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Emissions of nitrogen oxides from equatorial rain forest in central Africa:

origin and regulation of NO emission from soils

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ABSTRACT

Emissions of nitric oxide from soils of equatorial rain forest were measured in the Dimonika Natural Park (4°30'S, 12°30'E) in the Mayombe Forest in Congo. Three research campaigns were carried out in June and July 1991 and in February 1992. Fluxes were measured by dynamic chamber techniques using a chemiluminescence instrument Scintrex LMA3. NO fluxes measured on natural soils are in between 5 and 17×10^9 molecules $cm^{-2} s^{-1}$; they are of the same order of magnitude as those observed in similar tropical forest media. Soil treatment experiments show that the auto-decomposition of HNO_2 in these acid soils (pH# 4) (chemodenitrification) is a potentially important cause of nitric oxide production in this type of ecosystem. Nitrous acid comes from autotrophic nitrification all the year round, and also from biological denitrification, shown by N_2O emissions, during the rainy season. The regulation of NO release from soils is linked to ammonia production from litter mineralisation and to direct NH_4 input by throughfall.

1. Introduction

Nitrogen oxides play a key role in the chemistry of the atmosphere, and the knowledge of their sources and sinks as well as their spatial and temporal distribution are essential for atmospheric chemical models (Crutzen, 1979; Logan, 1983). On the other hand, nitric acid is one of the main components of rainwater acidity (Bolin and Arrhenius, 1977; Galloway et al., 1982; Andreae et al., 1990; Lacaux et al., 1992). Biomass burning is certainly the major source of reactive nitrogen compounds in Africa (Andreae, 1991; Lacaux et al., 1993), but soils can also be an important source of NO (Galbally and Roy, 1978). The emission depends on many ecological factors which make any extrapolation in time and space of measurements already carried out thoughout the world difficult. These measurements seem to show the importance of tropical soils, either in savannas (Johansson and Sanhueza, 1988; Johansson et al., 1988), or in rain forests (Kaplan et al., 1988; Bakwin et al., 1990) and even in dry forests (Davidson et al., 1991). However, grasslands and croplands appear to be more productive due to the use of fertilizers which multiplies fluxes by a factor of 5 to 100 (Slemr and Seiler, 1984; Johansson and Granat, 1984; Williams et al., 1988). An assessment of natural emissions on the different continents is urgently needed because extensive development of agriculture based on the use of fertilizers is rapidly occuring in the tropics.

Emission mechanisms of nitric oxide by soils are still not well known. A conceptual model of NO and N_2O emission mechanisms was proposed by Firestone and Davidson (1989). In this "hole-in-the-pipe" model NO and N_2O emissions appear as losses occuring during biological nitrification and denitrification processes. On the other hand, different authors have established by laboratory experiments that the chemical decomposition of nitrites in acid soils can be an important cause of NO volatilization from soils, especially in the

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tropics (Laudelout et al., 1977; Blackmer and Cerrato, 1986). The importance of these chemical processes in soils has not really been studied by field experiments. Nevertheless, the instability of nitrites in soils has been known for a long time (Robinson, 1923; Cady and Bartholomev, 1960; 1963; Galbally and Roy, 1978; Smith and Chalk, 1980; Van Cleemput and Baert, 1976; 1984). The chemical nature of the phenomenon was demonstrated by liming at the beginning of this century (Robinson, 1923) and sterilization of the soil (Tyler and Brodbent, 1960; Bulla et al., 1970).

The emission of nitric oxide from soil is therefore rather complex. As tropical rainforests have been shown to be a significant source, three research campaigns were conducted in June and July 1991 and February 1992 in the Mayombe Forest in the Congo. The objectives of these campaigns were, on one hand, to investigate the various processes regulating the NO emission from tropical forest soils, and, on the other hand, to study the influence of such emissions on the atmospheric chemistry within the forest and the boundary layer.

