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Trace element budget in an African savannah ecosystem

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Abstract. The concentration of selected trace elements (Co, Cu, Fe, Mn, Mo, Se, and Zn) were analysed in soils, grass, bush, and tree samples from the Mole National Park, Ghana. The distribution of the essential nutrients: cobalt, copper, manganese, and selenium is controlled by bedrock geology, whereas iron, molybdenum, and zinc distribution is controlled by soil and hydrological processes. In the soils, iron, manganese, and cobalt are largely fixed in the mineral fraction while most of the copper, molybdenum, and selenium in the soils can be extracted by disodium ethylenediaminetetracetate. Copper, cobalt, and manganese appear to be preferentially concentrated in grass species while molybdenum and selenium are concentrated in browse plants.

Variations in uptake exist between wet and dry seasons with all trace elements studied, except iron and manganese, showing a marked increased availability in the wet season and increased concentration in the residual fraction of the mineral and organic soils in the dry season. In the dry season the plant concentration of molybdenum and selenium decreased while copper and zine showed increased concentrations and this may be related to a lower pH of the groundwaters at this time.

A budget of metal input and out put in the ecosystem at Mole has been computed. From this potential dietary deficiencies in cobalt can be observed, however for other metals soil and plant concentrations are sufficient to prevent straightforward deficiencies while the concentrations of molybdenum and selenium are sufficiently low to be considered safe.

Introduction

Terrestrial ecosystems receive inorganic matter from the atmosphere and from their geological substrates. In an undisturbed ecosystem, the principal source of major cation nutrients, such as calcium, magnesium, potassium, and sodium is the weathering of rocks underlying the ecosystem. The loss of these major cation nutrients to stream water greatly exceeds input from atmospheric sources, such as rainfall, or through other inputs (Likens et al. 1977; Gilliam & Richter 1991). Even though such transfers are small in comparison to the total quantity of nutrient cations in the ecosystem, it is reasonable to assume that it may only be sustained if sufficient nutrient cations are released from the substrate by weathering. In the same way the availability of trace element nutrients in an undisturbed ecosystem is determined largely by the balance between weathering and hydrological mobility. Trace elements may also be deposited from an atmospheric source and this input will reflect the dissolved and particulate contamination in the air with such phenomenon as bush fires intermittently affecting the atmospheric input of trace elements (Brookman-Amissah et al. 1980).

A common approach to assess element cycles in ecosystems has been to quantify the distribution of elements in the different components of a well defined ecosystem (Hughes 1981). The analysis of watershed input and output, combined with the budget of ecosystem components and internal transfer of trace elements can be used to quantify element cycles in an ecosystem.

The need for quantifying the cycling of trace elements in natural ecosystems is becoming more important. Increasingly, wildlife species are being contained in well defined fenced sanctuaries to protect the animals from poaching and to protect crops and livestock. Animals in these parks are dependent on the chemical status of the soils to supply sufficient trace element nutrients in bioavailable forms. For many of the major cations, water soluble forms provide adequate levels for nutrition while trace elements such as cobalt and copper can only be gained at localized sites or by selective eating of plants with a high adsorption capacity (McCullagh 1969; Weir 1973; McNaughton 1990; Ben-Shahar & Coe 1992).

This study aims to examine the cycling of cobalt, copper, iron, manganese, molybdenum, selenium, and zinc in an African savannah ecosystem. These elements are considered as essential micronutrients for plant and animal life (Bowen 1979; McDowell et al. 1984). The widespread occurrence of cobalt deficiency in cattle of West Africa, enzootic marasmus (Wharton 1964), and the recorded effects of dietary deficiencies on African herbivores (McCullagh 1969) necessities such a study.

Ecology of the Mole National Park

The Mole National Park (Latitude 9°15′N, Longitude 2°W) is the largest and most 'developed' of Ghana's National Parks. It lies in the northern region of Ghana, approximately 170 km west of Tamale. The 2 500 km^2 area which comprises the national park, lies between 150 and 275 m above sea level. The topography includes two major ridges oriented along a north-south trend along the eastern and western boundaries. The central portion of the reserve is low plain with some minor hills in the northern part of the park. Several streams drain of these highland areas and

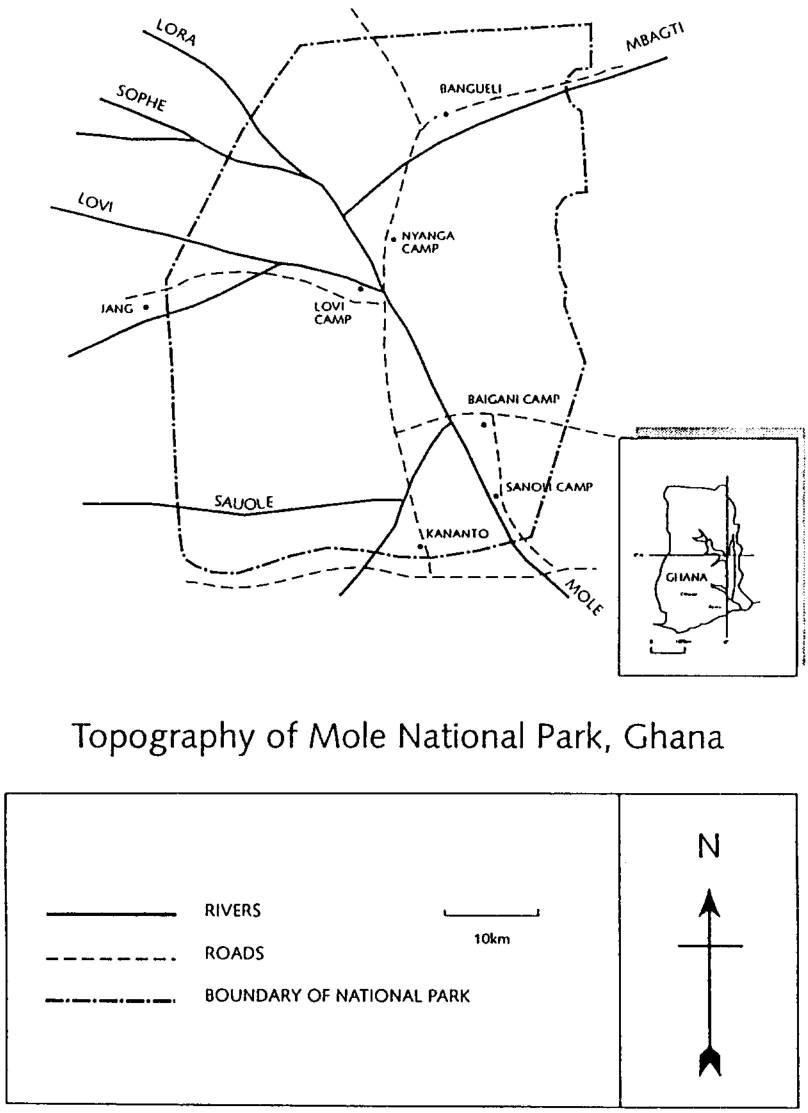

Fig. 1. Location map of Mole National Park, Ghana (after Survey of Ghana, 1961).

converge on the plain to form the Mole river (Fig. 1). Almost all the streams are ephemeral, with only stagnant ponds remaining in the Lovi and Mole rivers. Average daily temperature varies between 20—30 °C and mean annual rainfall exceeds 900 mm, which falls during September to December and March to June.

