

## Distribution and biogeochemistry of inorganic chemicals associated with forest conversion and pasture installation in Rondônia (Brazilian Amazon Basin)\*

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**Abstract:** Forest burning for pasture installation in tropical areas represents an important component on biogeochemical cycles. In order to get information about modifications within the element composition after forest burning, in this local study the attempt has been undertaken to provide a first overview about the total contents of a larger set of elements (29) and their distribution patterns in topsoils when forest is shifted for pasture use. The work was carried out in 1999 in Rondônia state (Brazilian Amazon Basin) focussing on a native forest site and 4 neighbouring pastures established in 1987, 1983, 1972 and 1911 after forest conversion. Mostly higher values of nearly all investigated macro- and micro-nutrients, but also of other elements (e.g. Sr, Cr, Ni, V or Pb) as well as increases of pH levels could be determined twelve years after forest burning in the pasture of 1987. Conversely, pH values of pH 7.6 five years after forest clearing in pasture 1987 (0-5 cm) and pH 5.5 in the same pasture after 12 years suggest a loss of basic acting cations in the present sandy soils due to high rainfall intensities. After initial element increases in pasture of 1987 the decreases of main nutritional elements (e.g. C, N, K, S) in the pasture of 1983 as well as again the enhanced levels in pasture 1972 and 1911 suggest both a persistent leaching and a function of pasture age where external element inputs exceed outputs. Ash deposition, animal excreta, accumulation of organic matter as well as natural soil conditions are discussed as influencing factors on the measured element budgets. Chemical fingerprint graphs of the pasture soils related to the chemical conditions in the forest soil illustrated different element distributions in the pastures. Nevertheless, in this particular area it can be suggested that continuous pasturing after forest clearing primarily enriched the

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\* A short first introduction into this overall topic has been given in: Herpin *et al.* 2002. Biogeochemical dynamics following land use change from forest to pasture in a humid tropical area (Rondônia, Brazil). A multi element approach by means of XRF-spectroscopy. *The Science of the Total Environment* 286: 97-109.

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soils in elements. From the ecotoxicological aspect the results showed low risks of toxic elements in the considered area compared to element ranges for unpolluted soils.

**Resumen:** La quema del bosque para el establecimiento de pastizales en áreas tropicales es un componente importante de los ciclos biogeoquímicos. Con el fin de obtener información sobre las modificaciones en la composición de elementos después de la quema del bosque, en este estudio local se intentó ofrecer una primera visión general sobre los contenidos totales de un conjunto más grande de elementos (29) y sus patrones de distribución en el suelo superficial cuando el bosque es eliminado para usar el terreno como pastizal. El trabajo se llevó a cabo en 1999 en el estado de Rondônia (cuenca amazónica brasileña) y se enfocó en un sitio de bosque natural y cuatro pastizales vecinos establecidos en 1987, 1983, 1972 y 1911, una vez que el bosque fue transformado. En el potrero de 1987, doce años después de la quema del bosque, se determinaron principalmente valores altos de casi todos los macro- y micronutrientes investigados, pero también de otros elementos (e.g. Sr, Cr, Ni, V o Pb), así como incrementos en los valores de pH. Por el contrario, los valores de pH de 7.6 observados cinco años después del aclareo del bosque en el potrero de 1987 (0-5 cm) y el pH de 5.5 en el mismo potrero después de 12 años, sugieren que hay una pérdida de cationes que actúan como bases en los actuales suelos arenosos debido a las altas intensidades de la precipitación. Después de un incremento inicial de los elementos en el potrero de 1987, los decrementos de los principales elementos nutricionales (e.g. C, N, K, S) en el potrero de 1983, así como de nuevo los niveles mejorados en los potreros 1972 y 1911, sugieren una lixiviación persistente y una función de la edad del potrero, en la que el ingreso externo de elementos excede a las salidas. Se discute el papel de la deposición de cenizas, las excretas animales, la acumulación de materia orgánica y las condiciones naturales del suelo como factores que influyen sobre los presupuestos medidos de los elementos. Las gráficas del perfil químico de los suelos de los potreros en relación con las condiciones químicas en el suelo forestal ilustraron diferentes distribuciones de los elementos de los pastizales. No obstante, para esta área en particular se puede sugerir que la presencia continua de potreros después del aclareo del bosque enriqueció principalmente a los suelos en términos de sus elementos. Desde una perspectiva ecotoxicológica, los resultados mostraron que los riesgos de que haya elementos tóxicos en el área considerada son bajos en comparación con los intervalos de los elementos para suelos no contaminados.

**Resumo:** A queima da floresta para a instalação de pastagens em áreas tropicais representa uma componente importante nos ciclos biogeoquímicos. A fim de obter informação acerca das modificações respeitantes à composição dos elementos químicos depois da queima da floresta, o estudo, neste sítio particular, foi efectuado para proporcionar uma primeira informação sobre o teor total de um grande conjunto de 29 elementos e sobre os padrões de distribuição na camada superficial do solo quando a floresta é transformada em pastagem. O estudo foi levado a cabo no Estado da Rondônia (Bacia Amazônica Brasileira) em 1999 focando uma estação florestal nativa e 4 pastagens vizinhas estabelecidos em 1987, 1983, 1972 e 1911 depois da conversão da floresta. Valores quase sempre mais altos de quase todos os macro e micro nutrientes já estudados, mas também de outros elementos (p.e. Sr, Cr, Ni, V e Pb), assim como, aumentos dos níveis de pH, poderiam ser encontrados doze anos após a queima da floresta na pastagem em 1987. Reciprocamente, valores de pH 7,6, cinco anos depois da conversão da floresta em pastagem 1987 (0-5 cm) e pH 5,5 no mesmo pasto, 12 anos depois sugerem uma perda básica da acção catiónica no presente solo arenoso devido à intensidade das chuvas. Depois dos aumentos iniciais de elementos na pastagem de 1987, a diminuição dos principais elementos nutricionais (p.e. C, N, K, S) na pastagem em 1983, assim como, o aumento dos níveis novamente nas pastagens de 1972 e 1911 sugerem um lixiviamento persistente e uma função da idade da pastagem onde as contribuições de inputs nutricionais externos excedem os outputs. Depósito de cinzas, excrementos de animais, acumulação de matéria orgânica, assim como, condições naturais do solo são discutidas como factores que influenciam nos balanços dos elementos medidos. Gráficos de caracterização dos elementos

químicos dos solos da pastagem relacionados às condições químicas nos solos das florestas ilustram diferentes distribuições de elementos nas pastagens. Não obstante, nesta área particular, pode ser sugerido que nas pastagens contínuas após conversão da floresta houve um enriquecimento dos elementos do solo. Do ponto de vista ecotoxicológico os resultados mostram baixos riscos de toxicidade na área considerada comparada com a gama de elementos nos solos não poluídos.

**Key words:** Amazon basin, biogeochemistry, land use change, multi-element analysis, XRF-spectroscopy.

## Introduction

The increasing activities of man to transform natural ecosystems for agricultural purposes are an important component of global environmental change. Particularly in the tropics, which represent today a region of most rapid land cover conversion, forest clearing for agriculture involves millions of ha annually (Melillo 1996). Especially the state Rondonia in the south-western Amazon Basin has been one of the focus of rapid deforestation with an increase of the deforested area from ca. 4200 to 53300 km<sup>2</sup> between 1978 and 1998 (INPE 2000). At present this converted land is predominantly used for years as pasture (Serrão & Toledo 1990). However, the conversion of natural forest for pasture land, mainly by slash and burn technique will invariably impact chemical and biological soil properties and processes of the surface soils.

Previous studies have described temporal alterations of carbon and nitrogen contents and the relation to changes in trace gas fluxes like CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> after land use changes (Bernoux *et al.* 1998; Feigl *et al.* 1995; Neill *et al.* 1998; Steudler *et al.* 1996). Changes in organic matter as well as increases in soil pH and exchangeable cations after forest burning and pasture installation were reported by Ewel *et al.* (1981); Andreaux & Cerri (1989); Maggs & Hewett (1993); Hölscher *et al.* (1997) and Giardina *et al.* (2000).

It is safe to assume that simultaneously with burning of natural vegetation there is a release of other elements of the Periodic Table, which were here accumulated in the vegetation in former periods of time by natural and anthropogenic pathways as well (Nriagu & Pacyna 1988). In general natural and anthropogenic induced element inputs

combine with the present state of the organic and the inorganic element fraction of the soil matrix constitutes their entire element store and may lead to modifications of the chemical inventory in soils as well (Raison 1979). Chemical elements of importance in agricultural soils are elements forming the soil matrix, essential elements for plants and animals and known toxic elements. Other elements are merely up to now without biological or any other function.

Nearly all chemical elements are involved in so-called cycles which are a basic requirement of the life processes known to take place on earth today (Bliefert 1994; Schlesinger 1991). Moreover, since each element and each class of material can be significant at some point in the ecosystem and due to the formulated assumption, that one element (or elements) can influence the others (e.g. synergistic or antagonistic effects), the biogeochemical aspect demand to involve the consideration of the entire element composition. Almost no information currently exists about inorganic element pools that point out alterations when forest is shifted to pasture land. Special emphasis is placed on nutrient physiology or toxicology because many elements are known to be of essential (structural, electrolytic, enzymatic) or ecotoxicological significance (Markert 1998). The introduction and use of multi-element techniques had opened up new opportunities in this field of modern ecosystem research and can provide relevant contributions in future (Markert & Friese 2000).

This study is focused on 4 different aged pastures established in 1987, 1983, 1972 and 1911 as well as a reference forest site in a region with representative soils of the Brazilian Amazon basin. This chronosequence was object of extensive previous studies mainly for C- and N dynamics after

land use changes (Moraes *et al.* 1996; Neill *et al.* 1995). The pastures were established in the same manner after forest clearing what make it suitable for comparative investigations and evaluations of the transition from forest to pasture and of the effects of continuous pasture use.

