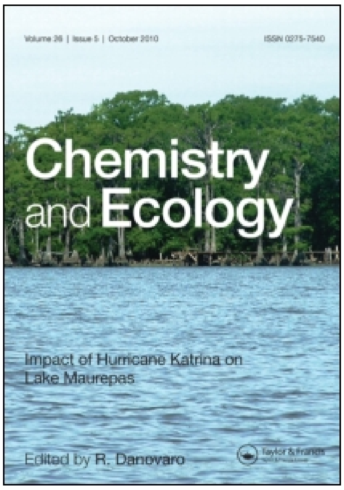

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RESEARCH ARTICLE

Biogeochemistry and cycling of zinc and copper in a dyked seasonally flooded savanna

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There is very little information on the cycling of heavy metals in natural savannas. Venezuelan flooded savannas are characterised by acid soils with redox conditions which might induce Zn and Cu solubilisation. In those flooded savannas a network of small dykes has been constructed to control floods. The biomass accretion after dyking and the abundance of clay particles in the vertisols, dominant in the overflow plains, might be responsible for an increase in nutrient uptake and immobilisation. Due to the redox and pH conditions prevailing during flooding, some questions arise on the fate of the heavy metals. Are they significantly lost as soluble and particulate forms, which in turn, can induce a potential risk of microelement deficiency? Or, on the contrary, are heavy metal inputs in precipitation waters retained somewhere in the terrestrial pools of the watershed allowing for an adequate micronutrient economy? By using input-output budgets, which consider the total atmospheric input and total output in stream runoff (soluble and particulate) for zinc and copper we concluded that in Mantecal flooded savannas, a net accumulation of micronutrient in soils is actually occurring through organic and inorganic complexes, a process that is counterbalanced by the losses of particulates through erosion.

Keywords: heavy metals; nutrient budgets; particulate; savannas; small watersheds; soil redox

1. Introduction

Inputs to natural and man affected ecosystems of trace elements through human activities have increased over the last century, particularly through the contribution of industrial and agriculture operations. There is relatively abundant information available about pools and fluxes of heavy metals in temperate forest ecosystems [1,2]; however, there is very little information on the biogeochemistry and cycling of heavy metals in natural savannas.

Zn and Cu are essential to the normal growth of plants and animals, but are also among the most environmentally concerning elements that have been reported to cause contamination of soil, water and food chains [3]. Venezuelan and Colombian flooded savannas are characterised by

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acidic soils and also by redox conditions which may induce Zn and Cu solubilisation; losses by leaching and external run-off (erosion) might reach limiting levels unless they are compensated for by the inputs due to precipitation or by weathering of Zn and Cu accessory minerals. Precipitation water in neotropical savanna ecosystems is in general slightly or definitely acid [4,5], therefore, macro and micronutrient levels in such water are not expected to be particularly high. Moreover, savanna ecosystems, and within them, alluvial overflow plains in Venezuela are distant from the ocean and with a non-significant anthropogenic activity; consequently the composition of rain water should be minimally affected by marine aerosols. Furthermore, the lack of an important tree canopy, characteristic of seasonally flooded savannas, accounts for a minimal interception of heavy metal aerosols.

The south-western lower Venezuelan llanos are seasonally flooded because of the convergence of numerous river courses, the presence of abundant vertisols or related ill-drained soils, and the extremely flat landscape that is described as an ‘internal delta’ [6]. Vegetation and soils vary along topographic catenas, which show differences of only 1 or 2 metres between the highest and lowest topographic level in the alluvial overflow plain. The upper part of the vegetation soil catena corresponds to the physiographic unit that border the stream, locally called Bancos [7,8], where sandy alluvium has been deposited. The lowest part of the catena corresponds to the physiographic unit called Estero, and is formed by slowly draining decantation cuvettes, where fine particles have settled leading to the development of vertisols or related type soils [7,8]. During the top of the rainy season only the Bancos remain unflooded, therefore the Esteros remain waterlogged from weeks up to several consecutive months.

In order to control floods and maintain water reserves during the dry season (November–April), a network of small dykes (2000–3000 ha of drainage area each) have been constructed. The superficial waters, however, are drained at a weir anchored to the clay layer at the outlet located in the Esteros unit.

In previous papers we described the input and output of nutrients in a flooded savanna, showing the role of precipitation water in the nutrient (cations and micronutrients) economy of those environments [4,7]. After the construction of the dykes, the biomass vegetation doubled and its species composition changed. This biomass accretion might be responsible for an increase in nutrient uptake and immobilisation. In temperate forest, it has been shown that the existent conspicuous humus layer is very effective in retaining heavy metals, particularly Pb and Cu [2]. The lack of a humus layer in seasonally unfertile savannas impairs an effective retention of heavy metals. However, the biomass accretion together with the abundance of clay particles in the vertisols or associated type soils which are dominant in the alluvial overflow plains might contribute to the terrestrial retention. On the contrary, the over flooding condition and low pH of the soils may account for heavy metal losses by leaching and external drainage.