The area is part of the Guinea savannah belt ecosystem (Sanford &

Isichei 1986). The fauna of this ecosystem has been listed in detail by Ingoldby (1929), Cansdale (1948), and Maze (1970) and the flora by Vigne (1936), Baker (1962), Lawson et al. (1968) and Hall & Jenik (1968).

The vegetation of the Mole National Park has been sub-divided into three units (Lawson et al. 1968); an upper-slope savannah, with the prevalent trees being *Detarim microcarpum*, *Burkea africana*, and an unidentified species of Combretceae; a middle-slope savannah, with *Daniella oliveri* and *Aformoria laxiflora* dominating the canopy and with the undergrowth dominated by *Combretum ghasalense*, *Maytenus senegalensis*, *Burkea africana*, and *Parinari curatellifolia*; and flat valley riverine woodland, with a deep undergrowth dominated by *Pilostigma thonningii* while the dominant tree species is *Terminalia avicennioides.*

Geology of the Mole National Park

Northern Ghana is underlain by early Proterozoic rocks of the West African craton. This supracrustal sequence comprises a volcano sedimentary 'Birimian' sequence (Kesse 1985) which is dominated by carbonaceous argillites with subordinate arenites and andesitic-rhyolitic tuffs. Within the Mole National Park, Birimian rocks occur in the west and central portions of the Park (Fig. 2). The whole sequence was tightly folded along NNE-trending axes and metamorphosed to chlorite-greenschist facies during the Burkinian (c. 2 400—2 100 Ma) and Eburnean (c. 2 000—1 800 Ma) orogenic events (Lemoine et al. 1990). The strata strike is approximately north-south and dips 50—80°W. The Birimian sequence is intruded by granodiorites, which form the western ridge and form inselbergs in the northern part of the park close to the deserted camps by Bugay and Nyanga (Fig. 2).

The Birimian is overlain unconformably in the region by shallow marine and continental sediments of the Voltaian system (K/Ar age, 800—600 Ma). These rocks are largely fine grained feldspathic-arenites with minor argillites, conglomerates, and marls, and are flat-lying with a dip of 3—5°.

Pedology of Mole National Park

A sub-division of the soils (following the FAO/UNESCO (1965) scheme) is:

(i) Ferralsol: This is the dominant soil type throughout northern Ghana (Survey of Ghana 1961; Brammer 1962; Ahn 1970) and these soils

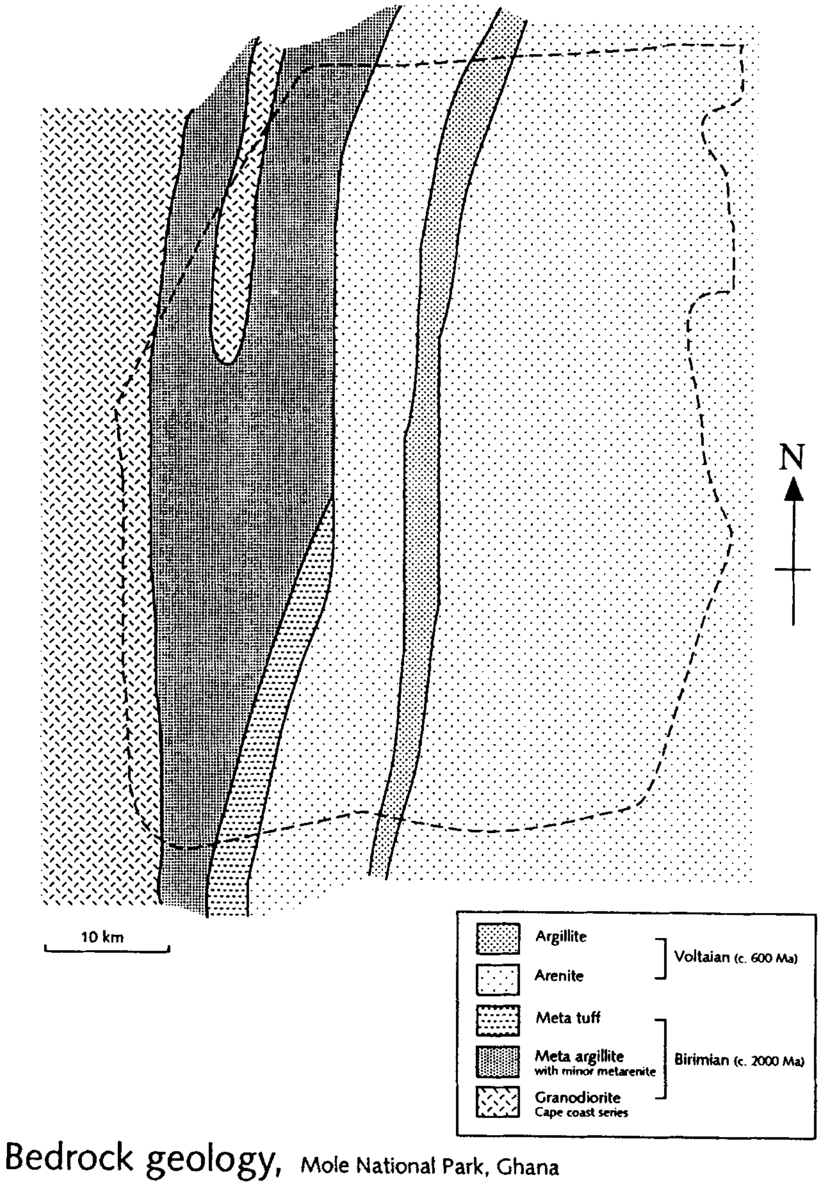

Fig. 2. Geology of Mole National Park, Ghana (after Survey of Ghana, 1961).