To study NO emission mechanisms, and test by field experiments the potential role of the chemical decomposition of nitrites in acid soils, soil treatment experiments were carried out, after measurement of NO emission from natural soils in different seasons. Biological denitrification was followed by measurements of N_2O emissions using static chambers, N_2O and N_2 being the main products of denitrification in soils because denitrifiers reduce NO more rapidly than N_2O (Betlach and Tiedje, 1981; Zafiriou et al., 1989).

2. Experimental sites and scientific approach

Experiments were performed in the Dimonika Natural Park forest in the Mayombe region of the Southern Congo. The Mayombe is a pre-Cambrian mountain chain, culminating at 900 m altitude. The forest forms a belt extending about one thousand kilometers along the Atlantic coast, from Angola to Gabon and over fifty to one hundred kilometers inland. The average annual rainfall is about 1400 mm. During the dry season, from June to October, rainfall does not exceed 5 mm per month (Clairac et al., 1989). Surface soil moisture presents a maximum in April–May, at the end of the rainy season (45 to 70% in mass relatively to the weight of soil dried at 105°C). Then it regularly decreases untill the end of the dry season (15–20% in September). Experiments were carried out on soils well-drained at least at the surface (plateau and mountain slopes), and on waterlogged soils at the bottom of slopes. The vegetation is of the ombrophilic guineo-congolese type, under a humid sempervirent or semi-sempervirent facies (Cusset, 1989). This type of vegetation can be found in spite of limited rainfall because of the permanent presence of fog during the dry season, reducing evaporation. Soils are lateritic oxisols with a sandy clay texture (Misset, 1989). Chemical characteristics of soil samples taken in various sites (mountain slopes, valley and flooded lowlands) in the Mayombe forest are given in Table 1. Soils are acidic with pH in water around 4. In the surface layer the carbon and nitrogen contents are 1.7–4.5% and 0.1–0.3% with a C/N ratio of about 15 (Table 1). Ammonium concentrations of 1.1 to 3.8 were mesured in various soil samples whereas nitrate concentrations are generally lower than the detection limit of the method. In this ecosystem, the nitrogen recycling results from litter fall, rain (R) and throughfall (T). Litter fall is very slight for a tropical rainforest: 4.4–5.2 tons of dry matter per hectare per year, representing an input of mineralizable nitrogen to the soil of 60 kg ha^{-1} yr^{-1} (Schwartz, 1993). The precipitation chemistry was studied over a two year period (1986–1988) at the Dimonika Station (Lacaux et al., 1992). This programme was followed by a study of the chemical composition of throughfall and rain over a rainy season period, from October 1988 to June 1989; 32 samples were collected during this period. The chemical composition of throughfall differs from that of rainwater due to the washout of aerosols deposed on leaf surface and of eventual plant exudations. Ammonium ions appear to be strongly enriched in throughfall, with an enrichment factor $T/R[NH_4] = 6.77$, whereas nitrate concentrations are almost the same, on average, in throughfall and rain ($T/R[NO_3] = 0.95$). Over the sampling period, the average rainfall was 1600 mm, and 1400 mm under the vegetation due to direct absorption by the leaves and evaporation. The total input of mineral nitrogen to the soil was about 16 kg(N) ha^{-1}, with more than 80% in the form of ammonium ions; occult precipitations in the dry season were not taken into account.