Input-output budgets are useful tools to describe the mobility, retention, and flows of substances, including heavy metals in the environment [2,9,10]. Most heavy metal budgets have been calculated in temperate ecosystems, particularly in forest sites. In this contribution we describe the atmospheric input and total output in stream runoff (soluble and particulate) for zinc and copper in a dyked seasonally flooded savanna. In addition, some internal pools of the biogeochemical cycle of those micronutrients associated with terrestrial environments (soil and vegetation) are described. For our analysis we were interested in the following questions:

(1) Due to the redox and pH conditions prevailing during flooding, are heavy metals significantly lost as soluble and particulate forms in dyked savannas which, in turn, can induce a potential risk of micro element deficiency?
(2) Or, on the contrary, are heavy metal inputs in precipitation waters retained somewhere in the terrestrial pools of the watershed, allowing for an adequate micronutrient economy?

2. Materials and methods

2.1. *Study site*

The site known as Módulo Experimental Mantecal (MEM) is located near Mantecal, Apure State, Venezuela (7° 8′N and 68° 45′W). The region has a marked seasonality with a dry season from November to May and a rainy season from June to October, with maximum precipitation from June to August. The total annual precipitation is 2389 mm, and the mean annual temperature is 27.4 °C with minor variations among months.

It is a seasonally flooded savanna developed under alluvial sedimentation processes forming an 'interior delta', as a consequence of particle deposition on very gentle slopes occurring along great tracts of savanna in Venezuela and eastern Colombia. MEM is a natural savanna with a drainage area of 2200 ha which have been dyked in order to control the floods and to retain water throughout the dry season.

The almost flat topography of the landscape produces a physiography composed of three zones. The highest zone is sabana de Banco, the middle zone is sabana de Bajío and the lowest zone is sabana de Estero. Each physiography unit is characterised by a particular association of soil and vegetation [4], at MEM, Bajio and Estero units represent most of the dyked surface.

At the highest level of the landscape (Banco), soils are less weathered coarse-textured acidic Entisols or Inceptisols; dominant plant species are *Leersia hexandra*, Swartz and *Panicum laxum*, Swartz. In the middle (Bajíos) and lower level of the landscape (Esteros), soils are fine-textured with more developed Vertisols or associated soil types, and dominant plant species are *Leersia hexandra*, Swartz and *Himenachne amplexicaulis* (Rudge) Ness [11].

2.1.1. *Soil sampling*

Soils were sampled in an area of 3.5 ha which is representative of MEM. Thirty surface (0–10 cm) samples mixed to form three composite samples were collected in the area of the Banco (Entisols) and the Estero (Vertisols) soils, respectively.

The main characteristics of the analysed soils are presented in Table 1.

2.1.2. *Collection of rain and stream waters*

Bulk precipitation for chemical analysis was sampled from all storms during one year from six gauges located in three different cleared plots within the study site (MEM). Collection was made in a 1 litre borosilicate glass cylinder protected with a plastic jacket attached 1 m above the soil

Table 1. Physical and chemical characteristics of the studied soils (0–15 cm)*.

Parameters	Entisol	Vertisol
Bulk Density (Mg m^{-3})	1.42	1.12
Sand (%)	54.2	7.8
Clay (%)	7.8	62.4
Textural Classification	Sandy	Clay
pH (1:1)	4.40	4.25
CEC (cmol kg^{-1})	4.1	38.2
Total N (%)	0.04	0.16
C (%)	0.80	3.00
C/N	20.0	18.8

*Adapted from López-Hernández et al. [13].

surface. Collectors were fitted with a polyethylene funnel 20 cm in diameter. The samples were collected in polyethylene bottles, which were first acid-washed and then rinsed with demineralised water, were analysed individually and averaged for monthly input. The rainfall was measured in a standard bureau manual gauge at MEM. Samples were rejected when contaminated by debris.

Streamflow was monitored and water samples taken at a rectangular concrete weir anchored to the clay layer at the outlet of the dyke located at the Estero physiographic unit of the MEM. Samples (six replicates) for stream chemistry were collected semi-weekly during May–December, because the floodgate was closed late in dry season, the floodgate cross section was sampled at various points in order to eliminate uneven distribution of dissolved and suspended materials. Samples were collected in 500 ml polyethylene bottles, which were first acid-washed and then rinsed with demineralised water. Prior to sample collection, at the collection site, bottles were flushed with stream water. All water samples were treated with chloroform ($1\ \mathrm{ml\,l^{-1}}$) and then refrigerated to reduce biological activity.

2.2. *Analytical methods*

2.2.1. *Fractionation of micronutrients*

Zinc and copper fractionation was performed according to the method originally proposed by McLaren and Crawford [12] for copper and used by López-Hernández et al. [13] for copper, zinc and cobalt fractionation.