are located on the upper slopes and over much of the arenite and granodiorite lithologies (Fig. 3). These soils are characterized by the development of a hard ferricrete pan at a depth of 0.2—1.2 m. Soil depth varies from less than a metre to five meters. The pH of the

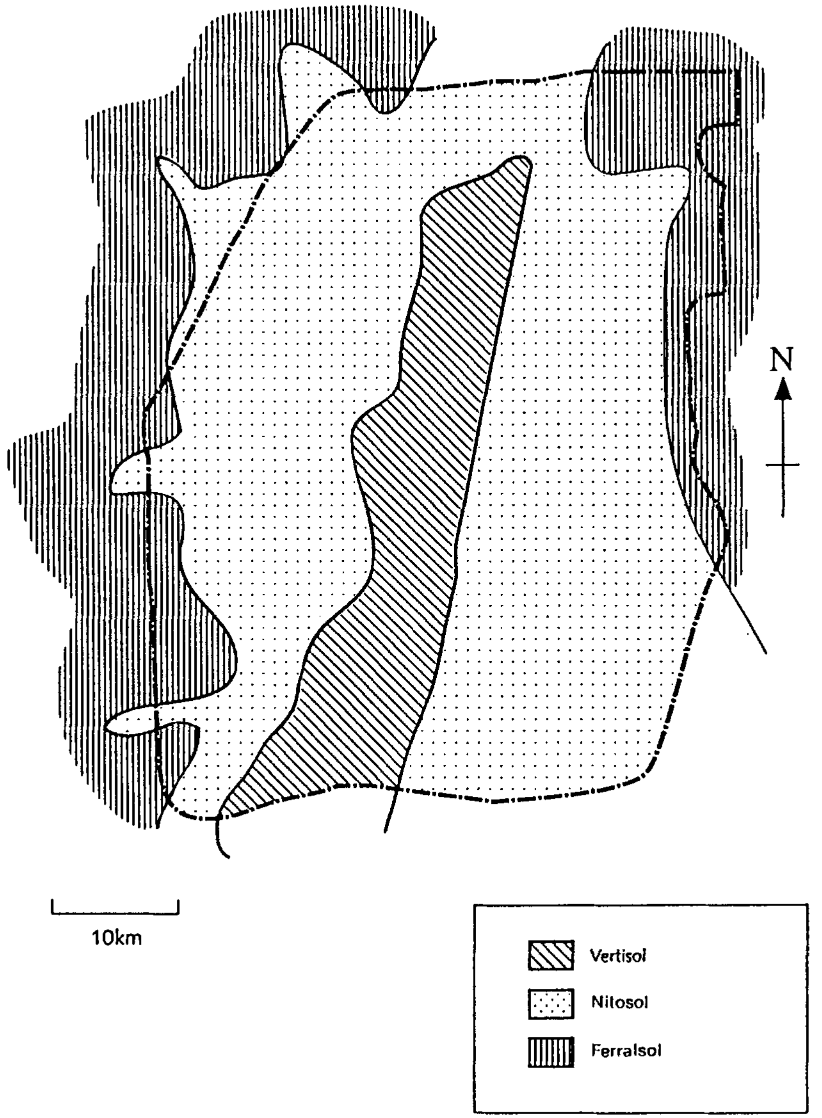

Fig. 3. Pedology of Mole National Park, Ghana (after Survey of Ghana, 1961).

soils varies between 4.9—6.1 and cation exchange capacity is less than 55 meq/100 g. Soil mineralogy consists of hydrous iron (±manganese) oxides, quartz, kaolinite, and minor gibbsite, illite, and rutile.

(ii) Nitosol: These soils are developed in the middle slope catena areas and on the flat valley plains away from streams. The soil depth varies from a metre to over ten metres, and pH varies between 4.9 to 6.5. The cation exchange capacity of the nitosol soils at Mole is between 15 to 87 meq/100 g. Soil mineralogy, as with the ferralsols, is dominated by hydrous iron oxides, quartz, and kaolinite but gibbsite is absent and complex clays such as smectite and vermiculite are present.

(iii) Vertisol: These are developed in the valley floor in the centre of the park. Often termed 'cotton soils' (Ahn 1970) and are organic rich (organic matter content is 2.1—15.9% of total soil volume). Depth of the profiles varies from one metre to seven metres and pH ranges from 4.5—5.8 except close to the streams where pH may be as high as 7.9 in the salt licks. Cation exchange capacity is greatest in the surface horizons (with high organic matter) and is up to 160 meq/100 g. The soil mineralogy is the same as the nitosols except that smectite and vermiculite are more common and chlorite and paragonite are present in soils developed overlying the granodiorite and tuff lithologies. Around the Lovi and Mole rivers, patches of saline soils (Halomorphic soils), termed Solonchaks have developed. These are important sources of trace nutrients of wildlife and show extensive utilization.

Sampling and analytical procedures

Surface soils (0—30 cm) were collected, where possible, on a regular 5 km × 5 km grid covering the National Park and adjacent area. Fieldwork was conducted during October 1988 and March 1990 to collect samples during the wet season and in January 1990 to collect samples during the dry season. A total of 125 soil samples and 96 vegetation samples were collected in the wet season and 125 soil samples and 82 vegetation samples in the dry season. Each soil sample was a composite of non sub-samples taken on a 3 m × 3 m grid using a 5 cm teflon coated soil auger. Samples were sieved in the field and the less than 1 mm size fraction retained.

Soil pits were excavated in each of the major soil types to a depth of 2—3 m, and examined for colour, texture, moisture, and pH. Measurements of pH were made in the field using a Cambridge instrument field Eh-pH meter, calibrated against known standards of pH 4, 7, and 9.

Trace elements geochemistry was obtained for all samples by X-Ray Flourescence spectrometry (XRF) using a Phillips PW1400 with a 3 kW Rh anode tube. Major elements were determined as fused beads and trace elements as pressed powder pellets (Potts 1985). This technique has a 2 σ of 1% for major elements and 5% for trace elements when concentration is above the detection limit (typically 100 μg/g for major elements and 1—2 μg/g for trace elements). Reliability of the data was assessed by analysis of two standard reference samples, a basalt (BHVO-1, USGS) and a laterite soil (K-3 Burke 1985).

Total selenium content was determined after gaseous hydride generation (Welz 1985) and analysis by graphite furnace atomic absorption spectrometry (Perkin Elmer 1100B).