The present analytical study using multi-element analysis forms an initial contribution to complete the intended establishment of worldwide "element concentration catalogues of ecosystems (ECCE)" (Lieth & Markert 1990). This program contributes to the goals of the International Geosphere-Biosphere Program (IGBP) which calls for descriptions of the environment for its inorganic chemical composition, for a better understanding of the chemical structure and the element fluxes in ecosystems on a global, regional and local scale. At present there are no data for the area of investigation which concern the transition from forest to pasture. So far attention has been focused mainly on data from the northern hemisphere.

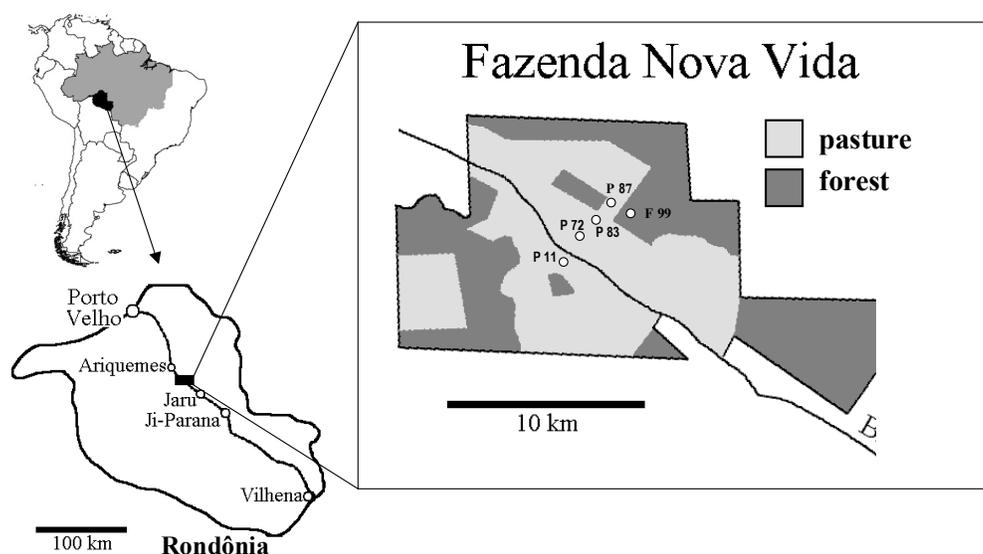
The purpose of this work is to provide a comparison between the forest and the pastures based on their chemical soil composition and to provide information about the possible enrichment, depletion or correlation of elements after forest conversion as well background concentrations in a tropical environment.

## Material and methods

### Study area

The forest and the pasture sites were located at Fazenda Nova Vida in Rondonia state (south-western Amazon Basin) within a distance of 5 km. In Fig. 1 the locations of the investigated sites (F99, P11, P72, P83 and P87) in the chronosequence are shown. The climate of Rondônia is humid tropical. The mean annual rainfall averages 2200 mm with a short, well defined dry season from June to August. The mean annual maximum and minimum temperatures range from 24.4 °C to 25.5 °C and 18.8 °C to 20.3 °C, respectively. The native forest vegetation is open humid tropical forest with large numbers of palm trees. According to Moraes *et al.* (1996) the investigated area can geomorphologically be divided into two landscape patterns. (1) for the sites F99, P87, P83 and P72 a sedimentary landscape of convex rolling hills with flat tops at about 200 m and (2) for P11 rocky hills with more irregular diameters and shapes because of a complex incision by a temporary river network. The altitude ranges between 130 and 170 m.

The area of investigation show similar topography (Neill *et al.* 1995) and two main soil types. The forest site (F99) and pastures created in 1987 (P87), 1983 (P83), and 1972 (P72) consists of a red



**Fig. 1.** Map of the Brazilian legal Amazon region and the location of Rondônia and Fazenda Nova Vida including the investigated forest (F99) and pasture sites (pasture installation after forest clearing in 1987 (P87), 1983 (P83), 1972 (P72) and 1911(P11)). BR 364 represents the most important highway in the area.

yellow podzolic latosol (EMBRAPA 1988). In the U.S. Soil Taxonomy it is classified as Kandiodult. According to Moraes *et al.* (1996) the A horizon is a sandy clay loam, weakly structured about 10 cm thick. The AB horizon extends to 25 cm. The B1 horizon is brown or yellowish red, gradually becoming sandy clay. The underlying B2 horizon is yellowish red to red, soft, porous and presents a sandy clay material. The lower part of this horizon may contain up to 50% of gravel and stones composed of flat ferruginous sandstone, sub-rounded ferruginous rocks, and angular and subangular quartz. The clay minerals consist of kaolinite and small amounts of gibbsite in both B and C horizon.

In the pasture created in 1911 (P11) the soil is a red yellow podzolic soil or Ultisol (Paleudult, Tropudult). The surface A horizon is about 5 cm thick and brown, with a sandy loam sand texture. A thin, 1 cm sand layer is encountered on the top soil. The B2 horizon is a yellowish red sandy clay loam or sandy clay and extends to more than 100 cm, with weak structural development. Saprolite is found at depths of 150-200 cm. Kaolinite, mica and feldspars are the mineralogical compounds of the clay fraction. In the upper part of the C horizon the mica content is very high. Both soil types are representative soils of the Brazilian Amazon basin and covering almost 60% of the basin area (Moraes *et al.* 1995).

The pastures were created by slashing and burning after the beginning of the rainy season and planting with pasture grass in December or January. No mechanical agricultural practices were used (Moraes *et al.* 1996). Information about fertilizing treatments (except P72, liming in 1998) were not available. In the sampling period the dominant plant species in the pastures was the tropical grass *Brachiaria* (*Brachiaria brizantha* (A. Rich.) Stapf.). All pastures were actively grazed at an average annual rate of 1-2 animal ha<sup>-1</sup>.

### *Sampling and analysis*

In the forest and pastures soil samples were collected at 5 sampling points (pits) (80x100 cm and 50 cm deep) within an area of 1 ha (100x100 m). The pits were located at a regular distance of 50 m. The samples were collected at 0-5 cm, 5-10 cm and 10-20 cm depths by using plastic equipment to reduce the risk of metal contamination and were subsequently stored in plastic bags.

Samples for C and N determination were taken by means of non-plastic materials. After drying at 50°C to a constant weight the samples were sieved at 2 mm, any remaining fine root fragments were removed using plastic tweezers. Bulk density was determined from three replicate samples collected at each depth using volumetric cylinders.

As in previous studies in Rondônia the pH of the dried and sieved soil samples was measured in deionized water (2.5:1). Total C and N contents were determined by using a C/N analyzer (Finnigan Delta E). For multi-element analyses the dried soil samples were ground in agate bowls by using a planetary mill (Fritsch, Germany). Pellets (40 mm diameter) were prepared by mixing 9 g sample and 1.5 g of Wax C micropowder PM (C<sub>38</sub>H<sub>76</sub>N<sub>2</sub>O<sub>2</sub>, (Hoechst, Germany)) and pressed for one minute at 119 MPa with a semi-automatic press (HTP40, Herzog, Germany). Major and minor and trace element determinations were performed by XRF spectrometry (PW2404, Phillips). Concentrations of 27 elements (P, K, S, Ca, Mg, Na, Mn, Zn, Cu, Mo, Co, Ba, Rb, Sr, Pb, Ni, As, Cr, V, Ti, Si, Al, Fe, Ga, Y, Nb, Zr) were determined.

The accuracy of the measurements were verified by use of international reference materials MESS-2 (marine sediment prepared by NRC (Canada)), TILL-1 and TILL-3 (soil samples from the combined B and C horizons prepared by CCRMP (Canadian Certified Reference Materials Project), TILL-2 and TILL-4 (till (glacial sediment) samples prepared by CCRMP. The measured and recommended values are given in Table 1.

## **Results**

The major results should be priority considered for the sequence from forest to the 12, 16 and 27 years old pastures (P87, P83, P72). The 88 year old pasture (P11) reported in this paper is not representative for the land use types in the Brazilian Amazon Basin due to initially different pasture management (e.g. stocking rates of animals). Moreover, mineralogical data indicate some divergent natural conditions in P11. However, P11 will be presented as an example of long term changes on soil properties after forest clearing.

### *Soil pH*

In Table 2 the pH values obtained in the present study in 1999 (sampling in July/August, dry

**Table 1.** Recommended values (recomm.) and measured value (m) of different soil reference materials (Mess-2, Till-1, Till-2, Till-3, Till-4).

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>
	(%)									
MESS-2 (m)	59.47	16.47	6.04	0.054	2.31	2.23	1.79	3.23	0.792	0.22
recomm.	59.40	16.2	6.22	0.047	nd	nd	nd	nd	nd	0.28
TILL-1 (m)	59.15	13.39	6.80	0.141	2.06	2.64	2.61	2.07	0.956	0.274
recomm.	60.90	13.70	6.82	0.180	2.15	2.72	2.71	2.22	0.980	0.220
TILL-2 (m)	62.78	17.46	5.64	0.088	1.73	1.28	2.50	3.25	0.978	0.171
recomm.	60.80	16.00	5.39	0.100	1.83	1.27	2.19	3.07	0.880	0.170
TILL-3 (m)	68.75	10.98	4.06	0.060	1.65	2.46	2.35	2.41	0.465	0.124
recomm.	69.10	12.20	3.92	0.060	1.71	2.63	2.64	2.42	0.490	0.110
TILL-4 (m)	63.74	14.28	5.85	0.060	1.19	1.23	3.04	3.22	0.849	0.201
recomm.	65.00	14.40	5.63	0.060	1.26	1.25	2.46	3.25	0.810	0.200

