

# Hydroecogeochemical effects of an epikarst ecosystem: case study of the Nongla Landiantang Spring catchment

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Received: 16 July 2010 / Accepted: 5 June 2012 / Published online: 14 July 2012  
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**Abstract** A typical small-scale epikarst ecosystem usually consists of an epikarst zone, soil and vegetation. In this study, to determine the hydro-eco-geochemical effects of an epikarst ecosystem in subtropical humid area, the samples of vegetation, soil, soil microbes, rainfall, throughfall, stem flow, soil water and epikarst springs of Nongla Village, Mashan County, Guangxi in China were collected and analyzed. The research results have shown in the epikarst ecosystem, the conductivity, temporary hardness and total carbon increased continuously in hydro-ecochemical cycle; the vegetation–soil system conducted the transformation and transference of carbon in hydro-ecochemical cycle; the vegetation layer was the major source for organic carbon, while the soil layer was of the important chemical field for the conversion of organic/inorganic carbon and  $\text{HCO}_3^-$ , which would affect the epikarst dynamical system; for most ions, the vegetation layer and shallow soil layer presented more leaching effect than absorption, in contrast, the deep soil layer behaved oppositely. The vegetation layer and shallow soil layer leached ions, and deep soil layer absorbed

them. With the plant community presenting in a positive succession, the epikarst ecosystem trended to be stabilized gradually, which made the hydro-eco-geochemical effects to be adjusted and controlled more effectively.

**Keywords** Hydro-eco-geochemical effects · Epikarst ecosystem · Vegetation · Soil microbes · Landiantang Spring

## Introduction

Epikarst zoon is the uppermost weathered zone of carbonate rocks with substantially enhanced and more homogeneously distributed porosity and permeability, which is due to stress release, weathering, dissolution and enhanced solution in the uppermost zone of the bedrock. The epikarst zone surface water system (S), groundwater layer (G), soil (S), vegetation (P) and atmosphere (A) form a complex ecological water cycle system (SGSPA; Wu 2001). Karst processes are controlled by the  $\text{CO}_2\text{--H}_2\text{O--CaCO}_3$  three-phase disequilibrium open system, which is a part of the terrestrial carbon cycle (Liu and Yuan 2000) and very sensitive to environmental change. To determine the hydro-eco-geochemical processes, it is desirable to consider the epikarst zone as a holistic ecological system to investigate. Some studies focused on water cycle processes, accommodation and storage, utilization and development in the epikarst zoon, but few study focused on hydro-ecological effects (China Geological Survey 2003). Jiang et al. (2001) compared microclimate, available water in the epikarst zoon and hydro-ecological effects through different vegetation layers. Thus, most of the hydro-ecological studies have focused on water quantity, but few on hydro-geochemical characteristics. A pilot study on the hydro-eco-geochemical effects of karst secondary forest

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was reported by Deng et al. (2007). Li et al. (2003) found that suitable biological communities can improve the water and soil conditions. In an ecosystem, hydro-eco-geochemical process is the key operator in the atmosphere–biosphere–soil–geosphere interactions, which is the principal path for transporting carbon from a terrestrial ecosystem to river deposition (Chen et al. 2004).

This paper reports on the catchment of Landiantang Spring as a typical sub-tropical epikarst ecosystem. Vegetation, soil characteristics and soil microbe populations were analyzed. Samples of rainfall, throughfall, stemflow, soil water and the epikarst spring were collected to investigate eco-hydrological processes in the karst peak–cluster depression. Their physical and chemical characteristics were analyzed both in the field and laboratory to measure carbon transformations in the ecosystem and provide a scientific basis for epikarst water use, epikarst ecosystem restoration and amelioration.

### The study area

The study was conducted at the karst dynamic monitoring site at Nongla, a village in Mashan County, Guangxi

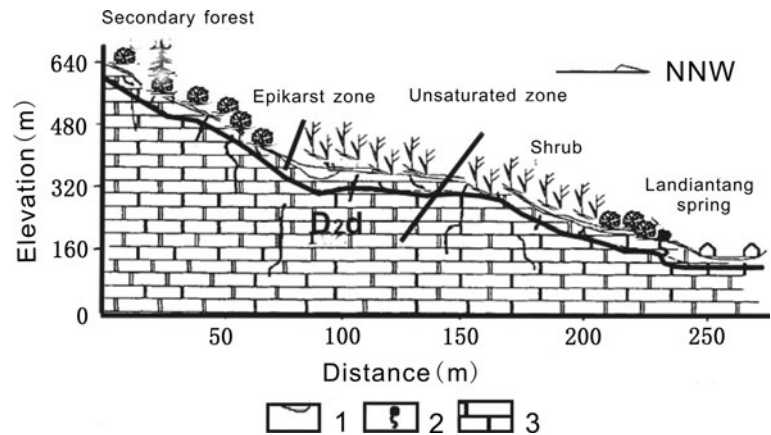
Zhuang Autonomous Region, China (23°29′N, 108°19′E; Fig. 1). It was a typical peak–cluster depression of the South China subtropical monsoon karst area. The local relief from depression rim to floor ranged from 120 to 260 m. The strata were Devonian D<sub>2</sub><sup>d</sup>, mainly argillaceous dolomite with purer limestone towards Landiantang and purer dolomite in the southwest.