Vegetation samples were taken at each site on the same grid. The dominant grasses *Hyparrhenia subplumosa, H. chrysargyrea, Parinari curatellifolia, Pilostigma thonngii,* and *Andropogon ascinodis* were collected along with leaves, bark, and roots of the trees *Isoberlina doka, Daniella oliveri, Combretum ghasalense, Maytenus senegalensis, Terminalia avicennioides, Afromosia laxiflora, Burkea africana, Detrium microcarpum,* and a species of Combretceae. Grass samples were collected over a 3 m × 3 m square with a scythe and leaves, bark, and roots collected within or near the sampling square. Samples were air dried at 80 °C for 48 hours. Total element concentration in dry ground vegetation was determined by graphite furnace atomic absorption spectrometry (AAS) after digestion in a hydrofluoric/perchloric acid mix.

Bioavailability of elements was determined by leaching in 0.25 M disodium ethylenediaminetetracetate (EDTA) at pH 4.6 for 2 hours in a water bath set at 40 °C. EDTA extraction gives a good estimate of element bioavailability of an element in a free and in a chelated form.

Results

Trace element concentration in soils

Iron concentration in the Park soils range from 100 000 to 590 000 μg/g with the highest concentration over tuffs and granodiorites, particularly on the upper slopes and hills where ferralsols are formed (Table 1). Where pH is high (greater than 6.8), on the valley plain, iron concentration is low (less than 125 000 μg/g). The dispersion of iron is controlled by hydrous iron oxides which are soluble at high pH (greater than 7).

Manganese has a strong lithological control with high concentrations over the Birimian lithologies overlain by ferralsol and vertisol soils (Table 1). This distribution is controlled by the presence of iron-manganese nodules in the Birimian argillites and tuffs and in the Voltaian shales but are largely absent from Voltaian arenites of Birimian granodiorites.

Table 1. Trace element geochemistry, Mole National Park, Ghana. Number of samples = 125. All concentrations expressed as μg/g

	Cobalt				Copper				Iron				Manganese			
	Range		Mean	SD	Range		Mean	SD	Range		Mcan	SD	Range		Mcan	SD
	min.	max.			min.	max.			min.	max.			min.	max.		
Ferralsol																
wet season	1.09	5.12	2.77	1.25	0.9	12.9	7.7	5.1	155000	590000	408000	281000	100	5500	3100	1800
dry season	1.12	5.98	3.22	1.21	0.9	13.2	8.2	4.3	187000	619000	495000	224000	200	7200	3400	2700
Nitosol																
wet season	4.34	9.8	6.91	1.57	1.9	10.2	7.39	3.06	171000	520000	239000	196000	200	6900	2900	2100
dry season	6.23	10.5	6.21	2.35	2.21	11.1	6.3	2.7	162000	543000	375000	117000	200	7200	3400	2700
Vertisol																
wet season	5.38	14.6	7.72	2.64	2.23	27.9	17.2	8.7	170000	265000	195000	17000	300	7300	4100	3000
dry season	5.29	16.9	8.21	2.11	5.41	29.9	16.9	9.2	189000	283000	205000	65000	300	6800	4300	2100
Solonchak																
wet season	1.56	4.5	2.51	1.04	0.98	2.64	1.22	0.42	102000	129000	115000	12000	900	5100	2700	1900
dry season	3.09	7.1	3.99	0.41	1.98	3.74	2.65	0.52	119000	128000	125000	26500	1000	6100	2100	1800

	Molybdenum				Selenium				Zinc			
	Range		Mean	SD	Range		Mean	SD	Range		Mean	SD
	min.	max.			min.	max.			min.	max.		
Ferralsol												
wet season	0.78	8.7	6.52	2.71	0.02	0.56	0.19	0.21	23	51	38	13.9
dry weason	0.89	9.1	5.21	3.72	0.11	0.66	0.37	0.11	29.8	70.9	52.1	17.9
Nitosol												
wet season	0.65	11.1	5.91	4.34	0.49	1.86	0.65	0.52	38.9	63.2	49.6	21.2
dry season	0.65	11.1	4.22	3.78	0.61	2.08	1.02	0.39	41.6	67.9	59.2	11.2
Vertisol												
wet season	0.62	10.2	4.22	3.21	0.43	2.16	1.49	0.62	21.5	123.9	69.5	33.2
dry season	0.62	10.2	3.99	2.21	0.55	3.86	1.04	0.42	27.9	167.9	78.3	32.7
Soonchak												
wet season	10.9	15.9	12.9	1.20	1.98	3.26	3.01	0.15	11.9	61.9	26.2	19.8
dry season	11.1	14.5	10.3	2.57	1.08	3.06	2.69	0.8	31.2	86.8	48.2	10.8

Cobalt, copper, molybdenum, selenium, and zinc are concentrated in soils overlying Birimian tuffs and argillites with the highest concentrations of cobalt and zinc in ferralsol and vertisol soils over the Birmian tuff and the highest copper, molybdenum, and selenium concentrations in similar soils overlying the Birimian and Voltaian argillites. In the salt licks and stream sediments, cobalt, copper and zinc are depleted but molybdenum and selenium are enriched with respect to soil levels elsewhere in the park. Copper shows very little evidence of supergene mobility and its soil distribution and appears to be strongly controlled by bedrock geology. Soils developed on this granodiorite intrusions in the north and west of the game park are enriched in cobalt and molybdenum compared to global average abundance and depleted in copper, iron, manganese, selenium, and zinc.

The total element concentration in the soils is similar in wet and dry seasons with only molybdenum and selenium showing greatly elevated concentrations in the wet and dry seasons (Table 1).

Sequential extraction of trace elements from the soil

The results of the selective extraction for cobalt, copper, iron, manganese, molybdenum, selenium, and zinc are given in Table 2 for the three soil types. The ready availability of elements in the salt lick is reflected by the high percentage of readily exchangeable elements (56% of total selenium, 31% of total molybdenum, 22% of total cobalt, 16% of total zinc, 8% of total copper, 5% of total iron and manganese) in the soils (Table 2). The low organic matter content of the mineral licks ($<4\%$) may explain the lower concentrations of molybdenum, selenium, and zinc in these soils, although copper shows a similar concentration in the salt lick as in the parent soil type (vertisol) away from the salt lick.

In the wet season the exchangeable concentration of all metals is greater than in the dry season. This is most noticeable for molybdenum, selenium, and zinc and to a lesser extent copper (Table 2). Cobalt, iron, and manganese are largely unaffected although in the solonchaks 30% more cobalt is bioavailable in the wet season than in the dry season.

Concentration of trace nutrients in grasses and plants

The concentration of cobalt, copper, iron, manganese, molybdenum, selenium, and zinc in plant samples from all three vegetation catenas are given in Tables 3 and 4.