Sample	As	Ba	Co	Cr	Cu	Ga	Mo	Nb	Ni	Pb	Rb	S	Sr	V	Y	Zn	Zr
	(µg g <sup>-1</sup> )																
MESS-2 (m)	21.1	972	11.3	116	41.5	17.4	1.93	17.1	50.8	20.0	165	1683	116	236	27	157	187
recomm.	20.7	nd	13.8	106	39.3	nd	2.85	nd	49.3	21.9	nd	1800	125	252	nd	172	nd
TILL-1 (m)	18.1	657	17.1	63	45.4	18.6	1.6	12	23.5	26.2	47.6	249	295	111	33	97	448
recomm.	18.0	702	18.0	65	47.0	nd	2.0	10	24.0	22.0	44.0	<500	291	99	38	98	502
TILL-2 (m)	26.0	569	13.5	77	159.3	19.1	14.2	22	38.5	32.6	161.3	334	155	91	38	155	407
recomm.	26.0	540	15.0	74	150.0	nd	14.0	20	32.0	31.0	143.0	<500	144	77	40	130	390
TILL-3 (m)	93.1	458	14.6	128	26.8	14.1	< 1.5	8	45.7	31.8	61.2	195	296	68	17	70	215
recomm.	87.0	489	15.0	123	22.0	nd	2.0	7	39.0	26.0	55.0	<500	300	62	17	56	230
TILL-4 (m)	114.4	413	7.2	59	251.8	16.6	15.8	18	16.8	52.6	178.4	898	136	78	26	95	381
recomm.	111.0	395	8.0	53	237.0	nd	16.0	15	17.0	50.0	161.0	800	109	67	33	70	385

**Table 2.** pH values of investigated soils in 1999 and in 1992\* (Moraes *et al.* 1996).

Sites	0-5 cm		5-10 cm		10-20 cm	
	pH (1992)*	pH (1999)	pH (1992)*	pH (1999)	pH (1992)*	pH (1999)
F99	5.1 ± 0.5	4.0 ± 0.2	4.7 ± 0.2	3.8 ± 0.1	4.5 ± 0.2	4.0 ± 0.1
P87	7.6 ± 0.5	5.5 ± 0.1	7.2 ± 0.3	5.4 ± 0.1	6.9 ± 0.3	5.3 ± 0.2
P83	6.1 ± 0.2	5.8 ± 0.1	6.1 ± 0.3	5.5 ± 0.3	6.3 ± 0.3	5.3 ± 0.3
P72	5.7 ± 0.4	5.2 ± 0.3	5.7 ± 0.3	5.0 ± 0.2	5.7 ± 0.3	5.1 ± 0.2
P11	5.9 ± 0.3	6.0 ± 0.3	5.9 ± 0.5	5.5 ± 0.2	5.9 ± 0.2	5.3 ± 0.2

season) are compared with pH values obtained in the same sequence in 1992 (sampling in July, dry season) published by Moraes *et al.* (1996). In both surveys, the forest site showed the lowest pH values. Compared to the forest levels the largest pH changes of about 2.5 units were determined in P87 at all depths in 1992 (pasture: 5 years old). In 1999 (pasture: 12 years old) less increases of about 1.5

units were observed. The pH values measured in 1999 are generally less at all sites and at all depths compared to 1992. Distinct decreases between 1999 and 1992 (more than 1.5 units) at all depths were found in P87. For the other pastures (P83, P72, P11) the values do not vary very much in both investigations.

**Table 3.** Total element contents (%) and bulk density ( $\text{g cm}^{-3}$ ) of major elements in soil samples at the forest site in 1999 (F99) and the pasture sequence. Values are mean  $\pm$  S.D.

	Bulk density $\text{g cm}^{-3}$	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	TiO <sub>2</sub> (%)	P <sub>2</sub> O <sub>5</sub> (%)	K <sub>2</sub> O (%)
0-5 cm							
F99	1.24 $\pm$ 0.02	78.2 $\pm$ 3.1	6.6 $\pm$ 0.6	4.0 $\pm$ 1.0	0.64 $\pm$ 0.05	0.06 $\pm$ 0.002	0.014 $\pm$ 0.005
P87	1.32 $\pm$ 0.03	73.0 $\pm$ 0.7	8.0 $\pm$ 0.4	5.1 $\pm$ 0.4	0.65 $\pm$ 0.04	0.08 $\pm$ 0.006	0.034 $\pm$ 0.009
P83	1.56 $\pm$ 0.04	70.2 $\pm$ 2.9	8.3 $\pm$ 0.9	6.0 $\pm$ 1.0	0.84 $\pm$ 0.07	0.08 $\pm$ 0.006	0.030 $\pm$ 0.008
P72	1.30 $\pm$ 0.11	75.4 $\pm$ 4.4	7.6 $\pm$ 2.0	3.9 $\pm$ 0.6	0.56 $\pm$ 0.08	0.08 $\pm$ 0.004	0.053 $\pm$ 0.022
P11	1.33 $\pm$ 0.05	75.5 $\pm$ 2.7	6.6 $\pm$ 0.9	3.7 $\pm$ 0.4	0.84 $\pm$ 0.11	0.13 $\pm$ 0.021	0.058 $\pm$ 0.010
5-10 cm							
F99	1.47 $\pm$ 0.04	71.3 $\pm$ 3.0	9.4 $\pm$ 1.2	4.4 $\pm$ 1.0	0.73 $\pm$ 0.04	0.07 $\pm$ 0.001	0.020 $\pm$ 0.008
P87	1.48 $\pm$ 0.03	69.7 $\pm$ 2.9	9.5 $\pm$ 1.1	5.7 $\pm$ 0.6	0.70 $\pm$ 0.06	0.07 $\pm$ 0.003	0.026 $\pm$ 0.011
P83	1.59 $\pm$ 0.05	64.7 $\pm$ 1.5	10.6 $\pm$ 0.3	6.6 $\pm$ 0.8	0.93 $\pm$ 0.04	0.08 $\pm$ 0.003	0.016 $\pm$ 0.007
P72	1.44 $\pm$ 0.03	75.3 $\pm$ 4.7	7.7 $\pm$ 2.1	4.1 $\pm$ 0.6	0.58 $\pm$ 0.10	0.07 $\pm$ 0.01	0.048 $\pm$ 0.022
P11	1.45 $\pm$ 0.05	77.2 $\pm$ 1.4	6.3 $\pm$ 0.4	3.8 $\pm$ 0.4	0.81 $\pm$ 0.10	0.11 $\pm$ 0.01	0.048 $\pm$ 0.010
10-20 cm							
F99	1.53 $\pm$ 0.01	68.0 $\pm$ 3.1	10.9 $\pm$ 0.9	4.7 $\pm$ 1.0	0.78 $\pm$ 0.04	0.07 $\pm$ 0.002	0.020 $\pm$ 0.008
P87	1.44 $\pm$ 0.02	60.9 $\pm$ 4.8	13.3 $\pm$ 2.4	6.2 $\pm$ 0.7	0.80 $\pm$ 0.08	0.07 $\pm$ 0.004	0.026 $\pm$ 0.011
P83	1.57 $\pm$ 0.04	60.3 $\pm$ 1.0	12.6 $\pm$ 0.8	6.9 $\pm$ 0.7	0.98 $\pm$ 0.05	0.08 $\pm$ 0.01	0.018 $\pm$ 0.006
P72	1.45 $\pm$ 0.13	67.6 $\pm$ 3.8	10.6 $\pm$ 2.0	4.6 $\pm$ 0.4	0.65 $\pm$ 0.05	0.07 $\pm$ 0.004	0.038 $\pm$ 0.013
P11	1.55 $\pm$ 0.01	74.0 $\pm$ 2.9	7.5 $\pm$ 0.9	3.9 $\pm$ 0.5	0.84 $\pm$ 0.11	0.10 $\pm$ 0.01	0.048 $\pm$ 0.014
	MgO (%)	CaO (%)	MnO (%)	Na <sub>2</sub> O (%)	C (%)	N (%)	S (%)
0-5 cm							
F99	0.11 $\pm$ 0.01	<0.001	0.04 $\pm$ 0.003	<0.004	1.08 $\pm$ 0.14	0.10 $\pm$ 0.01	0.009 $\pm$ 0.002
P87	0.13 $\pm$ 0.01	0.11 $\pm$ 0.01	0.06 $\pm$ 0.012	<0.004	2.82 $\pm$ 0.58	0.20 $\pm$ 0.03	0.024 $\pm$ 0.002
P83	0.12 $\pm$ 0.00	0.10 $\pm$ 0.01	0.07 $\pm$ 0.018	<0.004	1.81 $\pm$ 0.23	0.14 $\pm$ 0.02	0.015 $\pm$ 0.002
P72	0.11 $\pm$ 0.01	0.04 $\pm$ 0.01	0.05 $\pm$ 0.001	<0.004	2.28 $\pm$ 0.25	0.17 $\pm$ 0.01	0.016 $\pm$ 0.001
P11	0.18 $\pm$ 0.03	0.17 $\pm$ 0.06	0.07 $\pm$ 0.005	<0.004	2.48 $\pm$ 0.37	0.20 $\pm$ 0.04	0.022 $\pm$ 0.003
5-10 cm							
F99	0.10 $\pm$ 0.004	<0.001	0.04 $\pm$ 0.002	<0.004	0.87 $\pm$ 0.08	0.08 $\pm$ 0.01	0.009 $\pm$ 0.001
P87	0.11 $\pm$ 0.004	0.05 $\pm$ 0.01	0.05 $\pm$ 0.01	<0.004	1.35 $\pm$ 0.15	0.12 $\pm$ 0.01	0.012 $\pm$ 0.002
P83	0.10 $\pm$ 0.00	0.04 $\pm$ 0.01	0.06 $\pm$ 0.02	<0.004	1.09 $\pm$ 0.14	0.10 $\pm$ 0.01	0.008 $\pm$ 0.001
P72	0.11 $\pm$ 0.01	0.02 $\pm$ 0.01	0.05 $\pm$ 0.00	<0.004	1.29 $\pm$ 0.22	0.11 $\pm$ 0.01	0.011 $\pm$ 0.003
P11	0.13 $\pm$ 0.01	0.09 $\pm$ 0.02	0.07 $\pm$ 0.01	<0.004	1.65 $\pm$ 0.13	0.15 $\pm$ 0.02	0.017 $\pm$ 0.002
10-20 cm							
F99	0.10 $\pm$ 0.005	<0.001	0.04 $\pm$ 0.002	<0.004	0.68 $\pm$ 0.07	0.07 $\pm$ 0.01	0.008 $\pm$ 0.002
P87	0.10 $\pm$ 0.007	0.04 $\pm$ 0.01	0.05 $\pm$ 0.011	<0.004	0.93 $\pm$ 0.18	0.09 $\pm$ 0.01	0.009 $\pm$ 0.001
P83	0.10 $\pm$ 0.005	0.04 $\pm$ 0.01	0.06 $\pm$ 0.016	<0.004	0.82 $\pm$ 0.11	0.08 $\pm$ 0.01	0.007 $\pm$ 0.001
P72	0.10 $\pm$ 0.006	0.02 $\pm$ 0.01	0.05 $\pm$ 0.006	<0.004	0.79 $\pm$ 0.20	0.07 $\pm$ 0.01	0.006 $\pm$ 0.002
P11	0.13 $\pm$ 0.009	0.08 $\pm$ 0.02	0.07 $\pm$ 0.008	<0.004	1.19 $\pm$ 0.14	0.10 $\pm$ 0.01	0.010 $\pm$ 0.000