2.2.1.1 Soil solution and exchangeable Zn and Cu (M-CA) and Zn and Cu bound by inorganic sites (M-AAC). Ten grams of soil was extracted by shaking with 100 ml of 0.05 M of $CaCl_2$ into 250 ml centrifuge tubes for 24 h; at the end of the shaking period, suspensions were centrifuged at 1200 *g* for 10 min. The soil residue from the above extraction was shaken with 100 ml of 2.5% acetic acid for 24 h; suspensions were centrifuged at 1200 *g* for 10 min. The extracts of both fractions were kept for analysis by atomic absorption.

2.2.1.2 Zn and Cu bound by organic sites (M-PYR), occluded by free oxides (M-OX) and residual forms (M-RES). Two grams of soil were extracted by shaking with 200 ml 1.0 M potassium pyrophosphate overnight in a 250 ml centrifuge bottle. After centrifugation (15 min at 1200 *g*) Zn and Cu (M-PYR) were determined in the supernatant.

The residue from the pyrophosphate extraction was shaken with 50 ml deionised water which was discarded, and the soil washed with a small amount of water into an evaporating basin. After evaporating to dryness on a boiling water bath, 100 ml of the reagent (0.1 M oxalic acid, ammonium oxalate 0.175 M at pH 3.25) was added and the contents of the basin, still on the water bath, was exposed to U.V. light for 2 h 30 min; the liquid level in the basin was maintained during extraction with deionised water. When extraction was complete the contents of the basin were centrifuged (1200 *g* for 5 min) and the supernatant was collected together with further washings, using another 50 ml oxalate reagent. Supernatant was kept for later determinations (M-OX).

Residue from the oxalate extraction was evaporated to dryness and ignited at 600 °C in a muffle furnace. 0.5 g of the residue was dissolved with HF in a Parr digestion bomb. Zn and Cu were determined in the digest (M-RES).

2.2.1.3 Total Zn and Cu. Total Zn and Cu were determined in a soil sample (0.1 g) digested in a 25 ml acid digestion bomb (Parr, Illinois, USA) with a mixture of HNO_3-HCl and HF [14]. After digestion, the volume was made up with demineralised water to 100 ml.

Micronutrient analysis was done by atomic absorption in a Techtron AA6 instrument (Varian, Victoria, Australia).

2.3. *Chemical measurements*

In rain and drainage waters pH was determined with a pH meter PM62 with a glass electrode.

Zinc and copper in both precipitation and stream discharge waters were analysed by flameless absorption spectroscopy, but without preconcentration: an HGA 2100 heated graphite atomiser (Perkin-Elmer Connecticut, USA) was employed. Detection limits for Cu and Zn were 3 and $5\,\mu g\,l^{-1}$, respectively.

Particulate material was filtered under pressure from measured amounts (about 20 l) of the streamflow samples, and the collected sediments were weighed. A subsample of particulate (0.01–0.015 g) was digested in a 25 ml acid digestion bomb (Parr, Illinois, USA) with a mixture of HNO_3-HCl and HF [14]. After digestion, the volume was made up with demineralised water to 100 ml. Aliquots were analysed for Zn and Cu by atomic absorption.

2.4. *Statistical analyses*

Analyses were carried out with t-tests for paired samples on the difference between monthly concentration of Zn and Cu in precipitation and stream water.

3. Results

3.1. *Inputs by precipitation water*

Table 2 presents the weighted average Zn and Cu concentration and the corresponding inputs by precipitation water. There was little variation in the monthly weighted concentration of Cu, except for May and September, when significant decreases were recorded (10.4 and $9.8\,\mu g\,l^{-1}$, respectively). The monthly weighted average of Zn in precipitation water was high (33–$39\,\mu g\,l^{-1}$) at the beginning and middle of the rainy season (May–August), decreasing significantly (13.5–$14.4\,\mu g\,l^{-1}$) at the end of the season (September–November); in the scarce December precipitation, zinc concentration again rises ($33\,\mu g\,l^{-1}$). Total micronutrient input to the MEM is taken as the product of precipitation volume and chemical concentration. The zinc input to the ecosystem was almost three times higher than the copper inputs (Table 2).

3.2. *Outputs in drainage water*

Table 3 presents the information on discharge waters for zinc and copper at MEM weir. Zinc weighted average concentrations were highest at the beginning of the wet season with a significant

Table 2. Monthly pH, weighted average concentration ($\mu g\,l^{-1}$) and monthly inputs ($kg\,ha^{-1}$) in precipitation water during the wet season at MEM. Means followed by the same letter do not differ significantly.