Table 1. *Chemical characteristics of soil surface horizon (0–10 cm) in the Mayombe forest (Congo) from samples taken on different sites on mountain slopes, flooded lowlands and valleys*

SITE Mayombe forest	Organic C (%)	Total N (%)	C/N ratio	$N\text{-}NO_3$ (ppm)	$N\text{-}NH_4$ (ppm)	pH (water)
mountain slope-1	1.75	0.13	13.3	ND	0.50	3.9
mountain slope-2	5.19	0.33	15.3	ND	1.12	3.9
mountain slope-3	3.75	0.25	14.8	ND	1.34	3.9
flooded lowland-1	2.62	0.19	14.1	ND	3.58	4.0
flooded lowland-2	3.45	0.21	16.3	1.12	2.35	4.0
valley-1	2.70	0.19	13.8	ND	3.08	3.8
valley-2	4.57	0.27	16.8	ND	1.90	3.1
valley-3	2.25	0.15	14.9	ND	3.80	3.8

NO and N_2O emissions from soils are generally considered as a consequence of biological nitrification and denitrification processes. In fact, if NO is partly produced by hydroxylamine oxidation, the majority of NO and N_2O emissions comes from a "denitrification" of HNO_2 by nitifiers under low oxygen tension (Lipschultz et al., 1981; Anderson and Levine, 1986). Nitrifier denitrification is virtually an aerobic denitrification (Conrad, 1990). HNO_2 appears therefore as the key element in biogenic emissions of nitrogen compounds (Van Cleemput and Baert, 1984). The HNO_2 production is biological but its evolution depends heavily upon its chemical stability which is related to soil pH and and the presence of organic matter. Blackmer and Cerrato (1986) have established models of chemical NO production for soils having selected pH values and various organic C content. The relevant chemical reactions are (Van Cleemput and Baert, 1976):

$$2H^+ + 3NO_2^- \rightarrow 2NO(g) + NO_3^- + H_2O,$$

$$2HNO_2 \rightarrow NO(g) + NO_2(g) + H_2O,$$

$$NO_2(g) + NO_2^- \rightarrow NO_3^- + NO(g).$$

In acid soils of humid tropics, nitrite decomposition may be more effective than microbial production of NO (Galbally, 1989). It has been demonstrated through laboratory experiments and computer simulation that up to 50% of added ammonium nitrogen may be lost in acid soils when nitrification occurs at temperature prevailing in the humid tropics (Laudelout et al., 1977). Fig. 1, based on the model of NO production by chemical reaction of nitrite of Blackmer and Cerrato, shows that the chemical potential production of NO in the Mayombe forest soil is approximately 25 to 40 mg of NO/kg of soil. In-situ soil treatment experiments (Subsect. 3.2) were designed to control the occurence of this process in real time on natural soils.

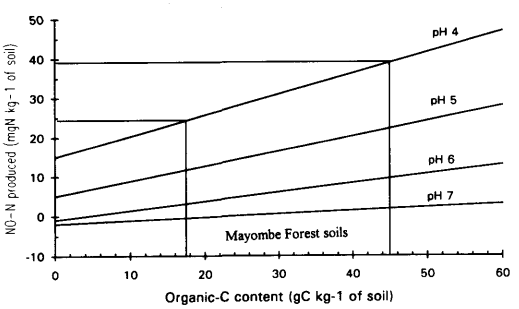

Fig. 1. Soil properties affecting formation of nitric oxide by chemical reaction of nitrite (from Blackmer and Cerrato, 1986): combined influence of pH and organic carbon leading to an estimate of potential production of NO in the Mayombe forest soils (average soil characteristics are given in Table 1).

3. Experimental methods

3.1. Flux measurement methods

3.1.1. Nitric oxide. NO emission from soil was measured using dynamic chamber techniques with a Scintrex LMA3 chemiluminescence instrument. This instrument detects NO_2 by a chemiluminescence reaction with a solution of Luminol. The air stream can be connected with a by-pass to a CrO_3 chemical converter which oxidizes NO

to NO_2; then the instrument detects $NO_x = NO + NO_2$. Nitric oxide level is determined by the difference of the two values. The instrument was calibrated just before and after each campaign, to within the range of 10–100 ppbv by means of standards of NO and NO_2 at 10 ppm diluted with pure nitrogen.