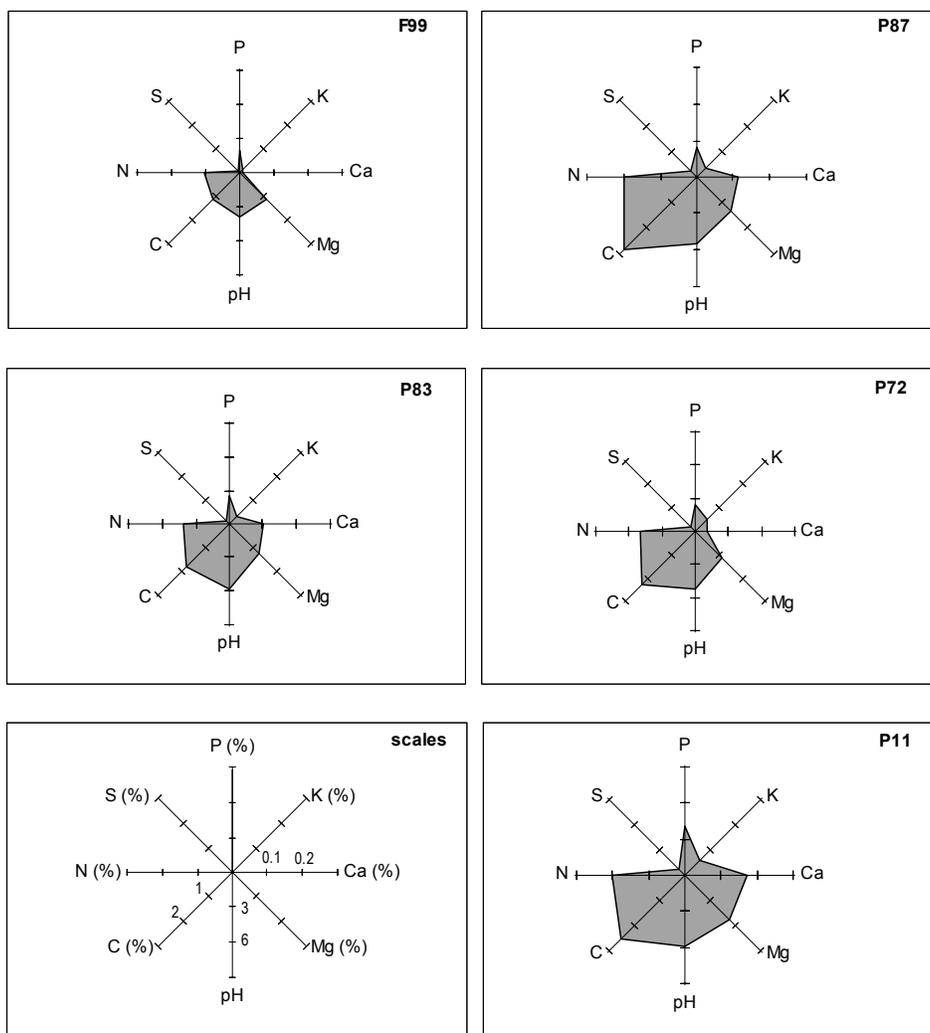
### Major elements in soils

The total contents of major elements in the soils (depths: 0-5 cm, 5-10 cm and 10-20 cm) are given in Table 3. Soils at all sites are mainly dominated by Si, Al and Fe with expected high Si contents.

For other major elements (e.g. essential elements like C, N and Ca), the lowest contents were found at the forest site in all layers. Ca could not be determined by the technique used at the forest site (detection limit 0.001%). Na was not detectable in the whole chronosequence (detection limit 0.004%).

Due to frequently small differences as well as partly high variabilities, the majority of the elements showed no clear differences from the top to the deeper layers (except for some macro elements such as Ca, C, N, S). At the forest site these elements displayed less differences between the layers compared to the pastures.

After an initial increase in P87 following forest burning (e.g. C, N, P, K, Mg, Ca, Mn and S) particularly in the top layer (0-5 cm) diminished values (distinctly for C, N and S) were measured in P83 (Table 3). Especially for C, N and S again ascending values could be found in P72 compared to P83. In contrast Ca showed a clear decrease in



**Fig. 2.** Comparison of main nutrients (total contents) and pH in a depth of 0-5 cm at the forest reference site and the pasture sequence at Fazenda Nova Vida. The axis for Ca represents the scale for all elements without inscription.

P72. P11 was more abundant in nutritional elements and exhibited the maximal values for P, K, Mg and Ca.

In order to illustrate the state of main nutrient pools for the top layer (0-5 cm) the element contents as well as the pH values were grouped in form of "nutrigrams" (Fig. 2). According to this illustration the forest site (F99) showed the lowest pools in relation to the pastures. In the chronosequence the highest values for C, N, S, P, K, Ca, Mg and pH with comparable distribution patterns were found in P87 and P11. The appearance of P83 and P72 revealed an intermediate place, whereas P72 showed a divergent image on the Ca-axis, in particular.

The total element inventories for macro nutrients are given in Table 4. The data were calculated by multiplying the element concentrations ( $\text{g } 1000 \text{ g}^{-1}$ ) with the mean soil bulk density ( $\text{g cm}^{-3}$ ) and the respective soil layers (cm). Subsequently the values were added.

The element stocks in the pastures, frequently with lower values in P72 (except C and K) showed generally higher stocks than the forest. The highest stocks of macro-nutrients for the entire soil profile (0-20) were found in pasture 11. The highest Al-, Fe and Ti-stocks were calculated for P83.

#### *Minor elements in soils*

In Table 5 the contents of minor elements in the individual layers are shown. In many cases the

element contents exhibited partly high variabilities. In these cases the difference in the distribution have to be considered as tendencies. At P87 for almost all elements higher values (except Co) could be determined in the first layer (0-5 cm) compared to the forest (F99). In P83 a further increase of the contents for all considered minor elements (except Ni and Rb) compared to P87 were found. The micro-nutrients Mo, Zn, Cu and Co gave different distribution patterns. Mo showed continuously higher contents from F99 to P72 where the highest values in all layers were measured. In P11 distinct less Mo concentrations were found. In contrast, the lowest values for Zn, Cu and Co were determined in P72 whereas the highest contents were measured in P11. In the forest and in P72 the Cu-contents were under the detection limit (detection limit:  $2.7 \mu\text{g g}^{-1}$ ).

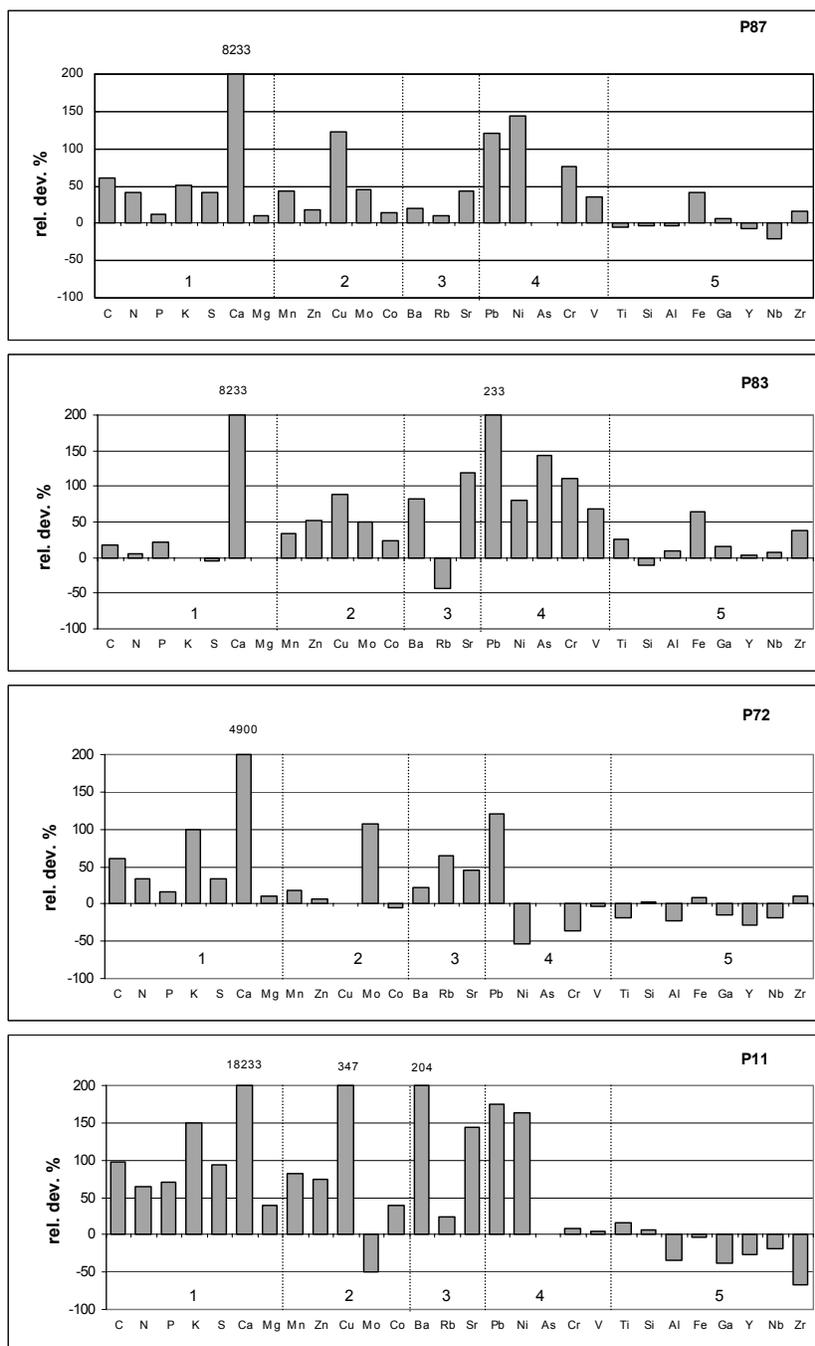
Potentially toxic elements such as As, Pb, Cr, or V were mainly enriched in P83. Ni showed the highest concentrations in P87 and P11. In the forest the Pb contents as well as the Ni-contents in P72 were under the detection limit (detection limit:  $\text{Ni}=2.3 \mu\text{g g}^{-1}$  and  $\text{Pb}=2.8 \mu\text{g g}^{-1}$ ). Arsenic (detection limit  $1 \mu\text{g g}^{-1}$ ) could only be detected in P83. In general, frequently the forest site and P72 were characterized by lower levels of these elements. Elements such as Y, Ga, Nb and Zr showed tendencies to higher values with the depth in the entire forest to pasture sequence and suggest a mineralogical background. Zr showed conspicuous low levels in all layers in P11.