The grass species *Hyparrhenia subplumosa*, *H. chrysargyrea*, *Parinari curatellifolia*, *Pilostigma thonngii*, and *Andropogon ascinodis* contain

Table 2. EDTA-extraction of trace elements of trace elements from the Mole soils. All concentrations in μg/g.

Wet Season	Co	Cu	Fe	Mn	Mo	Se	Zn
Ferralsol	0.17	2.42	11580	147	0.28	0.11	10.34
Total	2.90	6.90	579×10^3	4900	0.69	0.15	26.5
Nitosol	0.55	1.01	8850	152	2.48	0.42	25.03
Total	6.9	2.2	295×10^3	3800	5.9	0.55	58.20
Vertisol	1.74	5.70	2730	380	1.1	1.03	62.34
Total	7.9	9.2	182×10^3	1900	4.4	1.18	97.4
Solonchak	1.79	0.99	8890	224	12.2	1.97	7.02
Total	2.75	1.8	8.9×10^3	1600	14.3	2.05	11.9
Dry Season	**Co**	**Cu**	**Fe**	**Mn**	**Mo**	**Se**	**Zn**
Ferralsol	0.26	1.91	15750	104	0.39	0.14	9.63
Total	4.36	7.65	525×10^3	5200	1.33	0.22	32.1
Nitosol	0.29	1.60	7260	98	2.18	0.84	17.91
Total	5.98	8.90	363×10^3	4900	5.2	1.21	45.9
Vertisol	1.58	6.34	30600	612	1.45	1.11	56.05
Total	8.77	15.1	255×10^3	5100	6.9	1.41	101.9
Solonchak	0.43	0.48	1189	384	12.16	2.72	9.7
Total	5.35	2.31	12.1×10^3	4800	15.2	3.05	46.2

All concentrations in ppm.
EDTA = Ethylenediaminetetraacetic acid

Table 3. Concentration of trace elements in grass samples. All concentrations expressed in μg/g.

	Cobalt				Copper				Iron				Manganese			
	Range		Mean	SD	Range		Mean	SD	Range		Mean	SD	Range		Mean	SD
Species	min.	max.			min.	max.			min.	max.			min.	max.		
Hyparrhemia subplomosa																
wet season	0.71	1.23	0.89	0.12	14.2	18.3	16.1	0.96	6412	8622	6561	212	712	933	762	49
dry season	0.91	1.53	1.29	0.22	15.2	20.3	18.1	1.38	6422	6729	6520	80	722	933	822	89
Hyperrhemia chrysaryrea																
wet season	0.65	1.82	0.86	0.11	14.4	18.5	15.8	0.55	8811	7329	6923	322	495	632	539	42
dry season	1.05	1.92	1.44	0.25	15.6	21.5	18.7	2.62	6921	7529	7020	280	585	672	605	15
Schnizediyrins domingene																
wet season	0.75	1.02	0.91	0.11	13.5	18.2	15.2	1.08	5912	8553	6299	235	812	1021	918	77
dry season	0.75	1.05	0.87	0.13	17.5	20.5	18.7	2.16	6012	8655	6320	123	832	1211	1081	96
Androgen aecinodis																
wet season	0.52	0.92	0.77	0.19	15.8	20.9	16.5	0.53	7413	7805	7511	105	325	523	422	63
dry season	0.69	0.95	0.82	0.07	17.3	20.2	19.5	1.78	7419	7620	7520	108	396	743	558	159
Parineri curatellifolia																
wet season	0.67	0.82	0.71	0.04	14.1	22.3	17.1	2.25	6009	7119	6520	511	421	854	509	79
dry season	0.73	0.91	0.61	0.06	17.2	25.1	22.3	2.68	6109	7216	6522	357	478	762	595	112
Pilostigma thonningii																
wet season	0.55	0.87	0.62	0.09	12.9	16.7	14	1.96	6211	7091	6618	349	379	612	455	52
dry season	0.72	0.97	0.86	0.05	13.9	16.9	14.8	0.76	6210	7110	6498	211	429	678	552	108

Table 3 (Continued)

	Molybdenum				Selenium				Zinc			
	Range		Mean	SD	Range		Mean	SD	Range		Mean	SD
Species	min.	max.			min.	max.			min.	max.		
Hyperrhemia subplomosa												
wet season	0.01	0.08	0.05	0.03	0.01	0.06	0.04	0.02	33	81	49.3	10.2
dry season	0.01	0.06	0.03	0.02	0.01	0.05	0.03	0.01	44.2	86.5	69.2	11.9
Hyperrhemia chrysaryrea												
wet season	0.02	0.05	0.03	0.01	0.01	0.07	0.04	0.02	32	77.1	50.5	13.3
dry season	0.01	0.04	0.02	0.01	0.01	0.05	0.03	0.01	52	97.7	69.7	14.1
Schnizediyrins domingene												
wet season	0.02	0.05	0.03	0.01	0.01	0.06	0.04	0.02	44.1	77.5	56.2	10.1
dry season	0.01	0.05	0.03	0.01	0.01	0.04	0.02	0.01	64.2	102.5	79.5	9.2
Androgen aecinodis												
wet season	0.01	0.04	0.02	0.01	0.01	0.07	0.04	0.02	51	79.9	59.5	7.7
dry season	0.01	0.03	0.02	0.01	0.01	0.05	0.03	0.02	57	82.1	67.9	8.2
Parineri curatellifolia												
wet season	0.05	0.06	0.06	0.01	0.02	0.07	0.03	0.01	47.2	71.3	53.9	4.2
dry season	0.02	0.03	0.02	0.01	0.01	0.04	0.02	0.01	52.7	72.5	61.6	5.9
Pilostigma thonningii												
wet season	0.04	0.07	0.05	0.02	0.06	0.06	0.07	0.01	46.7	68.1	51.2	3.6
dry season	0.02	0.03	0.02	0.01	0.02	0.04	0.03	0.01	49.8	65.3	56.9	4.7

Table 4. Concentration of trace elements in bush and tree samples. All concentrations expressed in µg/g.