Epikarst zoon was about 10 m in thickness and developed everywhere across the peaks, cols and side slopes to their foot. The Landiantang epikarst spring was under the secondary forest; it had changed from a seasonal flow regime to a constant flow because of vegetation regeneration since the 1970s (Fig. 2). The annual runoff was about 20,000 m<sup>3</sup> in 2000, based on the record from a CTD300 multiple parameter recording instrument which was set-up in an observation station near the spring. The total area of the Landiantang Spring catchment was <0.02 km<sup>2</sup> (Deng et al. 2008). There was an obvious serial succession in vegetation due to the combination of physiography and restoration time: scattered shrubs → continuous shrubbery → second growth forest Shen et al. (2009). The dominant hydrological sequence in the catchment was rainfall → throughfall → stemflow → soilwater → epikarst fissure water → epikarst spring.



**Fig. 1** Study area location

**Fig. 2** Eco-hydrogeological profile of Landiantang Spring catchment. 1 Surface soil, 2 epikarst spring, 3 D<sub>2</sub>d argillaceous dolomite

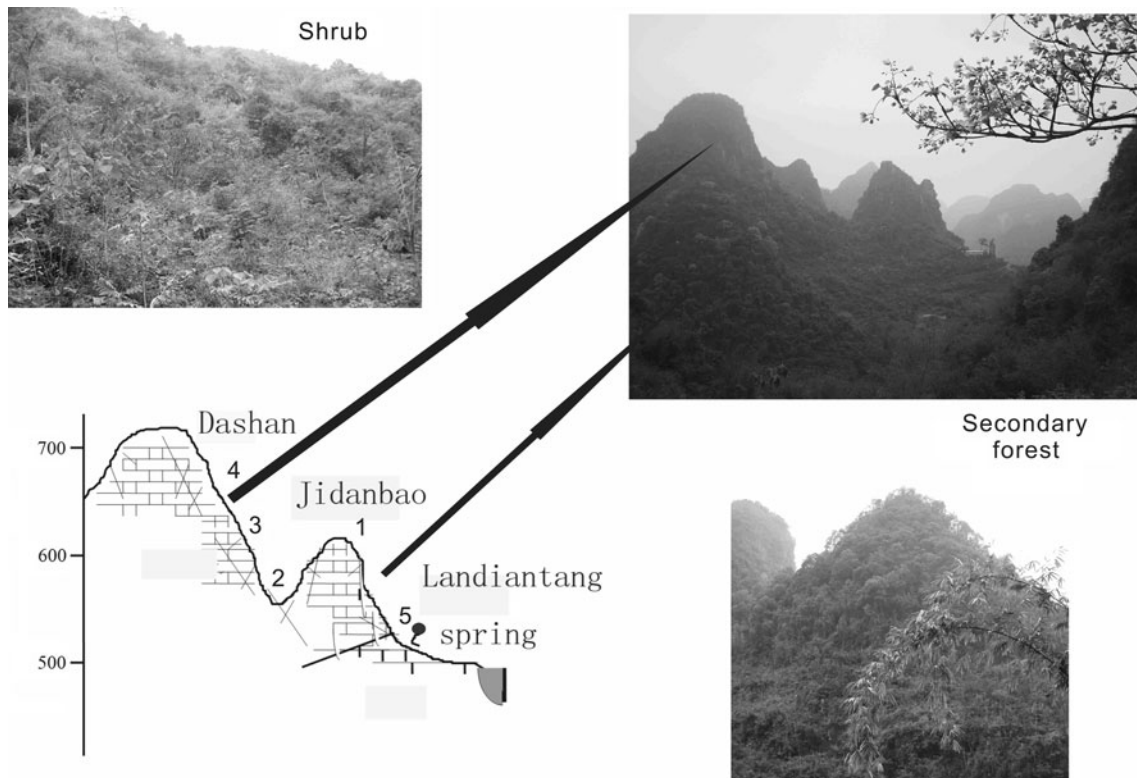


**Methods**

**Sampling**

Ecological data were collected in the Landiantang Spring catchment in 2006. Based on the hypsography, four quadrates of different typical communities were randomly selected along equidistant transect lines. An arboreal quadrant area was 20 m × 20 m. A shrub quadrant area was 10 m × 10 m. An herb quadrant area was 1 m × 1 m. Dominant canopy and undergrowth species were recorded. Diameters at breast height (DBH) of 1.3 m were measured

for each tree if its DBH is more than 10 cm and all individuals were identified by species and plotted on field notebook. Environmental factors, such as time elapsed since restoration began, elevation, percent bare rock, slope and aspect were recorded. Soil samples for soil chemistry, physiological and microbiological characteristics study were collected from the secondary forest and shrub quadrants (Harding and Ford 1993; Shen et al. 2009). A simplified sampling picture is shown in Fig. 3. Eleven rainfall events, with samples of throughfall, stemflow, soil water and the spring water were recorded in the Landiantang Spring catchment between May and July, 2006. Rainfall was collected in three plastic rain



**Fig. 3** Vegetation sampling design. 1–5 plot numbers, the same as in Table 1

gauges which were installed on a terrace of a four-storey building. Rain gauges were covered with nets to prevent insects and other matter from entering to avoid pollution of surrounding environment. Six polyethylene funnels of 26 cm diameter were randomly installed in the Landiantang Spring secondary forest to collect throughfall (He et al. 2001; Roberto et al. 2001). Polyurethane collars were attached to sample trees at breast height 1.3 m for stemflow: they were upward spirals draining into closed 596-ml polyurethane bottles attached to the tree (Likens and Eaton 1970). Soil water was collected using special lysimeters designed for soil water sampling in karst areas (Deng et al. 2007). The Landiantang epikarst spring water samples were collected by two 125-ml bottles immediately after each rainfall event.