We use rectangular stainless steel chambers of 800 cm^2 area (40x20 cm) and 15 cm height. A stainless steel frame is inserted into the ground several hours before the measurement which starts when adjusting the chamber on the frame, sealing being assured by a slot filled with water. The air inlet is on one side of the chamber; the air outlet on the other side is connected to the analyser with two meters of teflon tubing, so that the chamber is swept with an air flow only due to the pump of the instrument (1 l/min). The residence time of the air inside the chamber is approximately 12 min. Two different techniques were used to determine emission fluxes, and laboratory experiments were conducted to study the influence, on one hand, of ozone and NO_2, and on the other hand, of the ventilation of the chamber. This technical part is developed in the appendix, in order to simplify the presentation of the work itself.

3.1.2. Nitrous oxide. N_2O fluxes were measured using static chambers of the same design as those used for NO measurements. Air samples were taken from the chamber with 20 ml syringes, through a septum, every 15 mn for a 2-h measurement period. Air samples were then injected in pre-evacuated glass tubes closed by teflon septums. Analyses were performed in our laboratory in France, by gas chromatography, with a ^{63}Ni electron capture detector (ECD), within two weeks after sampling. Tests carried out with several series of tubes did not show any loss of N_2O (or CH_4 or CO_2) over several weeks.

NO and N_2O flux measurements on Mayombe forest soils were carried out during three campaigns: at the beginning of June 1991, i.e., at the end of the rainy season; at the end of July of the same year, in the dry season; and in the middle of the wet season, in February 1992. This allowed us to study the influence of soil moisture on emissions. In-situ soil treatment experiments were carried out in June 1991 and February 1992 to investigate NO emission processes, the order of magnitude of N_2O fluxes being considered as an indicator of the potential biological denitrification.

3.2. Field approach of chemodenitrification: soil treatment experiments

3.2.1. Experimental procedure. After measurement of natural NO emission, various chemicals dissolved in 1 liter water were added to the soil within the frames of the chambers. We first checked that the addition of 1 liter natural water on wet soils during the rainy season did not notably modify the flux.

- The key role of HNO_2 was shown by adding KNO_2 at doses equivalent to approximately 100 kg($N\text{-}NO_2^-$) ha^{-1} (too high) and then 1 kg ($N\text{-}NO_2^-$) ha^{-1}.
- The instability of nitrites in acid media was suppressed by liming with a saturated soda lime solution.
- The role of denitrification was studied by adding KNO_3 (100 kg($N\text{-}NO_3^-$) ha^{-1}).
- The role of nitrification was demonstrated by addition of specific ammonium monoxygenase inhibitors of like nitrapyrine (about 2 g/l), and acetylene (at about 10 kPa).
- The role of ammonium oxidation as a limiting factor was studied by input of urea, the hydrolysis of which being very fast in these soils. The dose used was equivalent to 100 kg($N\text{-}NH_4^+$) ha^{-1}.

4. Results

4.1. Natural emissions of NO and N_2O

The results of flux measurements carried out during the three campaigns are shown in Table 2. With fluxes included between 0.5 and $1.7x10^{10}$ molecules $cm^{-2}\,s^{-1}$ (0.4–1.5 kg[N] $ha^{-1}\,yr^{-1}$), NO emissions are in the lower part of the range of fluxes commonly measured on similar tropical soils (see the review in Conrad, 1990). They are comparable to the values found in the Amazon forest during the wet season (Bakwin et al., 1990), or in dry tropical forests (Davidson et al., 1991). However, these fluxes are some five times less intensive than those measured in the Amazon forest during the dry season (Kaplan et al., 1988). This may be due to differences in soil moisture between the two sites during the dry season. In the Mayombe forest the highest emissions seem to occur at the end of the wet season.