**Table 4.** Total element inventory of major elements ( $\text{kg m}^{-2}$ ) in the soil (0-20 cm) of the forest and different aged pastures sites.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	
	(kg m <sup>-2</sup> )						
F99	205 ± 11.8	27.7 ± 3.0	12.9 ± 3.1	0.12 ± 0.01	0.29 ± 0.02	<0.0017	
P87	188 ± 12.9	31.5 ± 5.02	16.5 ± 2.0	0.15 ± 0.03	0.31 ± 0.03	0.17 ± 0.03	
P83	201 ± 10.5	34.6 ± 3.1	20.8 ± 3.1	0.20 ± 0.06	0.33 ± 0.02	0.17 ± 0.04	
P72	201 ± 25.8	25.8 ± 7.6	12.2 ± 2.3	0.14 ± 0.02	0.30 ± 0.04	0.07 ± 0.03	
P11	221 ± 11.9	20.6 ± 2.7	11.3 ± 1.6	0.21 ± 0.03	0.42 ± 0.05	0.30 ± 0.09	
	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	Na <sub>2</sub> O	C	N	S
	(kg m <sup>-2</sup> )						
F99	0.05 ± 0.02	0.20 ± 0.01	2.1 ± 0.2	<0.0075	2.3 ± 0.3	0.23 ± 0.02	0.024 ± 0.01
P87	0.08 ± 0.03	0.21 ± 0.02	2.1 ± 0.2	<0.0075	4.2 ± 0.8	0.35 ± 0.05	0.034 ± 0.005
P83	0.06 ± 0.02	0.25 ± 0.03	2.9 ± 0.2	<0.0075	3.6 ± 0.6	0.31 ± 0.05	0.029 ± 0.005
P72	0.12 ± 0.05	0.20 ± 0.02	1.7 ± 0.3	<0.0075	3.6 ± 0.9	0.29 ± 0.05	0.027 ± 0.008
P11	0.15 ± 0.04	0.32 ± 0.04	2.5 ± 0.4	<0.0075	4.7 ± 0.7	0.39 ± 0.06	0.042 ± 0.005

**Table 5.** Total element contents ( $\mu\text{g g}^{-1}$ ) and standard deviation (n=5) of minor elements in soil samples.

	Co	Zn	Mo	Cu	Cr	Ni	V	As
	( $\mu\text{g g}^{-1}$ )							
0-5 cm								
F99	5.9 ± 1.2	15.4 ± 1.2	2.0 ± 0.4	- -	43.6 ± 13.4	4.5 ± 0.5	47.1 ± 6.8	- -
P87	5.7 ± 1.2	18.9 ± 1.7	2.5 ± 0.4	5.0 ± 2.9	60.1 ± 6.0	7.8 ± 1.1	59.2 ± 4.3	- -
P83	6.7 ± 0.4	23.6 ± 3.0	2.8 ± 0.3	5.7 ± 3.0	78.4 ± 14.3	5.6 ± 1.7	73.7 ± 6.5	1.4 ± 0.2
P72	4.6 ± 0.6	16.7 ± 1.2	4.1 ± 0.1	- -	28.3 ± 9.5	- -	44.0 ± 7.8	- -
P11	6.8 ± 0.6	27.8 ± 2.1	1.2 ± 0.3	7.4 ± 2.3	36.6 ± 3.4	7.8 ± 1.4	47.8 ± 2.5	- -
5-10 cm								
F99	4.5 ± 0.7	15.7 ± 1.6	2.4 ± 0.7	- -	44.2 ± 13.4	3.3 ± 0.7	51.5 ± 9.3	- -
P87	6.3 ± 1.5	17.4 ± 1.0	3.3 ± 0.4	5.1 ± 2.8	67.9 ± 6.5	7.8 ± 1.1	64.6 ± 6.8	- -
P83	5.5 ± 1.3	23.5 ± 1.8	3.2 ± 0.4	5.7 ± 3.1	76.9 ± 12.3	5.8 ± 1.3	80.0 ± 6.5	1.7 ± 0.3
P72	4.6 ± 1.5	16.4 ± 1.6	4.2 ± 0.4	- -	27.7 ± 10.6	3.3 ± 0.3	45.3 ± 6.9	- -
P11	6.5 ± 1.6	26.1 ± 1.4	1.2 ± 0.4	8.2 ± 1.5	41.0 ± 4.8	8.4 ± 1.7	49.6 ± 4.3	- -
10-20 cm								
F99	4.8 ± 0.8	16.1 ± 1.4	2.8 ± 0.1	- -	40.5 ± 11.4	3.2 ± 0.8	52.3 ± 9.1	- -
P87	5.1 ± 2.0	18.2 ± 1.6	2.7 ± 0.7	5.3 ± 1.9	65.7 ± 9.5	7.7 ± 0.8	67.4 ± 7.7	- -
P83	5.1 ± 1.0	23.1 ± 1.8	3.1 ± 0.6	4.5 ± 2.6	74.1 ± 16.4	5.4 ± 1.2	81.4 ± 4.8	2.2 ± 0.5
P72	4.1 ± 0.8	15.8 ± 0.7	4.0 ± 0.5	- -	29.6 ± 8.7	- -	48.2 ± 4.2	- -
P11	7.5 ± 1.1	25.2 ± 1.5	1.1 ± 0.2	7.6 ± 1.5	40.9 ± 2.4	8.3 ± 2.1	49.8 ± 5.0	- -
	Pb	Rb	Ba	Sr	Y	Ga	Nb	Zr
	( $\mu\text{g g}^{-1}$ )							
0-5 cm								
F99	- -	4.2 ± 0.8	15.6 ± 4.5	6.7 ± 1.6	20.9 ± 3.6	9.3 ± 1.2	20.3 ± 1.6	197 ± 82
P87	3.5 ± 0.5	5.7 ± 1.4	22.3 ± 8.6	12.4 ± 2.1	21.6 ± 3.5	11.0 ± 0.4	16.5 ± 1.3	337 ± 42
P83	6.8 ± 1.7	4.0 ± 1.3	33.8 ± 10.5	16.4 ± 5.2	23.4 ± 4.3	11.4 ± 1.5	22.5 ± 2.3	389 ± 89
P72	4.0 ± 0.7	8.7 ± 1.5	22.3 ± 12.7	9.2 ± 1.2	17.6 ± 4.7	9.9 ± 2.8	17.2 ± 1.5	404 ± 176
P11	4.9 ± 1.2	7.1 ± 1.8	45.3 ± 13.8	14.6 ± 2.9	20.4 ± 2.5	7.2 ± 0.9	17.6 ± 1.9	137 ± 59
5-10 cm								
F99	- -	5.6 ± 1.3	16.4 ± 4.7	5.9 ± 0.8	30.5 ± 9.0	12.0 ± 1.2	21.8 ± 1.8	415 ± 79
P87	4.9 ± 1.3	5.6 ± 2.0	19.7 ± 7.4	7.9 ± 1.2	24.7 ± 4.8	12.8 ± 1.2	17.7 ± 1.8	453 ± 114
P83	7.8 ± 2.9	4.1 ± 0.7	31.3 ± 7.6	13.8 ± 5.9	27.3 ± 2.8	13.8 ± 0.8	23.7 ± 1.2	543 ± 43
P72	4.2 ± 0.7	8.0 ± 3.0	25.2 ± 13.9	8.4 ± 0.8	18.0 ± 5.7	10.6 ± 2.9	17.9 ± 1.7	415 ± 186
P11	5.2 ± 0.9	6.1 ± 1.8	45.8 ± 7.8	13.1 ± 1.9	19.2 ± 2.8	7.4 ± 0.9	17.4 ± 1.0	113 ± 25
10-20 cm								
F99	- -	6.7 ± 1.7	15.4 ± 2.7	6.0 ± 0.8	33.7 ± 7.7	13.5 ± 1.0	22.3 ± 1.2	521 ± 76
P87	5.1 ± 1.8	7.2 ± 2.2	15.7 ± 4.8	6.4 ± 1.5	31.9 ± 6.2	15.9 ± 2.4	18.7 ± 1.5	668 ± 166
P83	8.3 ± 3.3	4.5 ± 1.8	31.1 ± 6.0	13.2 ± 5.5	33.4 ± 5.6	15.8 ± 0.5	24.3 ± 1.0	658 ± 23
P72	5.2 ± 1.0	7.4 ± 1.5	15.7 ± 7.1	7.1 ± 1.1	23.6 ± 4.4	13.4 ± 2.1	18.6 ± 1.0	680 ± 132
P11	4.9 ± 1.2	6.0 ± 2.4	40.3 ± 9.1	12.3 ± 2.0	24.4 ± 7.1	8.1 ± 0.6	18.1 ± 1.2	191 ± 74



**Fig. 3.** Fingerprint graphs of pastures soils by standardizing the values of the “reference soil site” in the forest and by graphically displaying positive and negative deviations of the pasture values from the forest values.