#### Analyzing methods

Bacteria, fungi and actinomycetes were measured by the dilution plate counting method (Zhao and He 2002). The diluting degrees were  $10^{-4}$  to  $10^{-6}$ ,  $10^{-3}$  to  $10^{-5}$ ,  $10^{-1}$  to

$10^{-3}$ . Four parallel tests were carried out for each sample. Different microbes were cultured using different media: beef peptone agar for bacteria, Gause's synthetic agar for actinomycetes, Rose Bengal and chloramphenicol martin agar for fungi. Soil chemical and physical characters were analyzed by standard methods (Yao and Huang 2006; Liu 1996).

All collectors and funnels were carefully cleaned with dilute nitric acid and rinsed 4–6 times with deionized water before use. Samples were first taken to the field laboratory and stored at 4 °C, and then analyzed in the laboratory of the Institute of Karst Geology, CAGS, Guilin.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^{-}$  by standard wet-lab method,  $\text{HCO}_3^{-}$  by neutralization titration,  $\text{Na}^{+}$  and  $\text{K}^{+}$  were measured by flame emission spectrometry,  $\text{SO}_4^{2-}$  by barium sulfate turbidity and free  $\text{CO}_2$  by acid–base titration. Total carbon (TC), total inorganic carbon (TIC) and total organic carbon (TOC) were measured by TOC-VCPN. The electrical conductivity and pH were measured in the field using the Multiline P3 instrument (WTW, Germany; Deng and Jiang 2009).

**Table 1** Community environment and dominant species of plots in Landiantang catchment

Plot	Layer	Years since deforestation	Slope	Aspect	Bare rock %	Layer coverage %	Dominant species
1	Tree layer	49	32	East	25	25	<i>Platycarya strobilacea</i> , <i>Quercus glauca</i>
	Shrub layer					40	<i>Cinnamomum migao</i> , <i>Zanthoxylum scandens</i>
	Herb layer					10	<i>Peteridium aquilinum</i> , <i>Woodwardia japonica</i>
2	Tree layer	40	5	Southeast	25	96	<i>Cinnamomum saxatile</i> , <i>Decaspermum esquiortlii</i>
	Shrub layer					85	<i>Pittosporum glabratum</i> , <i>Vitex negundo</i>
	Herb layer					60	<i>Eupatorium japonicum</i> , <i>Miscanthus floridulus</i>
3	Tree layer	25	30	West	20	90	<i>Pistacia chinensis</i> , <i>Platycarya strobilacea</i> , <i>Decaspermum esquiortlii</i>
	Shrub layer					40	<i>Zanthoxylum scandens</i> , <i>Acacia pennata</i>
	Herb layer					15	<i>Peteridium aquilinum</i> , <i>Woodwardia japonica</i>
4	Tree layer	40	23	East	35	–	–
	Shrub layer					80	<i>Vitex negundo</i> , <i>Callicarpa nudiflora</i>
	Herb layer					90	<i>Miscanthus floridulus</i> , <i>Nephrolepis auriculata</i>
5	Tree layer	45	15	West	45	95	<i>Calamus ochlandra</i> , <i>Clausena lasium</i>
	Shrub layer					20	<i>Callicarpa macrophylla</i>
	Herb layer					20	<i>Ophiorrhiza mungos</i> , <i>Pothos kerrii</i>

1 Jidanbao peak, 2 col between Dashan and Jidanbao, 3 Jidanbao west mountainside, 4 Jidanbao east mountainside, 5 Landiantang Spring, same below

**Table 2** Biodiversity index of vegetation plots in the Landiantang catchment

Plot	Tree layer					Shrub layer					Herb layer				
	Pa	Ga	H	D	Jsw	Pa	Ga	H	D	Jsw	Pa	Ga	H	D	Jsw
1	12	2.003	0.95	0.139	0.265	22	3.672	1.239	0.063	0.278	3	0.501	0.474	0.334	0.299
2	12	2.606	1.007	0.112	0.281	34	7.383	1.437	0.039	0.282	7	1.52	0.801	0.166	0.285
3	4	0.869	0.405	0.523	0.203	20	4.343	1.193	0.077	0.276	18	3.909	1.102	0.11	0.264
4	–	–	–	–	–	27	5.863	1.326	0.054	0.279	21	4.56	1.15	0.091	0.262
5	25	4.173	1.318	0.053	0.284	26	4.34	1.35	0.047	0.287	31	5.174	1.425	0.037	0.288

Pa Patrick index, Ga Gleason index, H Shannon–Wiener index, D Simpson index, Jsw Pielou index

**Data analysis**

The original data were analyzed with SPSS software (Version 13.0) and Excel software (Version 2003). Graphs were drawn with Origin software (Version 7.0). The mean values of water samples were used because the chemical and physical characteristics of the rainfall were influenced by local environment factors. Biodiversity indexes of Patrick, Gleason, Shannon–Wiener, Simpson, and Pielou were calculated for tree, shrub, herb layers based on the significance values (Song 2001).