Month	pH	Zn ($\mu g\,L^{-1}$) Weighted average	Zn ($kg\,ha^{-1}$) Inputs	Cu ($\mu g\,L^{-1}$) Weighted average	Cu ($kg\,ha^{-1}$) Inputs
May	5.8	37.0 a	0.094	10.4 b	0.027
June	5.6	39.0 a	0.182	12.0 a	0.056
July	5.4	39.0 a	0.157	12.3 a	0.049
August	5.5	33.0 a	0.080	16.1 a	0.037
September	5.6	13.5 b	0.023	9.8 b	0.016
October	5.4	14.4 b	0.022	12.1 a	0.019
November	5.1	20.0 b	0.034	11.5 a	0.020
December		33.0 a	0.007	13.2 a	0.003
Total annual			0.599		0.227

Table 3. Monthly pH, weighted average concentration ($\mu g\,l^{-1}$) and monthly outputs ($kg\,ha^{-1}$) in drainage water during the wet season at MEM. Means followed by the same letter do not differ significantly.

Month	pH	Zn ($\mu g\,l^{-1}$) Weighted average	Zn ($kg\,ha^{-1}$) outputs	Cu ($\mu g\,l^{-1}$) Weighted average	Cu ($kg\,ha^{-1}$) outputs
May	6.9	42.0 a	0.0128	9.0 a	0.0028
June	7.1	43.0 a	0.0727	9.2 a	0.0155
July	6.2	18.0 d	0.0369	9.2 a	0.0190
August	6.3	39.0 ab	0.0619	9.5 a	0.0150
September	6.3	29.0 bc	0.0174	7.9 a	0.0045
October	6.3	30.0 bcd	0.0096	8.7 a	0.0028
November	6.3	26.0 cd	0.0022	9.0 a	0.00077
December		24.0 cd	0.0002	9.0 a	0.00007
Total annual			0.214		0.06044

lower value at the month of July. There was not, however, any definitive trend for this element to increase in concentration towards the end of the wet season. Copper concentration apparently was independent of season with average weighted concentration ranging from 7.9–9.5 $\mu g\,l^{-1}$ (Table 3). Total micronutrient output to the MEM is taken as the product of drainage volume measured at the weir and chemical concentration. The zinc output to the ecosystem was three times higher than the copper output (Table 3).

3.3. *Particulate losses and Zn and copper budgets at MEM*

Table 4 presents the information for monthly and total annual losses of particulate material collected from discharge waters at MEM weir. Information is also presented for monthly and total annual losses for zinc and copper as particulate materials. Total annual losses as particulate materials reached 71.34 $kg\,ha^{-1}\,yr^{-1}$, from which 0.025 and 0.200 $kg\,ha^{-1}\,yr^{-1}$ correspond to Cu and Zn, respectively. Zn soluble losses were a little greater than those corresponding to the particulate forms, whereas Cu losses as particulate were half of the soluble forms (Tables 3 and 4).

In Table 5 the results for the micronutrients (Zn and Cu) budgets in the MEM are summarised. Assuming that most of the soils are poorly drained (vertisols or related badly drained soils), the percolation of water by internal drainage when the water content falls below field capacity becomes minimal; and losses of elements from the catchment by deep seepage should be negligible. Therefore, micronutrient budgets are calculated as the difference between annual input (entering in precipitation) and output (leaving in lateral drainage waters) for zinc and copper (*sensu* Likens et al. [10]). Zinc and copper outputs were lower than inputs; consequently net positive budgets were reported for those microelements when only soluble Zn and Cu forms are

Table 4. Monthly outputs of sediment ($kg\,ha^{-1}$), and of Zn and Cu ($g\,ha^{-1}$) contained in particulate material during the wet season at MEM.

	Total sediment losses ($kg\,ha^{-1}$)	Zn losses as sediments ($g\,ha^{-1}$)	Cu losses as sediments ($g\,ha^{-1}$)
April	3.25	12.68	3.25
May	2.34	13.34	1.40
June	26.26	91.91	7.88
July	15.40	26.18	3.08
August	10.82	24.89	2.16
September	9.31	21.84	5.59
October	3.96	9.11	1.58
Total annual	71.34	199.95	24.94

Table 5. Budgets for Zn and Cu at MEM (kg ha^{-1} yr^{-1}).

Element	Input (kg ha^{-1} yr^{-1})	Output (kg ha^{-1} yr^{-1})	Net gain (kg ha^{-1} yr^{-1})
Zn	0.599	0.214	0.385
Cu	0.227	0.060	0.167

