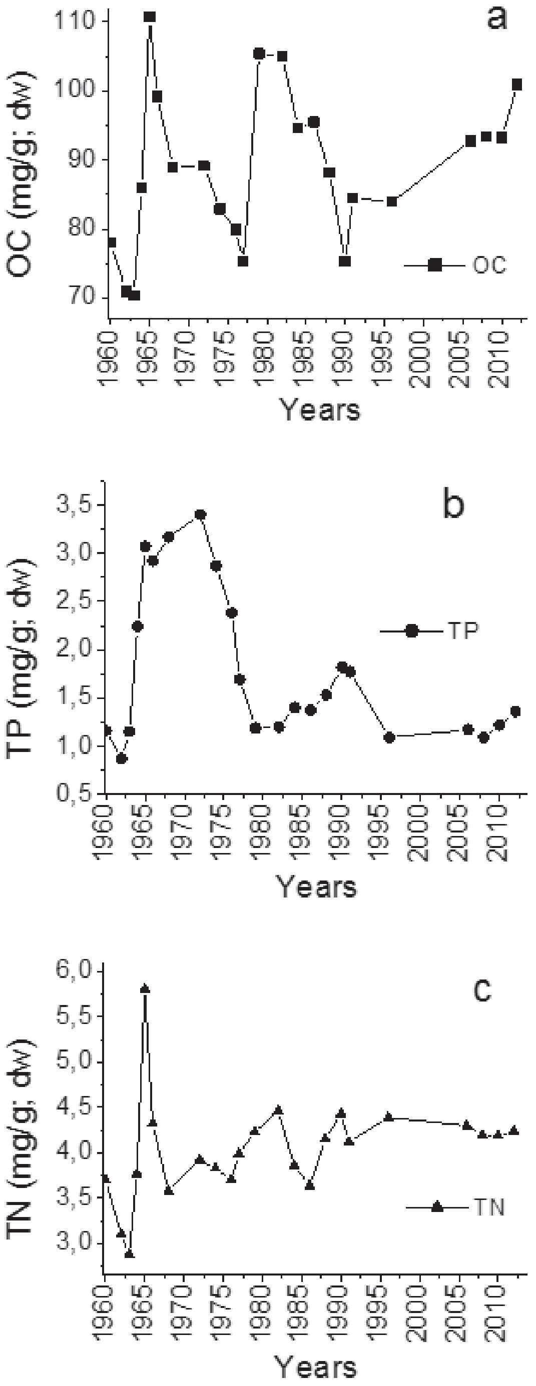

Figure 4. Organic carbon (a), total phosphorus (b) and total nitrogen (c) concentrations (mg/g; dw: dry weight), in sediment of Hanabanilla reservoir. *Concentraciones (mg/g; dw: peso seco) de carbono orgánico (a), fósforo total (b) y nitrógeno total (c), en el sedimento del embalse Hanabanilla.*

with Al, Si and K (Table 2). TP varied from 0.87-3.40 mg/g (dw) (Fig. 4b) and exhibited high concentrations from 1960 to 1976 and fairly low and stable concentrations (~1-1.5 mg/g) thereafter (Fig. 4). TP correlated positively with Mg and Fe and negatively with Ca/Al, Ca/Mg, Si/Al and Ca (Table 2). The concentrations of TN ranged from 2.88-5.81 mg/g (dw) (Fig. 4c). Minimal and maximum concentrations occurred in 1963 and 1965 respectively, and concentrations were fairly stable after that at 3.5-4.5 mg/g (dw) (Fig. 4). TN was correlated positively with Vmax (Table 2).