**Results and discussion**

**Characteristics of the epikarst ecosystem**

The second growth forest, dense shrubbery and scattered shrubs were the dominant plant community types in the Landiantang catchment. *Platycarya strobilacea* and *Quercus glauca* were dominant species of the forest on Jidanbao peak. Shrubbery was dominated by *Cinnamomum saxatile* and *Decaspermum esquirolii* on the col between the Jidanbao and the Dashan. Shrubs were dominated by *Vitex negundo* and *Callicarpa nudiflora* that covered most of the mountainside. The vicinity of Landiantang Spring was covered by the planted forest with the dominant tree *Calamus ochlandra*. *Clausena lasium* and shade herbs grew well in the dank environment around the spring (Table 1).

The number of species increased up the positive succession from shrubs to trees, but declined when the local climax community was attained. The tree layer was stable while shrub species and herb species were sharply reduced in a climax community (Table 2). Increase in plant diversity supplied more food to consumers in an ecosystem as well as habitats for soil microbes; thus it created rich heterogeneity in microhabitats and supporting greater biodiversity (Peng 2003). In the positive succession, the richness of secondary forest species was higher than the shrubs. Biodiversity of secondary forest in the Landiantang Spring was higher than the peak, because the spring supplied abundant water. The epikarst ecosystem was more stable and efficient, which induced complex hydro-ecogeochemical effects.

The secondary forest soil contained more organic carbon and effective N than the shrub soil, which suggested that the secondary forest was more effective than shrubs for soil improvement (Table 3). There are close relationships between soil physical and chemical characters and soil–microbe characteristics (Shen et al. 2007). Shrub soil was richer in soil actinomyces while the secondary forest was far richer than shrub in soil total microbes, bacteria and fungi. High and stable biodiversity in the vegetation assemblage provided favorable conditions for soil microbes, which enriched the number of species and quantities of individuals. It formed a stable microbe community which shown high diversity (Table 4; Fig. 4). Plant and soil microbes formed a biological system that

**Table 3** Soil physical and chemical characteristics of the shrub and secondary forest in Landiantang catchment

Soil layer	pH	TOC (%)	Effectivity K (mg/100 gK)	Effectivity P (mg/100 gK)	Effectivity N (mg/100 gK)	CaO (%)	MgO (%)	K <sub>2</sub> O (%)	Na <sub>2</sub> O (%)	Porosity (%)
SA	7.3	3.37	9.87	7.4	1.96	0.44	2.7	1.29	0.089	57.32
SB	7.3	2.28	8.1	9.2	2.23	0.47	2.71	1.32	0.089	56.33
FA	6.4	4.14	5.02	5	2.3	0.6	2.79	0.36	0.066	57.88
FB	7.4	1.22	3.31	8.8	1.6	0.57	3.04	0.3	0.063	50.72

SA shrub surface soil, SB shrub middle soil, FA secondary forest surface soil, FB secondary forest middle soil

**Table 4** Average number, standard deviation (in brackets) and percent ratio of soil microbes samples

Community	Soil layer	Bacteria		Actinomycetes		Fungi		Total 10 <sup>5</sup> /g
		10 <sup>6</sup> /g	Ratio %	10 <sup>5</sup> /g	Ratio %	10 <sup>4</sup> /g	Ratio %	
I	A	14.19 (11.24)	90.26	15.14 (5.80)	9.63	1.70 (9.95)	0.11	157.17
Shrub	B	2.76 (9.11)	87.55	3.78 (6.68)	12.01	1.36 (8.34)	0.43	31.49
	C	0.80 (6.99)	84.93	1.35 (9.22)	14.39	0.64 (11.15)	0.68	9.38
II	A	25.26 (7.41)	97.26	6.85 (9.36)	2.64	2.55 (16.72)	0.1	259.73
Secondary forest	B	1.43 (6.76)	94.61	0.65 (8.96)	4.31	1.64 (18.19)	1.09	15.14
	C	0.62 (7.27)	85.16	1.01 (7.68)	14.01	0.60 (7.77)	0.83	7.23

A 10–20 cm soil layer, B 20–40 cm soil layer, C 40–60 cm soil layer same below

improved soil physical and chemical characteristics (Kingsley 2004). The soil brought producer and disintegrator species. It was the link between the atmosphere and the geosphere, which played a key role in the bio-geochemistry of an epikarst ecosystem.

The quantity and quality of organic carbon in the plant litter are a significant factor of soil organic carbon content and soil structure (Su and Zhao 2005). Soil physical and chemical characteristics of the surface and middle soil may differ substantially, particularly with respect to soil organic matter, effective porosity and granule absorptive capacity. The content of organic carbon in the surface soil was higher than in the middle soil, because the stemflow was rich in organic carbon which was absorbed mostly by surface soil granules. In addition, the surface soil was rich in dead wood and soil microbes which metabolized more organic carbon.

#### Hydro-geochemical characteristics of the epikarst ecosystem

Certain ions in rainfall were adsorbed when passing through the cover of vegetation. Reduced Cl<sup>-</sup> concentrations in the vegetation layer demonstrated that sorption was more significant than leaching in throughfall and stemflow. The effects of aqueous leaching through dead wood and the surface soil increased the Cl<sup>-</sup> concentrations; however, the effects of sorption in the deeper soil (B layer) reduced the levels of Cl<sup>-</sup> in the spring water. It was close to rainfall after seeping in deeper soil and rock pores (Table 5).