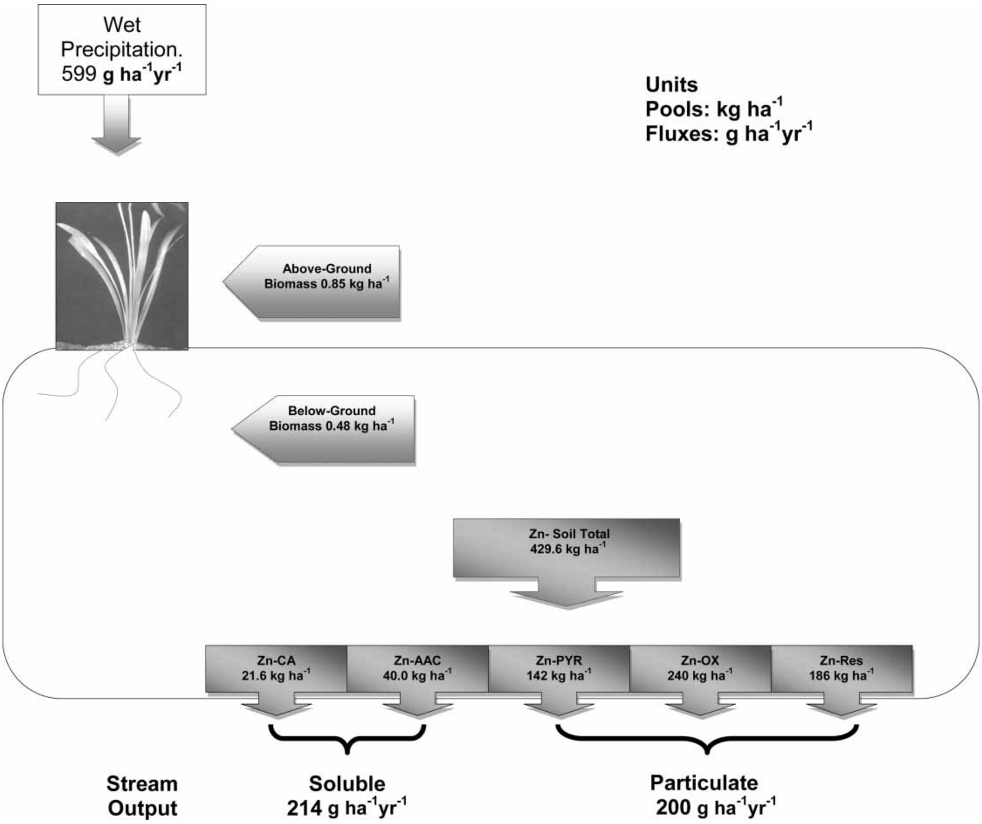

Figure 1. Detailed budget of Zn for dyked savannas at Módulo Experimental, Mantecal. Soil pools were calculated using Zn concentration in the different fractions and bulk density. Vegetation pools were calculated by using productivity values according to Bulla et al. 1980 [26], and Zn and Cu in vegetation according to Torres et al. 1990 [31]. Shown are fluxes (arrows) and pools (boxes) of Zn (no scale).

considered (Table 5). Important losses of both zinc and copper occurred as particulate material leaving by erosion processes from MEM, however (Table 4 and Figures 1 and 2).

3.4. *Zinc and copper fractionation in MEM soils*

The entisols representative of the Banco physiographic unit selected for zinc and copper fractionation presented a low pH (4.40) and a low content of organic matter (14 g kg^{-1}), a coarse texture (540 g kg^{-1} sand and 78 g kg^{-1} clay) and low CEC (4.1 cmol kg^{-1}), whereas the vertisols representative of the Esteros physiographic unit also presented a low pH (4.25), but a higher content of organic matter (51 g kg^{-1}), and a fine texture (128 g kg^{-1} sand and 624 g kg^{-1} clay) and a concomitant high CEC (38.2 cmol kg^{-1}). In the clayey vertisols vermiculite and interstratified