### *Fingerprints*

In order to compare the mean element contents in the pasture soils in relation to the forest

soil, in Fig. 3 chemical “fingerprint” graphs are shown. Concerning the objective to show element alterations after forest clearing and pasture instal-

lation the element contents at the forest site were defined as "reference points". The fingerprint graphs were generated by standardizing the values of the forest site and by graphically displaying positive and negative percentage deviations of the element values in pastures from the "reference" values in the forest. One advantage of this presentation is the possibility to portray element patterns within the soils despite different magnitudes of element concentrations. Likewise, by standardization to the "reference points" in the forest, not only extremely high concentrations are considered, but also minimal values of individual elements to the same degree (Breulmann *et al.* 1997; Markert 1996). Such comparisons plainly indicate not only an enrichments of elements but a reduction in these as well. Another useful aspect is the collective comparison of different element characteristics (nutritional, toxicological, pedological) in one image. The comparison was based on the medians of the elements contents for the depth 0-20 cm.

The fingerprints were defined in areas with priority known macro-nutrients (1), micro nutrients (2) intermediate elements (3), toxic elements (4) and mineralogical elements (5). It has to be emphasized that this functional grouping of elements is not exclusive, because many elements fit into two categories (e.g. Cr, V, Zn, Cu, Mn, Fe or Mo).

For the majority of elements all pastures showed partly high positive deviations compared to the forest site, particularly for Ca, Cu, Pb and Ba. Exceptions of this general pattern constituted the group of known soil elements (e.g. Ti, Si, Al, Fe, Ga, Y, Nb, Zr). Mainly, these elements showed comparable values like the forest (except for Fe) but negative deviations as well. Compared to the oldest pastures (P72, P11) the forest site exhibited mainly higher values. However, the distribution patterns of these elements in section (5) showed generally less distinctions than the other classified areas (1 - 4). Concerning the macro nutrients, P83 showed the lowest values up to equal medians (Mg, K) compared to the forest (except Ca). Conversely, the deviation pattern exhibited relatively high enrichments for a considerable amount of other elements, as already mentioned (e.g. toxic elements like Pb, As, Cr, V). The lowest as well as negative deviations for these elements were calculated in P72 (except Pb). Solely the micro-nutrient Mo showed the highest positive deviation within the entire consideration. Other micro-nutrients

(e.g. Zn, Cu, Mn, Co) were here irrelevant higher than the values of the forest (F99). Distinct element enrichments (nutrients and toxic elements as well) indicated by very high positive deviations were detected in P11. Particularly for Ca, Cu and Ba and substantially for C, K, Sr, Pb and Ni, positive deviations of around 100% and more were calculated. Molybdenum showed a considerable depletion in P11.

Generally, despite similar initial conditions after forest clearing the aging pastures (in particular P87, P83 and P72) reflected divergent element patterns, that indicate different time and site dependent influences.

#### *Interelement correlations*

Because of a lack of a complete mineralogical survey of the area the elements will be considered at first from the point of view of the Periodic Table in order to reveal general interactions between the elements and to get more insight about the element behaviour in a tropical soil (Ultisol). For this approach, the element concentrations of all locations and all layers were summarized in one set. The correlation matrix of the elements is given in Table 6. To get a more orderly overview of the results, only significant correlations ( $p=0.05$ ) with correlation coefficients  $> r = 0.5$  were considered. Moreover, the order of elements in the matrix were classified according to their main function in macro - and micro nutrients, intermediate elements as well as toxic elements and more pedogenic elements.

Two central areas in the matrix are recognizable. An agglomeration of high correlation coefficients in the so-called "nutrition sector" (C, N, P, K, S, Ca, Mg, Mn, Zn, Cu, Mo, Co) at the top of the matrix as well as in the "mineralogic sector". (Ti, Si, Al, Fe, Ga, Y, Nb, Zr) on the other side at the bottom of the matrix could be found. Regarding the nutritional elements the results reflected good relations between such elements which have important functions in living plants and suggest a main contribution of soil organic matter. Intermediate elements like Ba, Rb or Sr showed significant correlations with some macro- and minor elements (P, Mg, Ca, Mn, Zn), that could refer to chemical similarities (ionic radii, charge state), for example  $Ca^{2+}$  and  $Ba^{2+}$ ,  $Sr^{2+}$  or  $K^+$  and  $Rb^+$ . In general no positive correlations with main soil elements existed. On the other hand, some nutrients (e.g. Mg, S, K, N)



showed significant negative correlations with some soil elements (e.g. Ga, Nb, Zr, Fe, Al) and indicated a function of the soil depths due to mainly higher contents of mineralogical elements in the deeper layers compared to lower nutrient contents. Infrequent relationships between certain element pairs (e.g. Ni/Cu or V/Pb) may depend either on natural or anthropogenic causes. In the “mineralogic sector” mainly positive correlations between the elements predominated. Only silicon showed entirely high negative correlations and refer to weathering processes.

While the correlation matrix of the summarized elements of all locations are suitable to show specific element interactions, the correlation coefficients between elements at the individual sites could be useful as a tool to identify biogeochemical alterations in the forest to pasture or in the pasture to pasture sequence. In order to present this method of approach, as an example in Table 7 selected relations between major elements are shown. While there was no relationship between the macro-nutrients C and S as well as N and S in the forest, there were significant positive correlations in the pastures. Conversely, at all sites high degree correlations were detected for C and N. Considerable differences between forest and the pasture sites were found for C/P and N/P. In contrast to negative correlations in the forest, solely positive coefficients have been calculated for all pastures sites. Something different relations showed P83. In general, the differences or the time dependent shifting of element correlations could give a first indication of changes in chemical soil processes after land use change.

#### *Geochemical element-pairs*

The ratios of important geochemical element-pairs at the individual sites could be useful as a tool to identify natural soil conditions. In Table 8

**Table 7.** Correlation coefficients of selected element pairs at the forest site (F99) and the different pasture sites.

Sites	C/N	C/S	N/S	C/P	N/P
F99	0.965	0.026	0.142	-0.532	-0.595
P87	0.950	0.918	0.926	0.842	0.819
P83	0.980	0.933	0.927	0.361	0.443
P72	0.985	0.932	0.947	0.742	0.714
P11	0.973	0.934	0.920	0.734	0.711

selected element pairs, which are characteristic for the 10-20 cm layer at the individual sites are shown.

Considerable differences between forest and the pasture sites were found for P11. Generally, P11 showed the highest ratios for the element pairs compared to the other sites. The ratios Al/Ga, Ba/Sr, Nb/Zr at the forest and the other pastures revealed similar magnitudes. On the other hand, for the proportion of K/Rb, and especially for Ca/Sr, less ratios were found at the forest site. In general, based on this analysis the differences in the ratios indicates divergent natural soil conditions (e.g. P11) or changes in chemical soil processes after land use change (e.g. P87).

## Discussion

Because of the considerable significance of the soil as element reservoir as well as source within ecosystem biogeochemistry the aim of the present study is to provide an initial overview about the state of affairs of elements in the studied forest and pasture soils by using multi-element analysis in order to draw up a more detailed chemical soil characterisation. At first this study provided the total contents of a number of elements, which could be obtained by the used technique. However, as important as the total content of the elements are, their chemical forms determine their fate and bioavailability. But nevertheless, general statements about chemical changes, especially for nutritional or toxicological elements, can be suggested after land use alteration using the mentioned element fraction. Because of the proximity of the sites (5 km) we can expect the same climate conditions and similar soil types (except P11), which differ only with regard to the material input/ output over time.

**Table 8.** Selected ratios of important geochemical element-pairs at the forest reference site in 1999 (F99) and the pasture sequence at Fazenda Nova Vida.

Sites	Al/Ga	K/Rb	Ba/Sr	Ca/Sr	Nb/Zr
F99	8074	29.8	2.56	< 1.6	0.042
P87	8364	36.1	2.45	62.5	0.028
P83	7974	40.0	2.35	30.3	0.036
P72	7910	51.4	2.21	28.1	0.027
P11	9259	80	3.27	65	0.094

The initial high element contents twelve years after forest clearing in P87 confirms the transfer of former fixed elements to the soil by burning of natural vegetation (Kato *et al.* 1999). Fernandes *et al.* (1997) calculated nutritional element contents of ash of a primary forest site on oxisol at Manaus as follows: N= 80 kg ha<sup>-1</sup>, Ca= 82 kg ha<sup>-1</sup>, Mg= 22 kg ha<sup>-1</sup>, K= 19 kg ha<sup>-1</sup>, P= 6 kg ha<sup>-1</sup>, Zn= 0.2 kg ha<sup>-1</sup>, Cu= 0.2 kg ha<sup>-1</sup>, Fe= 58 kg ha<sup>-1</sup>, Mn= 2.3 kg ha<sup>-1</sup>. Therefore, also the significant increase of pH values from forest to pasture 87 (Table 2) is attributed to the release of basic acting elements (Ca, Mg, K) by ash deposition. More specifically, after an initial increase in the first 5 years after forest burning (pH 7.6 in pasture 1987 sampled in 1992), the decrease in the next 7 years (pH 5.5 in the same pasture sampled in 1999) indicate persistent leaching of these elements as a consequence of high rainfall intensities in the wet season accompanied by high drainage in the present soils (sandy clay, sandy clay loam). However, the less pH differences in P72, P83 and P11 in both investigations suggest that inputs and outputs of basic cations are nearly balanced. The amount of movement in Ca seems to play the decisive role in this context. Generally, the pH values still remained higher than the forest values for decades. The high Ca contents, and in a minor extent for many other elements in the pastures imply a depletion of the elements in the forest and indicate a characteristic feature found in acid forests due to natural decalcification, leaching processes and constantly recycling of elements (immediate uptake) by vegetation leading to element enrichments in living biomass. Also the less pH in 1999 in the forest compared to 1992 supports this assumption.