	Cobalt				Copper				Iron				Manganese			
	Range		Mean	SD	Range		Mean	SD	Range		Mean	SD	Range		Mean	SD
Species	min.	max.			min.	max.			min.	max.			min.	max.		
Isobolina dolia																
wet season	0.11	0.51	0.32	0.12	6.3	11.9	8.1	1.77	6720	6933	6800	108	237	259	248	6
dry season	0.18	0.51	0.38	0.1	7.3	13.9	10.2	1.7	6720	6879	8800	55	252	273	264	8
Afromosis laxiflora																
wet season	0.15	0.29	0.17	0.05	9.1	12.8	10.2	0.82	6821	7211	8921	89	221	256	233	9
dry season	0.167	0.22	0.19	0.02	9.7	13.1	11.3	1.23	6821	7321	7080	103	242	268	259	8
Burkea africana																
wet season	0.19	0.32	0.23	0.03	5.8	7.7	6.2	0.24	6305	6791	8550	180	251	286	265	12
dry season	0.29	0.42	0.37	0.04	6.1	9.3	7.9	0.96	6310	6820	8580	140	263	306	281	15
Detrim microcarpum																
wet season	0.04	0.08	0.05	0.02	11.7	14.8	12.5	0.53	7320	7850	7490	155	187	205	192	5
dry season	0.06	0.09	0.07	0.01	12.8	15	13.2	0.21	7320	7665	7482	122	196	222	205	9
Daniella oliveri																
wet season	0.06	0.11	0.09	0.01	9.6	12.5	10.7	0.89	8620	6970	6790	210	119	309	210	68
dry season	0.04	0.06	0.06	0.02	8.9	12.2	10.3	0.9	6100	6830	8550	250	102	312	225	86
Combretum ghasalense																
wet season	0.07	0.09	0.06	0.01	11.1	14.9	12.5	0.9	6700	7190	6910	190	221	260	249	72
dry season	0.05	0.07	0.06	0.01	9.2	11.3	10.5	0.6	6273	6960	6580	310	218	252	236	22
Maytenus senegaisis																
wet season	0.05	0.09	0.07	0.01	9.9	14.9	12.5	1.22	6730	7096	6850	260	240	271	258	13
dry season	0.03	0.09	0.05	0.02	9.3	14.8	11.3	2.1	6605	6960	6800	290	236	265	251	12
Terminalis avicennioides																
wet season	0.06	0.09	0.07	0.01	8.3	11.5	9.5	0.78	6955	7109	7080	95	226	256	245	9.8
dry season	0.02	0.05	0.04	0.01	8.5	12.1	10.2	1.9	6420	7200	6820	385	195	229	209	10

Table 4 (Continued)

	Molybdenum				Selenium				Zinc			
	Range		Mean	SD	Range		Mean	SD	Range		Mean	SD
Species	min.	max.			min.	max.			min.	max.		
Isobolina dolia												
wet season	0.69	0.91	0.79	0.08	0.09	1.21	0.52	0.29	45	55.5	48.3	2.2
dry season	0.52	0.83	0.62	0.06	0.04	0.96	0.63	0.18	46.1	56.6	52.5	4.1
Afromosis laxiflora												
wet season	0.52	0.77	0.68	0.1	0.55	0.81	0.65	0.09	42.3	65.2	51.5	8.9
dry season	0.48	0.68	0.56	0.11	0.35	0.59	0.42	0.18	48	67.2	53.5	3.8
Burkea africana												
wet season	0.75	2.2	1.39	0.42	0.61	1.81	0.95	0.24	40.8	61.6	50.9	7.2
dry season	0.45	1.45	0.72	0.26	0.33	1.28	0.62	0.28	43.8	70.8	62.1	4.7
Detrim microcarpum												
wet season	0.51	0.92	0.69	0.1	0.51	0.95	0.73	0.21	47.1	55.8	50.7	1.9
dry season	0.33	0.71	0.48	0.12	0.21	0.65	0.42	0.15	49.3	59.2	55.6	2.7
Daniella oliveri												
wet season	0.62	0.81	0.7	0.08	0.5	0.79	0.67	0.07	56.1	68.2	64.2	8.8
dry season	0.32	0.55	0.42	0.11	0.3	0.85	0.42	0.09	60.2	70.9	65.3	2.9
Combretum ghasalense												
wet season	0.59	0.82	0.67	0.08	0.7	0.99	0.8	0.09	50.1	68.7	59.2	5.9
dry season	0.29	0.62	0.46	0.13	0.5	0.7	0.63	0.06	52.1	69.5	60.9	5.3
Maytenus senegaisis												
wet season	0.62	0.91	0.72	0.07	0.56	0.74	0.67	0.11	65.2	78.9	69.3	3.9
dry season	0.3	0.69	0.42	0.19	0.48	0.69	0.55	0.11	67.8	76.9	71.2	2.5
Terminalis avicennioides												
wet season	0.62	1.4	0.83	0.16	0.42	0.8	0.63	0.13	52.3	71.6	62.7	5.8
dry season	0.45	0.8	0.56	0.1	0.31	0.62	0.43	0.05	55.9	74.2	63.6	4.1

higher concentrations of cobalt, copper, and manganese than the trees *Isoberlina doka*, *Afromosia laxiflora*, *Daniella oliveri*, *Combretum ghasalense*, *Maytenus senegalensis*, *Terminalia avicennioides*, *Burkea africana*, *Detrium microcarpum*, and Combretceae but lower molybdenum and selenium concentrations. Iron and zinc show a similar range of concentrations in both grasses and plants. Although iron uptake is antipathetic to cobalt, manganese, molybdenum and zinc and the uptake of zinc is also antipathetic to copper and molybdenum (Tables 3—4).

In the dry season the plant uptake of molybdenum and selenium is lower than in the wet season (Tables 3—4). However, the other trace elements show an increased concentration in the dry season in the plant samples. The lower pH of the groundwater (4—5.5) may be influencing the preferential dissolution of copper and zinc at this time.

Concentration of trace elements in the litter

The concentration of the trace elements in the litter are shown in Table 5. Essentially the concentration of trace elements in the litter increases downslope from the upper slope catena to the peneplain.

In the dry season, a lower concentration of trace elements are present in the litter than in the dry season. This reflects a greater retention of the nutrients, in the plants, owing to a decrease in element cycling.

Ecosystem budget

An ecosystem budget involves quantification of element distribution within an ecosystem and estimates of transfer between the main components of the ecosystem.

Table 5. Concentration of selected trace elements in the litter. All concentrations expressed in μg/g

	Co	Cu	Fe	Mn	Mo	Se	Zn
Upper catena							
wet season	0.17	0.52	11390	8900	0.25	0.13	12.92
dry season	0.22	0.53	10210	2290	0.12	0.05	13.12
Middle catena							
wet season	0.29	1.98	21390	11290	0.22	0.25	13.92
dry season	0.19	0.72	21580	3720	0.12	0.11	8.11
Lower catena							
wet season	0.37	2.55	19400	6500	0.22	0.27	25.95
dry season	0.22	0.98	12100	2700	0.18	0.16	18.22

The estimates of the budget (Fig. 4) were calculated using published methods (Parker et al. 1978; Hughes 1981). Estimates of total soil metal and bioavailable metal contents were calculated by $n \times 10^4$ mgm^{-2}, (where n is the mean measured concentration) and the total litter and vegetation metal transfer was estimated by $n \times 10^{1-2}$ mgm^{-2}.