There was not SO<sub>4</sub><sup>2-</sup> in the rainfall at Landiantang. SO<sub>4</sub><sup>2-</sup> concentrations in the soil water were significant due to leaching in the surface layers. It was suggested that the SO<sub>4</sub><sup>2-</sup> may come from soil microbe activity, especially surface layer soil sulfur bacteria catabolism. Sorption and dilution effects (Liu and Dreybrodt 2007) in the deeper layers of the soil decreased the SO<sub>4</sub><sup>2-</sup> concentrations which were found in the epikarst spring.

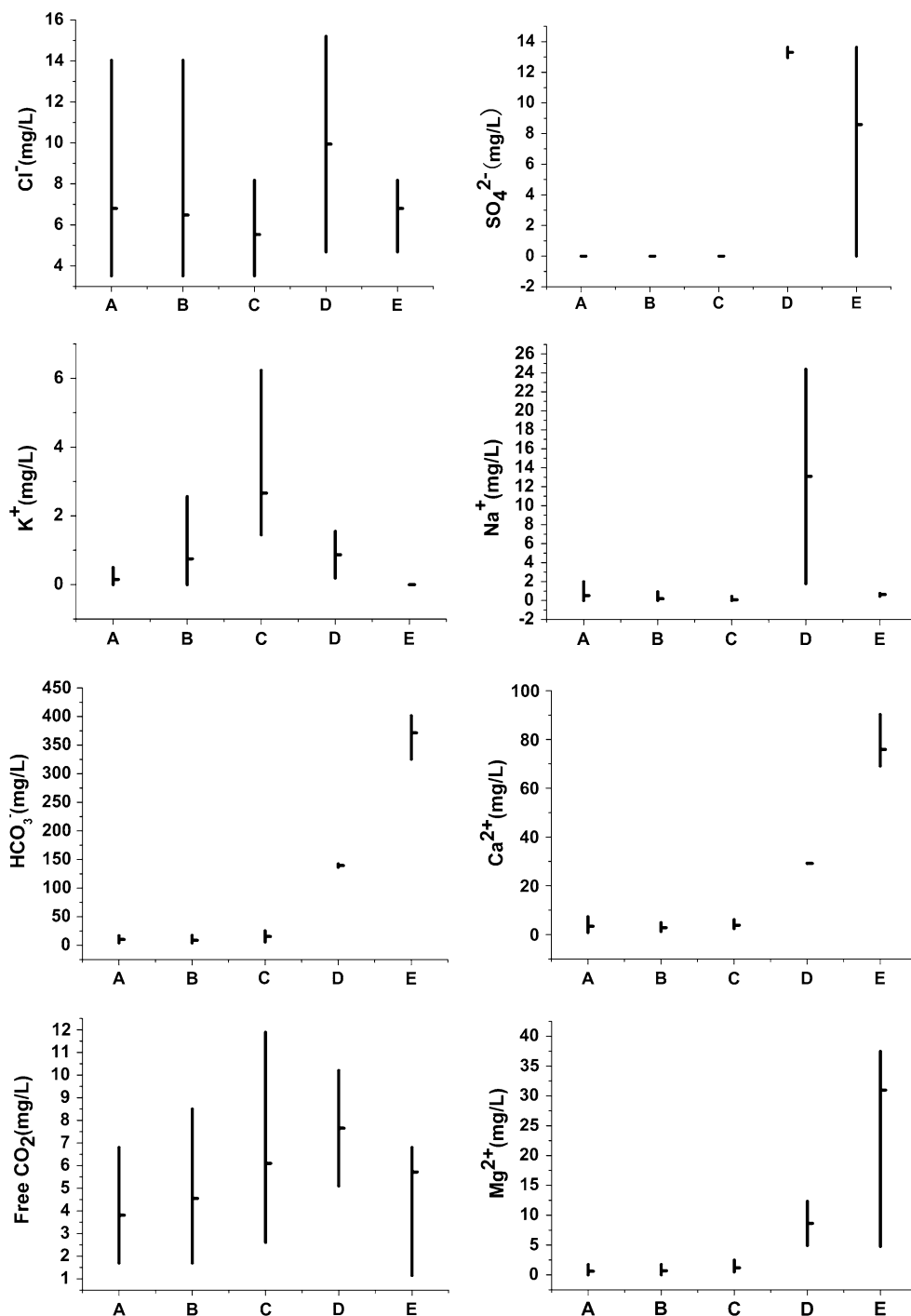
K<sup>+</sup> and Na<sup>+</sup> were leached and transported in water easily. Vegetation can leach K<sup>+</sup>. In contrast with other

cations, it increases significantly. K<sup>+</sup> net leaching in stemflow was 2.51 mg/L, with a leaching coefficient of 17.53, which was the highest record in the program. K<sup>+</sup> was not found in the epikarst spring during this study, but it was recorded in Landiantang Spring by Jiang (1997). The authors hypothesize that soil absorbed K<sup>+</sup> constantly and dilution also had effect. Vegetation may adsorb Na<sup>+</sup>: there was net leaching in the surface soil layer while adsorption in the deeper layer. Na<sup>+</sup> was low in the local atmosphere (Zhou et al. 2003). Rainfall was low in Na<sup>+</sup> content. It decreased in the throughfall and stemflow because of absorption by the vegetation. Na<sup>+</sup> increased rapidly after leaching through surface soil, but it was decreased again in the epikarst spring. It supposed that absorption in the deeper soil and dilution effects jointly played an essential role.