Mg, Al, Si K, Ca, Mn and Fe concentrations ranged from 14.8-23.5, 80.3-113.1, 156.3-203.5, 14.2-21.7, 16.2-79.7, 2.1-13.7, 69.15-143.5 mg/g (dw), respectively (Table 3). To assess processes related to sediment composition, atomic ratios of Si/Al, Si/K, K/Al, TP/AL, TP/Ca, TP/Fe, Ca/Al, Fe/Al, P/Si, Ca/Mg, Mn/Fe and Mn/Al were also determined (Table 3). Nutrient enrichment in the sediment column was evaluated by using the elemental ratios of organic matter. OC/TN, OC/TP and TN/TP ratios ranged from 22.0-29.1, 67-228 and 2.5-8.9, respectively (Table 3). OC/TP and TN/TP ratios registered a positive correlation with years (Table 2). The lowest values of OC/TP were observed in the first two decades of reservoir operations, whereas the highest values prevailed in more recent years, when TP registered relatively low concentrations.

Identification of the processes that influence sediment composition

PCA was conducted with the intention of reducing the large number of variables to a few combined variables, and then used to infer what processes influenced sediment quality in Hanabanilla reservoir. The results of PCA showed that three components accounted for 82.4 % of the total variance in the data matrix (Table 4). Component 1 was dominated by TP, TP/Al, TP/Fe, Fe/Al, TP/Si, TP/Ca, Mg and Fe (positive values) and OC/TP, TN/TP and Vmax (negative values), and accounted for 35.5 % of total variance. Component 2 was dominated by OC, TN, Ca/Al, Ca/Mg, Mn/Fe, Mn/Al, Ca, Mn (positive values) and Si (negative values), and accounted for 25.0 % of total variance. Component 3 was dominated by OC/TN, Si/Al, Si/K

Table 2. Significant correlations between variables and some ratios; positive (+) and negatives (-) correlations (* $p < 0.05$; ** $p < 0.01$) PS: particle size; Vmax: maximum volume. *Correlaciones significativas entre variables y algunos radios atómicos; correlaciones positivas (+) y negativas (-) (** $p < 0.05$*; ** *$p < 0.01$) PS: tamaño de partícula; Vmax: volumen máximo.*

	Correlations
Years	TP(-)*; TN(+)*; OC/TP(+)**; TN/TP(+)**; Vmax(+)**; TP/Ca(-)*; Ca(+)*
TP	OC/TP(-)**; TN/TP(-)**; Si/Al(-)**; TP/Al(+)**; TP/Al(+)**; Ca/Al(-)*; Fe/Al(+)**; TP/Si(+)**; Ca/Mg(-)*; TP/Ca(+)**; Mg(+)**; Ca(-)*; Fe(+)**
OC	Ca/Al(+)**; Ca/Mg(+)*; Mn/Fe(+)*; Al(-)**; Si(-)**; K(-)**; Ca(+)**; OC/TN(+)*
TN	Vmax(+)**
OC/TN	K(-)*; Si/Al(+)**; Si/K(+)*; Al(-)*
OC/TP	TN/TP(+)**; Vmax(+)*; Si/Al(+)*; TP/Al(-)**; Ca/Mg(+)**; Al(-)**; Mg(-)**; Ca(+)**; Fe(-)**
TN/TP	OC/TP(+)**; Vmax(+)*; Si/K(+)*; TP/Al(-)**; TP/Fe(-)*; Ca/Mg(+)**; Mg(-)**; Ca(+)*; Fe(-)**
PS<2µm	2-63 µm(-)**; Si/Al(+)*;
Vmax	TP/Ca(-)*; Ca(+)*
Si/Al	Ca/Al(+)**; Fe/Al(-)**; TP/Si(-)**; Ca/Mg(+)**; TP/Ca(-)**; Mg(-)**; Al(-)**; K(-)**; Ca(+)**; Fe(-)**
Si/K	Ca/Al(+)*; Al(-)**; K(-)**; Ca(+)*; K/Al(-)**
K/Al	TP/Fe(-)*; K(+)**
TP/Al	Fe/Al(+)**; TP/Si(+)**; TP/Ca(+)**; Mg(+)*; Fe(+)**; TP/Fe(+)**
TP/Fe	TP/Si(+)*
Ca/Al	Si/Al(+)**; Fe/Al(-)*; Ca/Mg(+)**; Mn/Fe(+)**; TP/Ca(-)**; Mn/Al(+)*; Al(-)**; Mg(-)**; Si(-)*; K(-)**; Ca(+)**; Mn(+)*
Fe/Al	TP/Si(+)**; Ca/Mg(-)*; TP/Ca(+)**; Mg(+)**; Ca(-)*; Fe(+)**
TP/Si	Ca/Mg(-)*; TP/Ca(+)**; Mg(+)**; Fe(+)**
Ca/Mg	TP/Si(-)*; Mn/Fe(-)**; Mn/Al(+)*; Mg(-)**; Si(-)*; K(-)**; Ca(+)**; Fe(-)**; TP/Ca(-)**; Al(-)**
Mn/Fe	TP/Ca(-)*; Mn/Al(+)**; Mg(-)*; Al(-)**; Si(-)**; K(-)*; Ca(+)**; Mn(+)**
TP/Ca	Mg(+)**; Al(+)**; Ca(-)**; Fe(+)**
Mn/Al	Si(-)**; K(-)*; Ca(+)*; Mn(+)**; Al(-)**
Al	Mg(+)**; Si(+)**; K(+)**; Ca(-)**; Mg(-)*; Mn(-)*; Fe(+)**
Mg	Ca(-)**; Fe(+)**
Si	K(+)**; Ca(-)*; Mn(-)**
K	Ca(-)**
Ca	Fe(-)**