Broadly similar patterns of metal distribution were found at Mole as has been reported elsewhere in temperate climates (van Hook et al. 1977; Whittaker et al. 1979; Martin & Coughtrey 1981). Atmospheric input is unknown for the Mole or any similar ecosystem so no estimate can be made. Roots are an important reservoir for copper and zinc, with more zinc in plants than in the litter suggesting more zinc is retained in the plants than any other trace element studied. The soil contains the highest proportion of all trace elements, as would be expected. The difference in element transfer between wet and dry seasons is also evident with lower concentrations of all elements available in the soils leading to lower concentrations in roots. Many trace elements, noticeably copper and zinc, are enriched in the grass and tree samples (Fig. 4). Either these elements are concentrated through loss of water or, in the acidic porewaters, they are more stable as dissolved complexes. Therefore despite lower concentrations of these elements being available for adsorption, what is available is far more efficiently adsorbed leading to enhanced concentrations in the plants.

The catenas developed on the lower slopes show a greater cycling of trace elements than on steeper gradients, possibly due to groundwater leaching of bioavailable nutrients (Fig. 4). This effect is even more pronounced in the dry season (Fig. 4b). The soil is the largest reservoir of nutrients, but on the vertisolic peneplain vegetation and the litter show appreciable concentrations of trace elements suggesting an active cycling of metals (Fig. 4), however on the steeper slopes the proportion of metals in the litter is less, due to lower concentrations of nutrients held by the vegetation and greater retention of the nutrients.

Where saltlicks are formed in the ephermal stream beds, molybdenum and selenium are concentrated and the soils contain lower concentrations of cobalt, copper, iron, manganese, and zinc (Fig. 4).

Discussion

Release of trace metals into the ecosystem

Trace metal release by weathering and subsequent soil transfer constitutes the major source of elements in the undisturbed ecosystem at Mole. Short

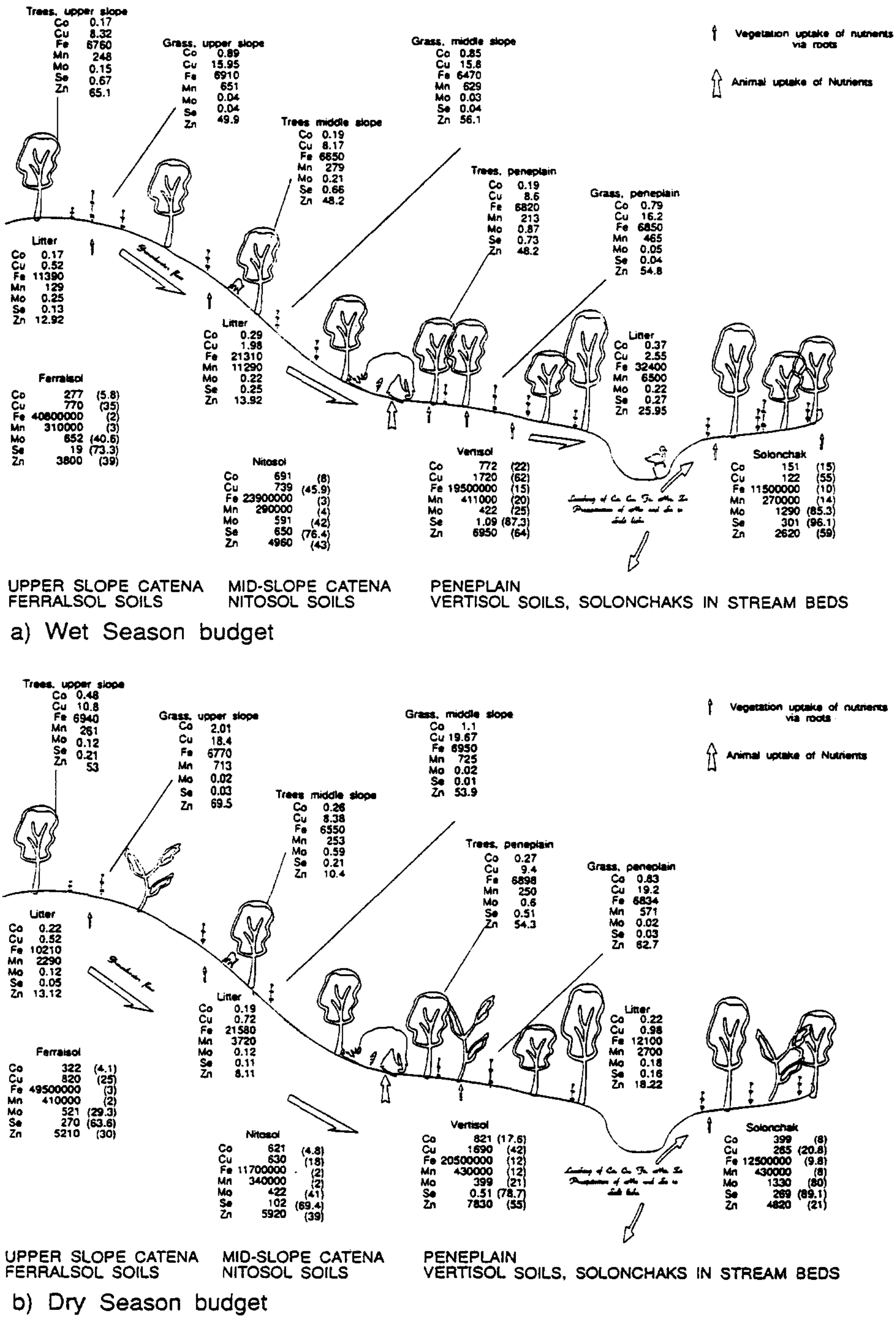

Fig. 4. Schematic representation of trace element transfer in soils at Mole National Park, Ghana. Element concentrations in mg/m^2. With soil geochemistry figure in parentheses in the percentage of element which is EDTA extractable. a) Wet Season; b) Dry Season.

term changes in soil pH, moisture, and redox conditions affect the form and bioavailability of trace elements. Soil pH is an important control on element availability in humid regions, such as Ghana, soil pH increases with depth. Although in the solonchak soils, where evaporation causes salt accumulation in the surface horizons, a decrease in pH occurs with depth. Generally, most trace elements are more mobile in acidic environments and pH increases usually reduce bioavailability. Two exceptions to this are molybdenum and selenium both of which increase in bioavailability with a pH increase. This may explain the decrease in plant uptake of molybdenum and selenium from the lower pH soils in the dry season and increased absorption of copper and zinc and to a lesser extent, cobalt, iron, and manganese.