In contrast to K<sup>+</sup> and Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> were not easily removed or leached in water. Both Ca<sup>2+</sup> and Mg<sup>2+</sup> content increased with HCO<sub>3</sub><sup>-</sup> after rainfall passed through the vegetation, soil and epikarst zone. The respiration of plants and soil microbes, decomposition of dead wood and leaves released abundant CO<sub>2</sub> into water, which raised the HCO<sub>3</sub><sup>-</sup> content and improved the capacity of water to dissolve Ca<sup>2+</sup> and Mg<sup>2+</sup>. These ions were leached from the vegetation layer into the surface soil and their concentrations in the water increased due to added CaO (lime). Absorption in the deeper soil made Ca<sup>2+</sup> and Mg<sup>2+</sup> contents higher than in the surface soil. The epikarst zone is developed in dolomites; therefore, general karst dissolution resulted in the great increase of Ca<sup>2+</sup> and Mg<sup>2+</sup> in the spring and the consumption of some free CO<sub>2</sub> (Fig. 4; Table 5). The standard deviation and variation coefficient of water samples were shown in Table 6.

Table 5 shows the ionic balance through the different layers of the epikarst ecosystem. Only K<sup>+</sup> and Mg<sup>2+</sup> increased a little in throughfall. The order of the leaching coefficient was K<sup>+</sup> > Mg<sup>2+</sup> > Cl<sup>-</sup> > HCO<sub>3</sub><sup>-</sup> > Ca<sup>2+</sup> > Na<sup>+</sup>. The concentrations of K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> increased in stemflow due to the leaching of nutrients from leaves and stems. The abundance of chemical elements and

**Fig. 4** Arithmetic means and ranges of chemical contents in different water samples. **a** Rainfall, **b** throughfall, **c** stemflow, **d** soil water and **e** spring. Unit mg/L limited by rainfall, etc, soil water samples  $n = 4$ , others  $n = 11$



contents in stemflow were affected by the shape of the cortex and the amount of time that the rainfall was retained in it (Luo et al. 2004; Liu and Shen 2003). The secondary forest canopy around the Landiantang Spring was 20 m in height, with a high biodiversity and a clear structure—tree, shrub and herb layers. The height and the variety of dominant species in the community greatly influenced the stemflow. The stemflow added chemical elements to the

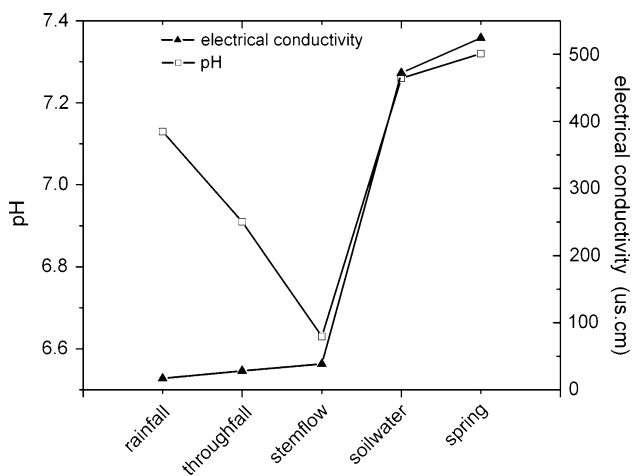
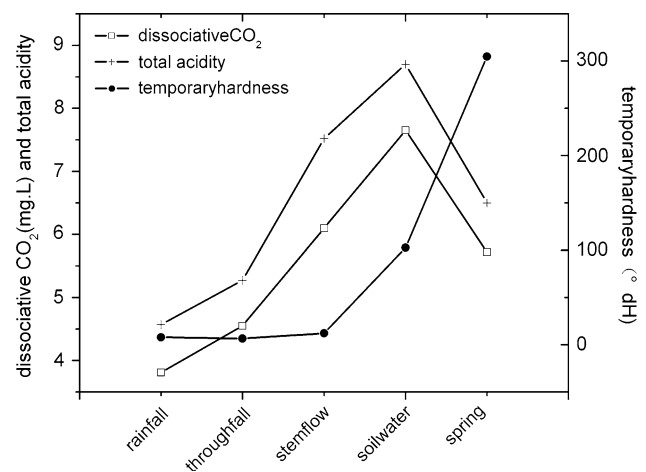
soil along roots. The leaching order of ions in stemflow was  $K^+ > Mg^{2+} > HCO_3^- > Ca^{2+} > Cl^- > Na^+$ . Water soluble elements moved rapidly through the soil medium, especially  $Na^+$  was enriched in the soil water. Microbial respiration produced high levels of  $CO_2$  which made the soil become a  $CO_2$  pump to trigger the release of  $HCO_3^-$  for carbonate dissolution. The leaching order of ions in soil water was  $Na^+ > Mg^{2+} > HCO_3^- > Ca^{2+} > K^+ > Cl^-$ .