(positive values) and particles < 2 µm, K/Al, Al, and K (negative values), and accounted for 21.9 % of total variance.

Because P and compounds that affect P cycling (Fe, Al, Ca, OC) were common dominant variables in component 1, it was related with the influence of geochemical cycling of P on sediment composition. Component 2 was related to compounds released to water during the mineralization of organic matter. Component 3 was

Table 3. Minimum (Min), maximum (Max), mean and standard deviation (SD) of the mass (mg/g; dry weight) of elements, and select ratios, in sediment of Hanabanilla reservoir. *Mínimo (Min), máximo (Max), media (Mean) y desviación estándar (SD) de la masa de los elementos (mg/g; peso seco), y algunos radios atómicos, en el sedimento del embalse Hanabanilla.*

	Min	Max	Mean	SD
OC/TN	22.0	29.1	25.6	2.3
OC/TP	67.6	228.4	146.6	55.1
TN/TP	2.6	8.9	5.7	2.1
Si/Al	1.9	2.4	2.1	0.1
Si/K	12.8	17.8	14.7	1.3
K/Al	0.1	0.2	0.1	0.0
TP/Al	0.0	0.0	0.0	0.0
TP/Fe	0.0	0.1	0.0	0.0
Ca/Al	0.1	0.7	0.4	0.2
Fe/Al	0.4	0.8	0.5	0.1
TP/Si	0.0	0.0	0.0	0.0
Ca/Mg	0.5	3.3	1.6	1.0
Mn/Fe	0.0	0.2	0.1	0.0
TP/Ca	0.0	0.2	0.1	0.1
Mn/Al	0.0	0.1	0.0	0.0
Mg	14.8	23.5	18.3	2.3
Al	80.3	113.1	95.8	9.3
Si	156.3	203.5	184.0	11.8
K	14.2	21.7	17.6	2.1
Ca	16.3	79.8	46.6	23.7
Mn	2.1	13.7	7.3	3.4
Fe	69.2	143.5	95.7	23.4

related to the contribution from the watershed to the sediment of the reservoir including entry of organic matter and weathering of silicates.

DISCUSSION

Composition, organic carbon, nutrients and in sediment

The record of the particles of major size in the deepest layers of the reservoir could be related with the presence of the original river bed frequently found in reservoir sediments. The predominant silt fraction (2-63 µm), is usually the most abundant in most of the reservoir sediments (López *et al.*, 2016) mainly in its downstream part (Snyder *et al.*, 2004).