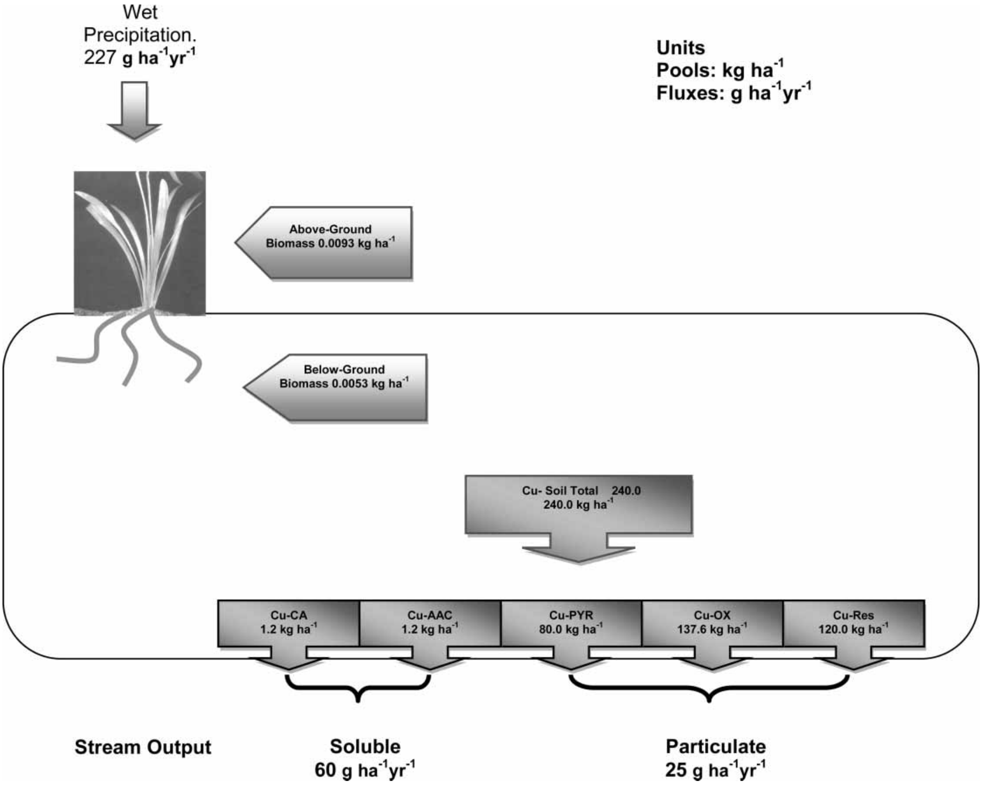

Figure 2. Detailed budget of Cu for dyked savannas at Módulo Experimental, Mantecal. Soil pools were calculated using Cu concentration in the different fractions and bulk density. Vegetation pools were calculated by using productivity values according to Bulla et al. 1980 [26], and Zn and Cu in vegetation according to Torres et al. 1990 [31]. Shown are fluxes (arrows) and pools (boxes) of Cu (no scale).

minerals were abundant, while in the entisols abundance of kaolinite, mica and goethite were reported [7].

Total Zn contents in the selected soils extracted by HF in vertisols were significantly higher than in sandy entisols (Table 6). Although both soils are originated from a similar parent material (weathered alluvial deposition), the abundant clay fraction in the vertisols allows for a higher proportion (the double) of Zn-bearing accessory minerals compared with sandy entisols. A similar distribution pattern was found in the case of copper contents (e.g. higher Cu concentration in vertisols with respect to entisols); however the difference for both soils on total Cu was less accentuated (Table 6).

Table 6. Mean values ($\mu g\, g^{-1}$) and standard deviations of zinc and copper in individual fractions in soils of Banco and Estero at MEM.

Element	Zn	Zn	Cu	Cu
Physiographic unit	Banco	Estero	Banco	Estero
M-CA	2.4 ± 0.3	10.8 ± 0.7	0.7 ± 0.1	0.6 ± 0.0
M-AAC	5.6 ± 0.5	20.0 ± 2.0	1.0 ± 0.0	0.6 ± 0.0
M-PYR	59.0 ± 3.0	71.0 ± 4.0	34.0 ± 1.0	40.0 ± 1.0
M-OX	83.0 ± 9.0	120.0 ± 2.0	8.7 ± 0.05	18.8 ± 0.06
M-RES	17.0 ± 2.0	93.0 ± 11.0	37.7 ± 0.05	60.0 ± 1.0
Total	167.00	214.8	82.10	120.0

In the fractionation of the vertisols, the largest proportion of zinc is associated with the oxides (Zn-OX), followed by the residual fraction (Zn-RES) and the form associated with organic matter (Zn-PYR) (Table 6 and Figure 1). As expected, a lesser, although important proportion, of this microelement exists in readily available forms (exchangeable and bound to inorganic sites). Regarding Cu, most copper appears in a residual form (Cu-RES, Table 6 and Figure 2), and, as in the case of Zn, an important part is also associated with organic matter (Cu-PYR), and the most available forms of Cu (Cu-CA and Cu-AAC) are very low (below 1 $\mathrm{mg\,kg^{-1}}$, Table 6).

4. Discussion

4.1. *Input of Zn and Cu*

The study site is 400 km distant from industrial activity or large populations; therefore, the chemical composition of rain water should not be strongly affected by industrial pollutants. In the more industrialised, northern part of Venezuela, highly acidic precipitation as a consequence of sugarcane burning [15,16] or industrial activity [16] have been reported. However, measurements of pH in Mantecal rain water were not particularly low, ranging from 5.1 at the end of the wet season (November) to 5.8 at the beginning of the wet season (Table 2), a value similar to that reported by Montes et al. [17] for the Trachypogon savannas of the Orinoco River.

In general, in pristine environments the weighted average Zn concentration in precipitation greatly surpasses the Cu concentrations [18]. Thus, Zn/Cu concentration ratios <10, have been reported several times in rain water [19,20]. However, in Mantecal precipitation water, weighted average Zn concentration only surpassed about three times Cu rain water concentration. The weighted average Zn concentration in precipitation in MEM (28.6 $\mu\mathrm{g\,l^{-1}}$) is higher than the values presented by Steinhardt and Fassbender [21] in a rain forest located in San Eusebio, Venezuela (2.4 $\mu\mathrm{g\,l^{-1}}$), and by McColl [22] in a eucalypt forest (16.1 $\mu\mathrm{g\,l^{-1}}$), but is lower than information reported by Golley et al. [23] in a Panamanian rain tropical forest (44 $\mu\mathrm{g\,l^{-1}}$), and by Liu et al. [19] in the Southern Yellow Sea, China (60–150 $\mu\mathrm{g\,l^{-1}}$). Cu concentration in rain water of MEM (about 12.1 $\mu\mathrm{g\,l^{-1}}$) is higher than the values presented by Steinhardt and Fassbender [21] in San Eusebio, Venezuela (2.79 $\mu\mathrm{g\,l^{-1}}$) and lower than the value presented by Golley et al. [23] for the Panamanian forest ecosystem (24.0 $\mu\mathrm{g\,l^{-1}}$) and by Muezzinoglu and Cukurluoglu [20] in Izmir, Turkey (19.7 $\mu\mathrm{g\,l^{-1}}$), and about the same as values presented by Liu et al. [19] in the coastal region of the Southern Yellow Sea, China (3–15 $\mu\mathrm{g\,l^{-1}}$).