**Table 5** Net leaching amounts and coefficients of different water samples

Water samples	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
Net leaching of throughfall (mg/L)	-0.32	-1.39	0.6	-0.33	-0.55	0.09
Net leaching of stemflow (mg/L)	-1.27	5.27	2.51	-0.44	0.48	0.58
Net leaching of soil water (mg/L)	3.14	129.36	0.72	12.57	25.82	8.03
Net moving of spring (mg/L)	0	361.33	-0.15	0.12	72.52	30.39
Leaching coefficient of throughfall	0.95	0.86	4.95	0.36	0.84	1.15
Leaching coefficient of stemflow	0.81	1.52	17.53	0.16	1.14	1.96
Leaching coefficient of soil water	1.46	13.73	5.8	25.16	8.68	14.16
Moving coefficient of spring	1	36.58	-	1.24	22.57	51.19

**Table 6** Standard deviation and Variation coefficient of water samples

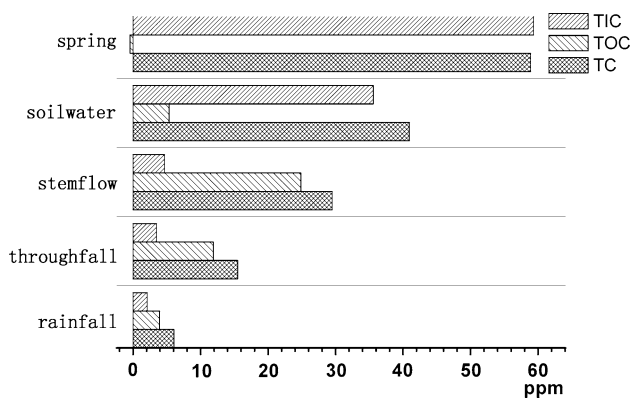
Compartments		Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Free CO <sub>2</sub>
Rainfall ( <i>n</i> = 11)	Standard deviation	2.99	-	4.44	0.18	0.72	2.14	0.53	1.74
	Variation coefficient	0.44	-	0.44	1.22	1.38	0.64	0.88	0.46
Through fall ( <i>n</i> = 11)	Standard deviation	2.97	-	3.93	0.90	0.30	1.25	0.61	2.02
	Variation coefficient	0.46	-	0.95	1.20	1.61	0.45	0.88	0.44
Stemflow ( <i>n</i> = 11)	Standard deviation	1.82	-	6.38	1.48	0.14	1.17	0.58	2.61
	Variation coefficient	0.33	-	0.41	0.56	1.68	0.30	0.49	0.43
Spring water ( <i>n</i> = 11)	Standard deviation	1.26	4.01	26.90	-	0.09	6.97	4.76	1.15
	Variation coefficient	0.18	0.47	0.07	-	0.13	0.09	0.15	0.20

**Fig. 5** Variation of pH and electrical conductivity in different water samples**Fig. 6** Variation of free CO<sub>2</sub>, total acidity and temporary hardness in different water samples

The soil was a major chemical catalyst in the epikarst ecosystem. Dynamic changes in HCO<sub>3</sub><sup>-</sup> were controlled by both CO<sub>2</sub> effects and dilution. The order of ions in the epikarst spring was Mg<sup>2+</sup> > HCO<sub>3</sub><sup>-</sup> > Ca<sup>2+</sup> > Na<sup>+</sup> > Cl<sup>-</sup> > K<sup>+</sup>. Vigorous karstification of epikarst zoon increased the content of Mg<sup>2+</sup>, Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> in spring and concentrations were two or three times higher than in the rainfall; karstification played a key role in the chemical composition of the spring.

Mean pH was 7.1 in the rainfall and then fell dramatically in the throughfall and stemflow, because the plant metabolization of matter acidified the water (Fig. 5). The secondary forest in karst area could acidify rainfall to some degree as it did in non-karst regions, such as the young second-rotation Chinese fir plantations in Huitong and Nanping, China, reported by Tian et al. (2002), Pan et al. (1996; 1999). The soil of this karst area was characterized by high calcium and an alkalinity trend which activated





**Fig. 7** TC, TOC and TIC content variation of different water samples

alkali elements and improved their effective states so that soil water quickly became alkaline with high-electrical conductivity. Karstification within the epikarst zone increased the pH a little further at the epikarst spring. Figure 5 demonstrated that leaching in the calcareous surface layer of the soil and vigorous karstification in the epikarst zone dominated the hydrogeochemical transformation in this representative karst area. Net leaching in throughfall and stemflow increased electrical conductivity only slightly. Then, it increased fivefold or more in the soil water, where the quantitatively predominant reactions took place. Figure 6 shows the behaviors of dissociative (free) CO<sub>2</sub>, total acidity and temporary hardness in the water. Dissociative CO<sub>2</sub> increased substantially through the vegetation and soil layers due to the respiration of plants and microbes, decomposition of dead wood and leaves releasing abundant CO<sub>2</sub>, which became available for dissolution in the epikarst zone; its content declined in the spring water. H<sup>+</sup> content became higher with higher dissolution of the dissociative CO<sub>2</sub>, which triggered the change in total acidity. The trends of free CO<sub>2</sub> and H<sup>+</sup> were identical (Fig. 6). Temporary hardness was produced by combinations of calcium ions and bicarbonate ions in the water. The decrease in HCO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup> in the throughfall reduced temporary hardness in dynamic equilibrium and dissolution in the epikarst zoon and then increased it dramatically. There was a close correlation with the electrical conductivity in Landiangtang data, indicating a comparatively simple bicarbonate karst system lacking complexity from heterogeneous ion effects.