OC concentrations were higher than those reported by other authors (Downing *et al.*, 2008; López *et al.*, 2016). In the watershed of this reservoir, there are several sources of organic matter pollution and a predominance of agricultural activities. The OC deposition appears high in small lakes that have steep catchment areas with agricultural land use (Kastowski *et al.*, 2011). The increase in OC in recent decades (Fig. 4) was likely related to use and management of the basin. In the last three decades, the population of the mountains was reunified in settlements with deficient or no waste treatment. For this reason, pollutant discharges were more intense with less possibility of natural degradation. In general, the last three decades were characterized by an increase of anthropic activities.

The high values of sediment TP found in the first years of the reservoir are likely due to the sediment of reservoir retaining high quantities of nutrients, especially P, during the first discharges of nutrient to the new reservoir (Sas, 1989; Rzymski *et al.*, 2015). According to Wetzel (1975) P can be retained more strongly in the sediments than N and C. This author also points out that both Fe and Al form compounds with P that are of limited solubility, especially Al. In the dammed waters of Hanabanilla reservoir concentrations of Fe and P have been found to covary (Sánchez, 2000). Besides, in the geologic formation of the basin there are rocks such as igneous granodiorite and diorite, amphibolic, micaceous and graffitic schists that contain structural Al, which is another factor to consider in the retention of P in sediments in the first years after reservoir construction.

The values found for TN are similar to those found in other reservoirs (Franzen *et al.*, 2010; Liu *et al.*, 2013; Winston *et al.*, 2014). Similarly, the percentage of OC was slightly higher when compared to a reservoir in Arkansas, USA (Winston *et al.*, 2014). This reservoir is 45 years old (Hanabanilla is 55 years) and lime rocks predominate in its basin; population settlements and farming activities are also located in the reservoirs basin. Nevertheless, the highest value of TP was 0.55 mg/g, below the lowest value observed in Hanabanilla (0.87 mg/g). These results reveal the influence of the geologic nature of basins on the preferential retention of P in sediments. In the basin of the Arkansas reservoir, the predominance of limestone was reported, while in the Hanabanilla there is predominance of igneous rocks with abundant presence of Al and Fe. The limited solubility of the phosphates of Al and Fe previously discussed explains observed differences in nutrient concentrations, especially P, in the sediments of both reservoirs.

Sánchez (2000) pointed out that the period 1992-1998 registered an increase in nutrient concentrations in water of Hanabanilla reservoir. This author reported also the use of fertilizers in coffee plantations in the basin, and this agrees with observed increases in TN concentrations in sediment relative to the previous decade.

Nutrient and metal ratios in sediment and Principle Components Analysis

Mass accumulation rates (MARs) of OC are better measures of delivery and preservation of organic matter to sediment than sediment OC concentrations (Meyers & Lallier-Vergès, 1999). Díaz-Asencio *et al.* (2017) measured MARs in Hanabanilla reservoir ranging from 0.09 to 046 g cm^{-2} y^{-1}, and observed high values in the first years of the reservoir likely related to intense rain events reported during that period which enhanced erosion in the catchment area and particulate loading and sedimentation in the reservoir. They concluded that sediment accumulation did not change significantly over the last 50 years.

While MAR is a useful metric, nutrient ratio has been used independently of sedimentation rate as a source indicator (autogenetic versus allochthonous) for organic matter (Kunz *et al.*, 2011; Winston *et al.*, 2011; Huo *et al.*, 2013). Although layers with different sedimentation rates can have diverse process that affect the elemental composition of sedimentary organic matter, changes (immobilization, remineralization, and others) are not commonly large enough to erase the large C/N differences between organic matter derived from vascular land plants and nonvascular algae (Meyer & Lallier-Vergès, 1999). C/N ratios greater than 20 (values of all layers of this study) are due to allochthonous organic matter of terrestrial origin (Meyers, 1994). Organic matter derived from vascular plant material has C/N ratios > 20 and can be distinguished from algal biomass (C/N of 8 to 10) (Meyers & Teranes, 2002). This allochthonous matter appears to constitute the main source of OC to Hanabanilla sediment.