Clay minerals, produced by the breakdown of primary silicates, are also an important component for trace metal fixation in soils due to a large surface area and permanent negative charge. The cation exchange capacity (CEC) increases with surface area, such that kaolinite, which is common in the ferralsol soils, with a small area (5—100 m^2/g) has a low CEC (3—20 meq/100 g) while smectite, common in the vertisol soils, has a large surface area (700—800 m^2/g) owing to relatively weak interlayer bonding which allows soil porewaters into the lattice and as a result has a high CEC (80—120 meq/100 g). Consequently in the Mole soils the smectite rich vertisols have a higher capacity to retain trace metals than the kaolinite-gibbsite-goethite ferralsols. However, clays rarely exist in a pure form in soils and commonly form intergrowths with humic substances and hydrous iron oxides. The combined organoclay phase is a more effective colloid in sorbing metals and plays an important role in metal retention in the soils (Farrah & Pickering 1979).

Apart from inorganic agents soil organic matter, particularly humic substances, can also adsorb cations either by chelation, through attached functional groups, or by colloidal adsorption onto the humic structure (Baker 1973; Schnitzer 1984). Non-humic compounds include unaltered biochemicals released during decay such as amino acids, carbohydrates, organic acids, fats, and waxes (Tissot & Welte 1978).

Redox reactions in the soils can also affect nutrient availability, but are frequently slow unless catalysed by soil organisms which consume oxygen thereby reducing the system (Sposito 1983). The precipitation of iron oxides initially produces ferrihydrite ($Fe_5(O_4H_3)_3$) which gradually alters to geothite. Ferrihydrite co-precipitates other essential trace elements nutrients such as Cu, Mn, Mo, and Zn and can act as a scavenger for oxyanions such as HPO_4^{2+}. This reduction of ferrihydrite may be assisted by the action of specialized bacteria such as *Thiobacillus ferroxidans* (Pepper & Miller 1981).

Plant uptake of trace elements

The litter (Fig. 4) receives decaying organic matter, including exudate, mucilage, dead cells, and their lysates (Marschner 1986; Yossef & Chino 1991). These organic compounds enrich the litter with contained nutrients and encourage microbial activity which causes metal solubility For example the release of phenolic acids by microbial activity is known to influence the dissolution and mobility of Fe^{3+} and Mn^{4+} compounds (Marschner 1986). Metals which follow a similar absorption mechanism are likely to compete for the same sites and will therefore be antagonistic to each other. For example, copper uptake is inhibited by high concentrations of ammonium, calcium, hydrogen, molybdenum, potassium, sodium, and zinc (Graham 1981). Once in the plant, metals can be transported into the xylem and there moved throughout the whole plant (Tyler 1971; Chaney & Giorando 1977; Thurman 1981; Przemeck & Haase 1991). In leaves, metal ions can be incorporated into proteins or migrate around the leaf in the phloem with photosynthates (Thurman 1981; Chongpraditnun et al. 1991).

Implications for wildlife nutrition

The cycling of trace nutrients in the Mole ecosystem is influenced by geology, groundwater flow, and adsorption by plants. In the wet season, the bioavailability of most elements is much greater than in the dry season suggesting that trace nutrient deficiencies will be unlikely. In the dry season many trace nutrients are retained by the vegetation, although the actual cycling of elements is lower. However, deficiencies may occur for some elements such as cobalt, based on recommended levels for domestic livestock (Underwood 1977). The partitioning of cobalt in the ecosystem, as well as its bulk concentration, reveals a potential deficiency in this element. The low molybdenum concentrations throughout the ecosystem are unlikely to induce copper deficiency.

However, the evaluation of trace nutrient requirements is based on the needs of domestic ruminant livestock which are less tolerant than non-ruminant livestock to cobalt deficiencies, which would lead to a deficiency in vitamin B_{12} (Purcell & Kotz 1977) and of increased molybdenum levels which induces hypocuprosis (Underwood 1977). In studies of wildlife nutrition in Kenya, Maskall & Thornton (1991) found a close correlation between high molybdenum in soils and copper deficiency in impala (*Aepyceros melampus*, Lichtenstein). Ruminant wildlife, such as forest buffalo (*Syncerus caffer beddingtoni*, Lyd), western hartebeest (*Bubalis major*, Blyth), and the red flanked duiker (*Cephalophus rufilatus*, Gray) may also be sensitive to similar soil nutrient deficiencies than non-ruminants such as the African elephant (*Loxodonta africana*, Blumbach). This, however, assumes that wildlife responds to nutrient deficiencies in the same way as domestic livestock (Wharton 1964; McDougall et al. 1984; Ben-Sharhar & Coe 1992). Other sources of nutrition such as salt licks may be used to compensate for dietary deficiencies or wildlife may merely adapt to the lower concentrations available (Rodger 1975).

It is clear that enhanced concentrations of trace nutrients may arise in any component of an ecosystem where accumulation exceeds loss.

The pattern of retention varies according to the trace nutrient involved. The mean values of trace nutrient concentration have been used here to be representative of the burden in that biotic component. This may not always be the case as frequency distributions of trace nutrients is often skewed (Garten et al. 1977; Wallace et al. 1977), with trace nutrients tending to be more skewed than essential elements (Garten et al. 1977). High soil concentrations of trace metals in the dry season may explain the extensive utilization of soil by elephants, buffalo, and hartebeest.

Conclusions

Trace elements have characteristic modes of dissolution, uptake, retention, and loss in ecosystems. Soils are by far the biggest pool of trace nutrients in Mole National Park. Litter is the next biggest source, except for copper which is largely concentrated in the vegetation. Metal transfers are much lower in the dry season than in the wet season due to a lower availability and greater retention of nutrients by the vegetation. From this study a potential dietary deficiency in cobalt is apparent for both plants and wildlife. The concentration of other trace elements appears to be sufficient, in plants and soils, to provide dietary requirements and the concentration of potentially antagonistic elements such as selenium and molybdenum are low enough not to prevent a hazard.

Further work is required to study the response of wildlife to low concentrations of trace nutrients in their habitat, and to quantify nutritional requirements of ungulates.

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