There was continual carbon input throughout these eco-hydrological processes. Changes in total carbon and total inorganic carbon were similar and systematic: spring > soil water > stemflow > throughfall > rainfall. Total carbon in the rainfall was 6.04 ppm. It increased 23.46 ppm after passage through the vegetation, so total carbon of stemflow was 29.50 ppm. The further 11.44 ppm was through the soil layer and another 17.95 ppm in the

epikarst zone between soil water and the spring. Total carbon of spring was 58.58 ppm, so the epikarst spring gained 52.58 ppm from the vegetation, soil and epikarst (Fig. 7).

Total carbon was an index that denoted total organic matter by carbon content. In the epikarst ecosystem, the trend of total carbon was stemflow > throughfall > soil water > rainfall > spring. CO<sub>2</sub> was absorbed by plants through photosynthesis and was stored in leaves as organic carbon (Stern et al. 2004). In comparison with rainfall, the organic carbon in the throughfall increased 7.97 ppm due to plant surface leaching. Abundant organic carbon was leached when the water flowed along the bole so that the organic carbon in stemflow increased 20.94 ppm when compared with rainfall. The discrepancy between the increment of organic carbon in stemflow and throughfall indicated that the organic carbon was mainly stored within the vegetation layer. Soil organic carbon was a dynamic carbon transfer medium and the main circulation route for carbon in the karst ecosystem (Pan and Cao 1999). Soil microbes turned organic carbon into inorganic carbon and CO<sub>2</sub> via mineralization and thus carbon was accumulated in the soil or output in the form of HCO<sub>3</sub><sup>-</sup>. From stemflow to soil water, organic carbon decreased 19.5 ppm while the inorganic carbon increased 30.96 ppm (Fig. 7). Soil was an important carbon sink. A δ<sup>13</sup>C stable isotope trace indicated that more than 60 % of the HCO<sub>3</sub><sup>-</sup> in the epikarst spring derived from soil CO<sub>2</sub> transformations. The negative value for total organic carbon at the spring was illogical, a product of a slight excess of TIC over TC; it was presumed that dilution effects created this anomaly. It emphasized that there was a nearly complete loss of organic carbon in the reactions within the epikarst zoon, depleting the spring water as much as 5.78 ppm as compared to the soil water. Active karstification and these soil organic carbon transformations increased the total inorganic carbon as much as 23.72 ppm (Fig. 7) (Pan et al. 1998).

The variety of total carbon, organic carbon and inorganic carbon concentrations encountered in this analysis of the hydro-eco-geochemical processes occurring in an epikarst ecosystem reflects the complexity of the transformations through the air–vegetation–soil–carbonate mediums. Further quantitative studies are needed to fully evaluate “the loss of carbon” in epikarst ecosystems (Cheng 1999).

### Conclusions

1. Water played a key role in the plant community successions in karst area. The structure and biodiversity of the communities determined soil microbe species, their abundance and distribution. Plant and soil microbes

affected soil characteristics and organic contents. Karst secondary forest was much more productive than shrubs. The presence of springs in the epikarst helped to maintain complex communities with high biodiversity.

2. Different ions interacted differently in the epikarst ecosystem. A proportion of initial  $\text{HCO}_3^-$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions were leached by vegetation.  $\text{Cl}^-$ ,  $\text{SO}_4$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and free  $\text{CO}_2$  were removed more strongly in the surface soil layer. The deeper soil absorbed  $\text{Cl}^-$ ,  $\text{SO}_4^-$ ,  $\text{K}^+$ ,  $\text{Na}^+$ . Karstification in an epikarst zoon consumed free  $\text{CO}_2$  while increasing the  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  content of epikarst springs.
3. Total carbon content in water increased with the hydro-ecogeochemical processes in an epikarst ecosystem. The vegetation–soil system dominated carbon transformation in the cycle within the ecosystem. The vegetation layer was the main source for organic carbon and the soil layer was the most important zone for the inorganic carbon, organic carbon and  $\text{HCO}_3^-$  transformations operating in the karst dynamic system.
4. Epikarst ecosystem became more stable as a plant community succession progresses because this boosted the air–vegetation–soil–rock chemical interactions. The quantity and species of ions determined changes of electrical conductivity.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration played the key role in temporary hardness. Both electrical conductivity and temporary hardness increased during the hydro-eco-geochemical reactions within the epikarst ecosystem.

**Acknowledgments** This research could not have been developed without the support of Key Technologies Research and Development Program of the State Tenth Five Year Plan Project (2006BAC01A10); National Key Technologies R&D Program (2008BAD98B07); the Hunan Education Office Excellence Youth Project (08B093); the Formation Processes and Evolution of Karst Secondary Forest in Guangxi (08KE01); NSFC (40872214); Preparation and Technology of Environmentally Friendly anti-UV PVA Film (2010GK2029). Many thanks are extended to Prof. F.N. Wei for his invaluable support in the identification of the botanical specimens. Thanks to Y.Q. Xie for his suggestion on illustrations. Prof. Derek Ford, Prof. Julia Ellis Burnet and Q.K. Luo kindly edited the text for English style.

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