Table 4. Percentage of variance explained by the three principal components (total variance 82.4 %) and loads for the variables introduced in the PCA analysis. Only values higher than 0.5 are given (PS: particle size; TR: residence time of water; Vmax: maximum volume). *Porciento de la varianza explicada por los tres componentes principales (varianza total= 82.4 %) y contribuciones de las variables introducidas en el PCA. Sólo se muestran los valores mayores a 0.5 (PS: tamaño de partícula; TR: tiempo de residencia del agua; Vmax: volumen máximo).*

	Component		
	1	2	3
% Variance explained	35.5	25.0	21.9
TP	.973		
OC		.741	
TN		.596	
OC/TN			.763
OC/TP	-.889		
TN/TP	-.941		
PS <2µm			-.597
Vmax	-.626		
Si/Al			.802
Si/K			.888
K/Al			-.573
TP/Al	.956		
TP/Fe	.832		
Ca/Al		.669	
Fe/Al	.857		
TP/Si	.962		
Ca/Mg		.646	
Mn/Fe		.909	
P/Ca	.758		
Mn/Al		.882	
Mg	.721		
Al			-.746
Si		-.866	
K			-.814
Ca		.643	
Mn		.853	
Fe	.773		

N/P ratio in water is commonly used as a nutrient limitation index for algal growth; according to Smith (1982) when the N/P is < 15 the limiting nutrient is N. The values of N/P ratio in water (period 1990-1999) indicated N limitation predominance (Sánchez, 2000). This is possibly associated with the retention of P in the sediments (Fig. 4b). P can precipitate bound inorganic material or be in a dissolved form in sediment pore waters (Pettersson, 1998). The potential source of P in the surficial sediments is very large in comparison to the pools in the water column (Boström *et al.*, 1982), meaning that even if only a very small amount is released, it will have a significant impact on P concentration in the reservoir water. In some cases, P can become the limiting nutrient when external N inputs increase to a reservoir (Anderson *et al.*, 2002). If N and P in the sediments are generated from the same source, they should have a good correlation. However, there was no correlation between N and P in Hanabanilla sediment, showing that the nutrients had different sources. In the case of our study site, the dominant source of P in sediment appears to be authoctonous (internally cycled) while the source of N in sediment appears to be allocthonous (terrestrial origin).

Elevated C/P and N/P ratios in sediments are indicative of increased anthropogenic input of nitrate and phosphate, while low N/P ratios have been associated with substantial losses of mineralized N (Giblin *et al.*, 1997). An increase of agricultural activities and settlements in the basin occurred in the last decades of the study years, and this matches with positive correlations between OC/TP and TN/TP ratios with years (Table 2). Sánchez (2000) reports that there was some tree cutting and burning activities in the basin, which meant a contribution of organic matter of vascular plants to the reservoir. He also reports the death of aquatic vegetation at the edge of the reservoir due to changes in the water volume, an additional source of organic matter.

Component 1 was related with the influence of geochemical cycling of P on sediment composition. The principal geochemical parameters involved with TP cycling at the water-sediment interface in lentic environment are: Fe, Mn, Al, Ca and OC (Franzen *et al.*, 2010). The Fe concentration in sediment showed significant correlation with Al concentrations ($p < 0.01$, r = 0.643) indicating that Fe has a predominantly terrigenous origin. Fe, as well as Al, is a major constituent of a large variety of mineral structures such as feldspars, clay minerals and amorphous aluminosilicate gels (Bortleson & Lee, 1972). Those minerals are present in the watershed of the reservoir. The atomic ratio of Fe/Al showed significant correlation with sediment TP concentrations ($p < 0.01$, r = 0.942). The ratio of Fe/Al is linked to the authogenic precipitation of iron oxides and it appears clearly related to the TP/Al ratio in sediments. Because iron precipitation is one of the most efficient processes removing dissolved phosphate from water, considering together Fe/Al and TP/Al in sediments may give a good estimation of the capacity of sediments to act as a P sink (López *et al.*, 2006).