In general, Mantecal weighted average Cu concentrations in precipitation were higher than values presented in other sites around the world; information that is surprising, if it is taken into account that MEM is far from heavy industrial and anthropogenic activities. On the contrary, the Zn concentrations in rain water are not much different from literature data.

The zinc input in Mantecal's savannas (599 $\mathrm{g\,ha^{-1}\,yr^{-1}}$) was much higher than the value (30 $\mathrm{g\,ha^{-1}\,yr^{-1}}$) reported by Steinhardt and Fassbender [21] for a rain forest located at San Eusebio, Venezuela, and about the same as the value presented by Liu et al. [19] in coastal regions of the Southern Yellow Sea (428 $\mathrm{g\,ha^{-1}\,yr^{-1}}$); however, Zn input at MEM was very much lower than the value presented by Heinrichs and Mayer [24] in an industrialised central European forest ecosystem (3900 $\mathrm{g\,ha^{-1}\,yr^{-1}}$). Copper input in Mantecal precipitation water (227 $\mathrm{g\,ha^{-1}\,yr^{-1}}$) also exceeded the 45 $\mathrm{g\,ha^{-1}\,yr^{-1}}$ presented for San Eusebio, Venezuela [21] and, because of the relatively high weighted average, Cu incorporated into Mantecal's savannas was similar to the value reported by Heinrich and Mayer [24] in a heavy industrialised central European forest ecosystem (224 $\mathrm{g\,ha^{-1}\,yr^{-1}}$).

4.2. *Output of Zn and Cu*

Elements in the drainage waters come from at least four sources: (i) partly from rain water composition; (ii) as elements dissolved and released from exchangeable soil sites; (iii) mineralised from organic forms, and (iv) released by oxide-reduction processes.

At MEM, Zn and Cu are mobilised from soil pools to drainage water as soluble ionic forms and organic and inorganic complexes in the suspended particulate material. Also, when the site is exposed to copious precipitation, element concentrations of lateral drainage waters might be mainly controlled by rain water composition. The values of pH in discharge water increased (around 6.5, Table 3), when compared with precipitation water (5.1–5.8, Table 2) as a consequence of the considerable amounts of bases (Ca, Mg, and K) that were released [4] from the stagnant water by leaching and decomposition processes of the accumulated biomass within the dyke (10–17 Mg ha^{-1} according to Escobar and González-Gimenez [25], and Bulla et al. [26]). Such biomass accumulation is particularly important at the end of the wet season and during the dry season (November–April). Therefore, important differences between pH in rain and discharge waters appeared at the beginning of the rainy season when the deposited biomass is actively decomposed, in fact during June differences reached 1.5 units (Tables 2 and 3). It seems possible that the increment in basicity of the drainage water at the beginning of surface runoff could be related with the decrease (60%) of soluble Zn concentration occurring from June to July (Table 3).

Redox conditions are important in the mobilisation of heavy metals in anoxic environments [18]. In savanna ecosystems an increment is to be expected in soluble forms of Zn and Cu when dyked savannas are flooded; therefore reducing conditions in vertisols increases the solubility of heavy metals and may increase potential leaching from soils with the concomitant risk of micro nutrient limitation. That process, however, was not observed in the case of Zn and Cu dynamics; on the contrary, drain water concentration appears to be more related to the original rain water concentration, and therefore apparently independent from flooding conditions (Table 3).

4.3. *Particulate losses of Zn and Cu*

Geological substrate, plant cover and, to a minor extent, annual precipitation, play a major role in determining the amount and composition of chemicals lost in stream water.

Important losses as particulate matter tend to occur with elements with a sedimentary cycle which, in turn, can form insoluble organic and inorganic complexes, such as in the case of Zn and Cu.

Therefore, the cycling behaviour of those sedimentary elements is in accordance with their peculiar chemical properties. They tend: (i) to form insoluble complexes with inorganic and organic materials [3]; (ii) to be adsorbed in the cation exchange complex [3,27,28].