In P83, the decrease of macro nutrients (e.g. C, N, K, Mg, S) on levels comparable to the forest ranges (except Ca), as well as the enhanced levels in P72 and P11 suggest both a continuous leaching of these elements and a function of pasture age where external element inputs exceed outputs.

Animal excreta can contribute to the higher element contents in the pasture soils compared to the forest. Especially the high amounts of C, N, S, P compared to the forest values and ascending contents since 1983 as well as the highest element contents of P, S, N, K, Mg and Ca in P11 support this fact. Beneficial effects of animal manure on element levels are well known. Tsakelidou *et al.* (1999) reported increases of pH by cat-

tle manure due to high contents of CaCO<sub>3</sub>. Kennedy & Siebert (1975) showed the quantity of sulfur consumed, recycled and excreted by cattle. For faecal and urinary they calculated an excretion of 2380 mg day<sup>-1</sup>, compared to an input of 1790 mg day<sup>-1</sup>. On grazed pastures Mathews *et al.* (1994) found accumulations of N, P, K in soils (0-15 cm) close to shade, water sources and supplement feeders. West *et al.* (1989) identified enhanced element zones near to water sources caused by a net transfer of elements by grazing animals via excreta over five grazing years and postulate an increase of these zones over the main body of the pasture over time. Mc Naughton *et al.* (1997) provided evidence that free-ranging mammalian grazers accelerate nutrient cycles in a natural ecosystem in a way that enhances their own carrying capacity. The chemical composition of excreta can be extended by supplemental feed (common management practice in the investigated area using concentrated by-products). However, the high leaching behaviour of tropical soils can lead to impacts on groundwater aquifers.

The quantity of organic matter reflects another factor contributing to element differences in the forest and the pasture soils. Pagel (1975) reported a linear relationship between C-content and cation exchange capacity (CEC), that represents the total of all cations adsorbed. For instance, the mean increase of 0.88% C in F99 to 1.36% C in P72 means an increase of 1.5% to 2.3% organic matter (C (%) x 1.72). This factor was established to provide an indication of the total amounts of organic matter presents (FitzPatrick 1983) and indicate an increase of the CEC related to organic matter. Schroeder (1984) reported a CEC of organic matter of 150-300 me 100 g<sup>-1</sup>. As shown in the fingerprints in P72 and particularly in P11 the high positive deviations of the C-contents linked with higher amounts of the main part of macro nutrients is obvious and suggest element enrichments associated with organic matter in these pastures compared to the forest site. However, despite higher contents of organic matter as mentioned above, particularly Ca showed a decrease in P72, but remained higher than the forest level. That result seems to be peculiar, because moreover a superficial liming was carried out in December 1998 (pers. comm. farm manager). Probably leaching or erosion effects accounted for the unexpected less contents.

Furthermore, mineral components can cause element differences at the sites. At P83, for instance, high positive deviations for many minor elements associated with less organic matter content similar to the forest were found. The Al- and Fe deviations suggest a higher presence of sesquioxides (hydrous-oxides). Fendorf *et al.* (1994) reported that metal cations and anions tend to form inner-sphere surface complexes with hydrous oxides (e.g.  $\text{Pb}^{2+}$  or  $\text{AsO}_4^{3-}$ ) and are more strongly retained by soil.

The highest deviations (positive and negative) compared to the forest but also in comparison to the other pastures frequently occurred in P11. Concerning the homogeneity over the sampling area, e.g. the soil texture refer to more sandy conditions in P11. Despite variations there is a general correlation between texture and mineral content due to the relations between mineral composition and particle size. Sands contain mainly primary minerals (quartz, silicates) and clays mainly secondary minerals (clay minerals such as kaolinite) (Schroeder 1984). According to Moraes *et al.* (1996) the clay minerals in the forest and in P87, P83 and P72 mainly consist of kaolinite associated with very low cation exchange capacity (CEC), (e.g. kaolinite:  $\text{CEC} = 30\text{-}150 \text{ mmol}_c \text{ kg}^{-1}$ ) (Schroeder 1984). In P11 aluminosilicates such as micas and feldspars with naturally higher contents of K, Ca or Mg occur and indicate divergent natural soil conditions (e.g. weathering degree) as well as different exchange capacities (e.g. mica:  $\text{CEC} = 100\text{-}400 \text{ mmol}_c \text{ kg}^{-1}$ ) (Schroeder 1984). Moraes *et al.* (1996) found higher initial cation stocks (Ca, Mg, K) in the red yellow podzolic soil at the original forest close to P11, compared to the original forest site over red yellow podzolic latosol close to P87, P83, P72. On the other hand, the initial carbon and nitrogen contents at both forest sites showed here comparable values.

Because mineral components (low inherent CEC) and organic matter (high CEC as mentioned above) represent the main cation exchange opportunities as well as the element store in soils, organic matter probably seems to be the decisive part in the exchange of elements at the sites and, beside the mineralogical conditions, responsible for the element differences in the forest and the pastures.

The highest negative deviations in the fingerprints particularly for Zr may also refer to the dif-

ferent mineralogical conditions at P11. Zircon ( $\text{ZrSiO}_4$ ), a stable and resistant mineral against weathering, is taken frequently as an index mineral for the determination of the weathering degree (Scheffer & Schachtschabel 1992). Generally, highly weathered soils contain less unstable minerals and more minerals stable to weathering (Schroeder 1984). The data indicate that the mineral zircon ( $\text{ZrSiO}_4$ ) seems to be absent in P11 compared to the forest and the other pasture sites and suggest different weathering stages. Also other anomalies such as the depletion of Mo can be attributed to the mineral composition. These results suggest no constant bedrock/soil conditions. The ratios of geochemical element-pairs at the individual sites indicate this aspect as well (Table 8). Generally, P11 showed the highest ratios for the element pairs compared to the other sites. The partly different ratios in the forest (e.g. Ca/Sr, Nb/Zr) and the other pastures as well indicate moreover small scale variabilities in the sequence.

Beside of nutritional and mineralogical aspects from the ecotoxicological point of view the contents of toxic elements in the soils of the investigated area seem to be less although some papers have proved, that also toxic elements are being deposited after forest burning in considerable scales (Artaxo *et al.* 2000; Lacerda & Marins 1997). The present study showed only less increases after forest burning. Generally, by considering element ranges of unpolluted soils for example Pb ( $2\text{-}60 \mu\text{g g}^{-1}$ ), Zn ( $10\text{-}80 \mu\text{g g}^{-1}$ ), Cu ( $2\text{-}40 \mu\text{g g}^{-1}$ ), Ni ( $5\text{-}50 \mu\text{g g}^{-1}$ ), As ( $1\text{-}15 \mu\text{g g}^{-1}$ ) (Scheffer & Schachtschabel 1992) the ranges of the calculated element means in the pastures showed clearly less concentrations (Pb =  $3.5 - 8.3 \mu\text{g g}^{-1}$ , Zn =  $16.7 - 27.8 \mu\text{g g}^{-1}$ , Cu =  $<2.7 - 8.2 \mu\text{g g}^{-1}$ , Ni =  $<2.3 - 8.4 \mu\text{g g}^{-1}$ , As  $<1 - 1.4 \mu\text{g g}^{-1}$ ) On the other hand, the high leaching behaviour of tropical soils can result in a draining of deposited elements followed by possible impacts of contaminants on groundwater aquifers.

In general, the results for the elements, particularly for a number of minor elements, frequently showed no clear or uniform pathways as well as high variability. Logan (2000) gave to consider that the minor element content of surface soil can vary naturally by several orders of magnitude. More specifically, the individual element behaviour concerning mobilization, immobilization or precipitation is influenced by a number of parameters, e.g. the actual binding affinity, the chemical

nature (speciation), redox potential, element interactions, moisture conditions, soil clay mineralogy, and soil acidity (Adriano 1986). Additionally, the variability in the element results could be enlarged by heterogeneities laterally across a landscape as well as vertically within the soil profile (Buol *et al.* 1989). Also Fernandes *et al.* (1997) emphasise that upland soils in the Amazon can be highly variable. This variability extends from the soil order to short range variability occurring within a distance of a few meters. According to West *et al.* (1989) soil element studies in pastures are complicated due to variability in native chemical and physical soil characteristics, fertilizer applications, and the distribution of animal excreta. Veldkamp (1994) reported about high heterogeneities of element data mainly under pastures that accentuate a solid investigation also on small scale level.

Also the present comparison between forest and pastures based on their chemical compositions is influenced by the complexity of these factors.

## Conclusions

Within ecosystem biogeochemistry one focal point represents the broad field of biogeochemical consequences after land use change. Until now no research concepts existed that e.g. attempted to quantitatively characterize a larger set of elements that concern the transition from forest to pasture land. As a complementary contribution to multidisciplinary research approaches in the area of investigation, the present study was conducted to provide a first overview about soil chemicals and properties. The results showed for the vast majority of macro- and micro and other elements as well higher contents in the pastures when compared to the initial forest values.

Furthermore, element differences occurring in the different old pastures are time and site dependent. Ash deposition, organic matter content, animal excreta, texture, erosion, percolation, mineralogy all contribute to differences in soil chemicals and properties and influence the high variability of the soils, which is a common feature in the Amazon. The rapid increase in the amount of pastures in the Amazon underlines a reliable determination and evaluation of the effects of forest conversion and pasture installation on soil chemicals. The present study can be considered as a first approach to evaluate this type land use change on

basis of such a large scale of chemical elements. In general, development of new knowledge through modern multi-element research represents an essential step to understand the dynamics and characteristics of chemical elements for a forward-looking land use in a tropical system.