Component 2 was related to compounds released to water during the mineralization of organic matter. Organic matter can adsorb ions such as Ca, Al and Mn and form stable complexes in water (Franzen *et al.*, 2010). During organic matter mineralization, these ions are released and can precipitate (Marchand *et al.*, 2011). Ca/Al ratio have been related to water mineralization in other reservoirs (López *et al.*, 2006).

Component 3 was related to the external contribution from the basin to the sediment of the reservoir, including allocthonous entry of organic matter (C/N ratio) and the contribution of mineralogy from the basin. Si, Al and K are the main elements associated with the alumino-silicate fraction, and these are present in silicates as feldspars (López *et al.*, 2006). Ratios Si/Al and Si/K, are used to infer mineralogical composition of basins, mainly weathering of silicate rocks (López *et al.*, 2006, Marchand *et al.*, 2011). The Si/Al ratio can also be used as a surrogate for grain size: coarse samples are Si enriched, while fine samples are Al enriched (Bouchez *et al.*, 2011). However, there was a positive correlation between Si/Al and PS < 2 μm (Table 2).

To improve the quality of waters and sediments, it is necessary to stabilize the extraction of the dammed waters and to protect the useful area of the reservoir. If the basin of a reservoir is in a mountainous zone, practices of proper management which mitigate contamination should be implemented. Mitigations should include: growing permanent plants to mitigate farming activities; the treatment of the human and cattle waste; the use of organic fertilizers; and the implementation of rational tree cutting practices.

CONCLUSIONS

During 1960-2012 period, the Hanabanilla reservoir basin was used mainly for temporary crops, cattle breeding and human settlements. These activities generated residuals rich in nutrients and organic matter that were stored in sediments. Also, large fluctuations in the water volumes of the reservoir influenced the characteristics of the sediments.

Nutrients and OC registered high values and were related to the use of the basin. Both TN and OC recorded high values in the last years of the study, which coincided with the increase in anthropic activities. In the first years of the study the sediments functioned as a P sink, with its highest values for TP in sediment. These sediments were related with the highest percent of particle size < 2 µm.

The PCA allowed for the distinguishing of reservoir operation and geochemical cycle of P as the most important processes on sediment composition. The influence of the P biogeochemical cycle was also confirmed by the high positive and negative correlation of Fe and Al, respectively, with TP. The other influential processes were the mineralization of the substances present in the water of the reservoir, the washing of silicates, and the contribution of organic matter from the basin.

The relationships between nutrients and organic matter revealed the increase of anthropic activities in correspondence with the use and management of the basin. Also this relationship allowed us to identify the allochthonous character of sediment organic matter and TN, and the autochthonous origin of sediment TP.

ACKNOWLEDGEMENTS

We would like to thank the technicians and specialists of the Laboratory of Environmental Assays of Centre of Environmental Studies of Cienfuegos (CEAC), the workers of the Hanabanilla Reservoir, and the Institutes of Hydraulic Resources (INRH) of Villa Clara and Physical Planning (IPF) of Cienfuegos, Cuba. We also thank Laura Castellanos (CEAC) for providing the site map, and to MSc Clara Esther Gómez Gonzalvo for review of the first version of the manuscript. This study was financed by the Nuclear and Advanced Technologies Agency (AENTA) 200.2002 Project (Solutions to specific problems of integrated management of basins and coastal areas in Cuba, through isotopic and nuclear techniques: sea acidification, CO_2 cycle and sequestration, toxic algal blooms, invasive species, environmental pollution, erosion-sedimentation-transport of nutrients and contaminants, eutrophication and water quality of reservoirs), and the ARCAL CXXXIX (RLA7019/2014) Project (Developing indicators to determine the effect of pesticides, heavy metals and emerging contaminants on continental aquatic ecosystems important to agriculture and agroindustry FAO-IAEA).

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