In addition to dissolved chemical substances, both organic and inorganic particulate matter may be exported by erosion from ecosystems in stream water [10]. At MEM total losses as particulate reached 71.4 kg ha^{-1} yr^{-1}, a value that doubled in the study by Likens et al. [10] for the Hubbard Brook forested ecosystem (33 ± 13.4 kg ha^{-1} yr^{-1}). Additional information found for non dyked savannas at Mantecal, Venezuela, reported lower particulate losses (data not presented).

At MEM, apart from soluble forms of Zn and Cu (Table 3), particulate materials in suspension could transport appreciable amounts of those elements in complex forms (Figures 1 and 2). Losses of zinc and copper as particulate at MEM corresponds to 48.3 and 29.4% of the total losses of the respective element (Table 7). The comprehensive results presented in Tables 4 and 7 for Zn and Cu particulate losses are lower than the information previously presented by López-Hernández [7]. Likens et al. [10] reported that 63.2 and 100% of the average annual gross output of the phosphorus and iron, respectively, occurred as particulate matter in the undisturbed forest ecosystem at Hubbard Brook, USA.

Table 7. Losses of Zn and Cu as soluble and particulate matter (kg ha^{-1} yr^{-1}) at MEM.

Output	Zn	Cu
Soluble form (kg ha^{-1} yr^{-1})	0.214	0.060
Particulate form (kg ha^{-1} yr^{-1})	0.200	0.025
Total (kg ha^{-1} yr^{-1})	0.414	0.085
% losses as particulate	48.3	29.4

4.4. *Internal cycling*

Total zinc concentration extracted by HF in the vertisols were higher than the values presented by Han et al. [29] for vertisols of the Mississippi River Delta, they also found that Zn in the soils was mainly in the residual fraction (60–70%), followed by the oxide and organically bound fraction. Average values of Zn at MEM (entisols and vertisols) were also higher than those reported by Dabkowska-Naskret [30] in agricultural soils of the Kujawy region, Poland.

Total Cu concentration in MEM soils were higher than the values presented by McLaren and Crawford for 24 British soil series that ranged from 4.4–63.5 mg kg^{-1}; also the total Cu values given by Han et al. [29] for vertisols of the Mississippi River Delta (41–52 mg kg^{-1}) were below the information here presented, in fact Cu concentration values in MEM are higher than mean concentration of world soils but below the mean concentration of metal-rich soils [3]. Although the parent material of both savanna soils (entisols and vertisols) is the same alluvial sediment, the clay fraction abundant in the vertisols is supposed to be richer in minerals of Zn and Cu than the coarse sediment. Besides, organic materials abundant in the clayey vertisols contribute to retain the relatively scarce level of micronutrients arriving by precipitation to the savanna ecosystem.

The Zn and Cu cycles at MEM are characterised by large internal soil pools (Figures 1 and 2), particularly for Zn. These pools largely occur as mineral (oxide occluded and residual) and organic (M-PYR) in the case of Zn; and as residual (M-RES) and organic (M-PYR) for Cu (Figures 1 and 2).

Zn and Cu are plant micronutrients and therefore the rate of uptake is important particularly for Zn which presents higher plant requirements than Cu.

At MEM the amount of Zn and Cu in vegetation pools (calculated by using productivity values according to Bulla et al. [26], and Zn and Cu in vegetation according to Torres et al. [31]) were small (Figures 1 and 2) compared with soil pools; moreover, according to Torres et al. [31], plant measurements reported Cu deficiency in the MEM vegetation, a fact that is anomalous due to the relative high concentrations of this element in soil (as total Cu) and in rain water, however the information is in correspondence with the also relatively low amounts of Cu found as exchangeable and soluble forms (0.6 mg kg^{-1}, Table 6) (Figure 2). On the contrary, the Zn pool in vegetation was important and related well to the higher contents of Zn-CA (10.8 mg kg^{-1}) and Zn-AAC (20.0 mg kg^{-1}), therefore, vegetation measures indicate an adequate level of Zn for plant production, and values were within the range present in vegetation [32].

Although information at eco-system level of trace elements is not abundant, literature shows a net accumulation of trace elements in soils [24,33,34]. Information that contrasts with input-output budgets reported for exchangeable bases are generally negatives, particularly if the ecosystems are in a steady state [2,4,9,10].

López-Hernández et al. [35] have studied the micronutrient balances in sugar-cane agroecosystems, where a net accumulation of the elements was found when the budget did not include the losses by cane export; once this last flux was included the budgets were negative, except in the case of Zn.

5. Conclusions

The Zn and Cu budgets (taking into consideration input and output of soluble and particulate forms) reported here are positive, showing that most of the atmospheric inputs of Zn and Cu were retained somewhere within the soil and vegetation pools of the watershed. In Mantecal flooded savannas, since the export of nutrients by harvesting are of minor significance and the atmospheric input is important, particularly in Cu, a net accumulation of micronutrient in soils is actually occurring through organic and inorganic complexes, a process that is counterbalanced by the significant losses of particulates through erosion. Our watershed retention values were positive, although the study did not include dry deposition, since aerosol interception by the scarce tree canopy is of minor relevance in flooded savannas.

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