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## References

- Adriano, D.C. 1986. *Trace Elements in the Terrestrial Environment*. Springer Verlag, New York.
- Andreaux, F. & C.C. Cerri. 1989. Current trends in the research on soil changes due to deforestation, burning and cultivation in the Brazilian tropics. *Toxicology & Environmental Chemistry* **20/21**: 275-283.
- Artaxo, P., R. Calixto de Campos, E.T. Fernandes, J.V. Martins, Z. Xiao, O. Lindqvist, Fernández-Jiménez & W. Maenhaut. 2000. Large scale mercury and trace element measurements in the Amazon basin. *Atmospheric Environment* **34**: 4085-4096.
- Bernoux, M., C.C. Cerri & J.F.L. Moraes. 1998. The use of stable isotopes for estimating soil organic matter turnover rates. *Geoderma* **82**: 43-58.
- Breulmann, G., B. Markert, U.S. Leffler, V. Weckert, U. Herpin, H. Lieth, K. Ogino, P.S. Ashton, J.V. LaFrankie, H. SangLee & I. Ninomiya. 1997. Multi-element analysis in different compartments of Euphorbiaceae species from tropical rain forest ecosystem in Sarawak, Malaysia. *Tropical Ecology* **38**: 181-191.
- Bliefert, C. 1994. *Umweltchemie*, VCH, Weinheim.
- Buol, S.W., F.D. Hole & R.J. McCracken. 1989. *Soil Genesis and Classification*. 3<sup>rd</sup> edn., Iowa State University Press.
- EMBRAPA. 1988. Sistema brasileiro de classificação de solos. 3<sup>rd</sup> Approximation Empresa Brasileira de Pesquisa Agropecuária, Serviço Nacional de Levantamento e Conservação de Solos, Rio de Janeiro, R.J. Brazil.
- Ewel, J., C. Berish, B. Brown & N. Price. 1981. Slash and burn impacts on a Costa Rica wet forest site. *Ecology* **62**: 816-829.

- Feigl, B.J., J.M. Melillo & C.C. Cerri. 1995. Changes in the origin and quality of soil organic matter after pasture introduction in Rondônia (Brasil). *Plant and Soil* **175**: 21-29.
- Fendorf, S.E., D.L. Sparks, G.M. Lamble & M.J. Kelley. 1994. Application of X-ray absorption fine structure spectroscopy to soils. *Soil. Science Society of American Journal* **58**: 1583-1595.
- Fernandes, E.C.M., Y. Biot, C. Castilla, A.C. Canto, J.C. Matos, S. Garcia, R. Perin & E. Wanderli. 1997. The impact of selective logging and forest conversion of subsistence agriculture and pastures on terrestrial nutrient dynamics in the Amazon. *Ciência e cultura. Journal of the Brazilian Association for the Advancement of Science* **49**: 34-47.
- FitzPatrick, E.A. 1983. Soils. *Their Formation, Classification and Distribution*. Longman, London and New York.
- Gardina C.P., R.L. Sanford, I.C. Dockersmith & V.J. Jaramillo. 2000. The effects of slash and burning on ecosystem nutrients during land preparation phase of shifting cultivation. *Plant and Soil* **220**: 247-260.
- Hölscher D., B. Ludwig, R.F. Möller & H. Folster. 1997. Dynamic of soil chemical parameters in shifting agriculture in the eastern Amazon. *Agriculture Ecosystems & Environment* **66**: 153-163.
- INPE (Instituto Nacional de Pesquisas Espaciais). 2000. Monitoramento da Floresta Amazônica Brasileira por Satélite - Monitoring of the Brazilian Amazonian Forest by Satellite (1998 - 1999). Ministério da Ciência e Tecnologia.
- Kato, M.S.A., O.R. Kato, M. Denich, & P.L.G. Vlek. 1999. Fire-free alternatives to slash-and-burn for shifting cultivation in the eastern Amazon region: the role of fertilizers. *Field Crops Research* **62**: 225-237.
- Kennedy, P.M. & B.D. Siebert. 1975. Sulphur metabolism in sheep and cattle fed tropical forages. *Sulphur Institute Journal* **11**: 6-11.
- Lacerda, L.D. & R.V. Marins. 1997. Anthropogenic mercury emissions to the atmosphere in Brazil: The impact of gold mining. *Journal of Geochemical Exploration* **58**: 223-229.
- Lieth, H. & B. Markert (eds.). 1990. *Element Concentration Cadasters in Ecosystems: Methods of Assessment and Evaluation*. VCH, Weinheim, New York, Tokyo.
- Logan, T.J. 2000. Soils and environmental quality. pp. G155-G169. In: M.E. Sumner (ed.) *Handbook of Soil Science*. CRC Press, Boca Raton, London, New York, Washington, D.C.
- Maggs, J. & B. Hewett. 1993. Organic-C and nutrients in surface soils from some primary rain-forests, derived grasslands and secondary rain-forests on the Atherton Tableland in north-east Queensland. *Australian Journal of Soil Research* **31**: 343-350.
- McNaughton, S.J., F.F. Banyikwa & M.M. McNaughton. 1997. Promotion of the cycling of diet-enhancing nutrients by African grazers. *Science* **278**: 1798-1800.
- Markert, B. 1996. *Instrumental Element and Multi-Element Analysis of Plant Samples. Methods and Applications*. John Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore.
- Markert, B. 1998. Distribution and biogeochemistry of inorganic chemicals in the environment. pp. 165-222. In: G. Schürmann & B. Markert (eds.) *Ecotoxicology- Ecological Fundamentals, Chemical Exposure and Biological Effects*. John Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore.
- Markert, B. & K. Friese (eds.). 2000. *Trace Elements. Their Distribution and Effects in the Environment*. Elsevier Science, Amsterdam, Lausanne, New York, Oxford, Shannon, Singapore, Tokyo.
- Mathews, B.W., L.E. Sollenberger, V.D. Nair & C.R. Staples. 1994. Impact of grazing management on soil-nitrogen, phosphorus, potassium and sulphur distribution. *Journal of Environmental Quality* **23**: 1006-1013.
- McNaughton, S.J., F.F. Banyikwa & M.M. McNaughton. 1997. Promotion of the cycling of diet-enhancing nutrients by African grazers. *Science* **278**: 1798-1800.
- Melillo, J.M., R.A. Houghton, D.W. Kicklighter & A.D. McGuire. 1996. Tropical deforestation and the global carbon budget. *Annual Review of Energy and the Environment* **21**: 293-311.
- Moraes, J.F.L., C.C. Cerri, J.M. Melillo, D. Kicklighter, C. Neill, D. Skole & P. Steudler. 1995. Soil carbon stocks of the Brazilian Amazon basin. *American Journal of Soil Science Society* **59**: 244-247
- Moraes, J.F.L., B. Volkoff, C.C. Cerri & M. Bernoux. 1996. Soil properties under Amazon forest and changes due to pasture installation in Rondônia, Brasil. *Geoderma* **70**: 63-81.
- Neill, C., M.C. Piccolo, P.A. Steudler, J.M. Melillo, B.J. Feigl & C.C. Cerri. 1995. Nitrogen dynamics in soils of forest and active pastures in the western Brazilian Amazon Basin. *Soil Biology and Biochemistry* **27**: 1167-1175.
- Neill, C., C.C. Cerri, J.M. Melillo, B.J. Feigl, P.A. Steudler, J.F.L. Moraes & M.C. Piccolo. 1998. Stocks and dynamics of soil carbon following deforestation for pasture in Rondônia. pp. 9-28. In: R. Lal, J.M. Kimble, R.F. Folett & B.A. Stewart. (eds.) *Advances in Soil Science: Soil Processes and the Carbon Cycle*. CRC Press, Boca Raton, Boston, New York, Washington, London.
- Nriagu, J.M. & J.M. Pacyna. 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* **333**: 134-139

- Pagel, H. 1975. *Grundlagen des Nährstoffhaushaltes Tropischer Böden*. VEB Deutscher Landwirtschaftsverlag Berlin.
- Raison, R.J. 1979. Modification of the soil environment by vegetation fires, with particular reference to nitrogen transformations: A review. *Plant and Soil* **51**: 73-108.
- Scheffer, F. & P. Schachtschabel. 1992. *Lehrbuch der Bodenkunde*. Ferdinand Enke Verlag, Stuttgart.
- Schlesinger, H.W. (ed.). 1991. *Biogeochemistry: An Analysis of Global Change*. Academic Press, Harcourt Brace Jovanovich, Publishers, San Diego, New York, Boston, London, Sydney, Tokyo, Toronto.
- Schroeder, D. 1984. *Soils Facts and Concepts*. International Potash Institute, Bern.
- Serrão, E.A. & J.M. Toledo. 1990. The search for sustainability in Amazonian pastures. pp. 195-214. In: A.B. Anderson (ed.) *Alternative to Deforestation: Steps Towards Sustainable Use of the Amazon Rain Forest*. Columbia University Press, New York.
- Stuedler, P.A., J.M. Melillo, B.J. Feigl, C. Neill, M.C. Piccolo & C.C. Cerri. 1996. Consequence of forest to pasture conversion in CH<sub>4</sub> fluxes in the Brazilian Amazon Basin. *Journal of Geophysical Research* **101**: 18547-18554.
- Tsakelidou, K., N. Karagiannidis & S. Bladenopoulou. 1999. Effects of calcium carbonate and organic matter on soil aluminium, manganese, iron, zinc and copper and their concentration in corn plants in Greek acid soils. *Agrochimica* **43**: 89-100.
- Veldkamp, E. 1994. Uncertainty of  $\delta^{13}\text{C}$  method in soil organic studies. *Soil Biology and Biochemistry* **26**: 153-160.
- West, C.P., A.P. Mallarino, W.F. Wedin & D.B. Marx. 1989. Spatial variability of soil chemical properties in grazed pastures. *American Journal of Soil Science Society* **53**: 784-789.