Nitrous oxide (N_2O) emissions appear to be linked to the hydrous state of soils and therefore

Table 2. *Nitric and nitrous oxide emissions from natural soils of the Mayombe forest during the 3 campaigns: 4–6 June 1991, 15–22 July 1991, 9–12 February 1992*

	Nitric oxide emission			Nitrous oxide emission		
Campaign and season	n	average flux–range (10^{10} mol. cm^{-2} s^{-1})	average flux (ng[N] cm^{-2} h^{-1})	n	average flux–range (10^{10} mol. cm^{-2} s^{-1})	average flux (ng[N] cm^{-2} h^{-1})
June 1991 (end of rainy season)	11	1.74 5.02–1.11	1.44	6	12.49 20.75–3.43	20.7
July 1991 (dry season)	6	0.78 2.39–0.03	0.65	8	<0.10	<0.17
February 1991 (rainy season)	6	0.50 1.39–0.23	0.41	8	1.18 1.76–0.30	1.96

n denotes the number of measurements; fluxes are in 10^{10} molecules N-NO cm^{-2} s^{-1} and in ng[N] cm^{-2} h^{-1}).

to biological denitrification, which implies the presence of nitrates or nitrites and of anaerobic conditions. Fluxes are almost zero on flooded soils during the rainy season (absence of nitrification) and on well drained soils during the dry season (absence of anaerobic conditions). The data obtained during the three campaigns is compatible with most of the measurements carried out in various sites in the Amazon forest, where average N_2O flux is in the order of 1 to 2×10^{10} molecules/cm^2/s (Keller et al., 1983; 1986; 1988; Livingston et al., 1988; Matson et al., 1990).

Because measurements were taken in the different seasons of the year, it is possible to give a rough estimate of annual fluxes of NO and N_2O from the Mayombe forest soils. If we consider, on a yearly average, NO and N_2O emissions of $1x10^{10}$ and $2x10^{10}$ molecules cm^{-2} s^{-1} respectively, the nitrogen loss from soils would be 0.73 kg[N-NO] and 2.9 kg[N-N_2O] ha^{-1} yr^{-1}. A few measurements of total denitrification carried out by adding acetylene at 10 kPa to the chambers, to inhibit the N_2O-N_2 transformation (Klemedtsson et al., 1988), gave the ratio $N_2O/N_2O + N_2 = \frac{1}{6}$. Therefore total denitrification in soils would represent a nitrogen loss of 17.4 kg[N] ha^{-1} yr^{-1} and a little more than 18 kg[N] ha^{-1} yr^{-1} if NO release is taken into account. Although our measurements were not numerous enough to assure the generality of this result, it can be noted that the order of magnitude is in close agreement with the nitrogen input by throughfall (16 kg[N] ha^{-1} yr^{-1}). It also corresponds to the value (14 kg[N] ha^{-1}), derived from the nitrogen balance in two coastal rivers basins in the forested zone of the southern Ivory Coast (Servant et al., 1984).

4.2. *Origin and regulation of NO emission from acidic soils*

Nitric oxide emission processes from acid soils of the Mayombe forest were studied through in-situ soil treatment experiments. The existence of chemodenitrification as a step of the nitrogen cycle in these acidic soils, suggested by the works of soil scientists (Section 1, e.g., Blackmer and Cerrato, Laudelout et al.), was first tested by addition of nitrites on three different plots followed by an artificial increase of soil pH by liming. During the first experiment in June 1991 a sequence of experiments was conducted on a single plot to study the origin and the control of nitrite production in soil. The results are presented in Table 3 and Fig. 2. Complementary experiments were carried out in February 1992 to confirm and complete the first set of observations.

4.2.1. Role of nitrites. The addition of heavy doses of nitrites (equivalent to 100 kg[N] ha^{-1}) leads to a sudden release of NO which saturates immediately the chemiluminescence instrument. At a dose of 1 kg[N-NO_2^-] ha^{-1} measurement becomes possible (Fig. 2A; 1–1b) but the flux is still one hundred times higher than natural flux (Table 3). The reaction appears a few seconds after the addition of nitrite to the soil, suggesting a purely chemical reaction confirmed by the pH modification.

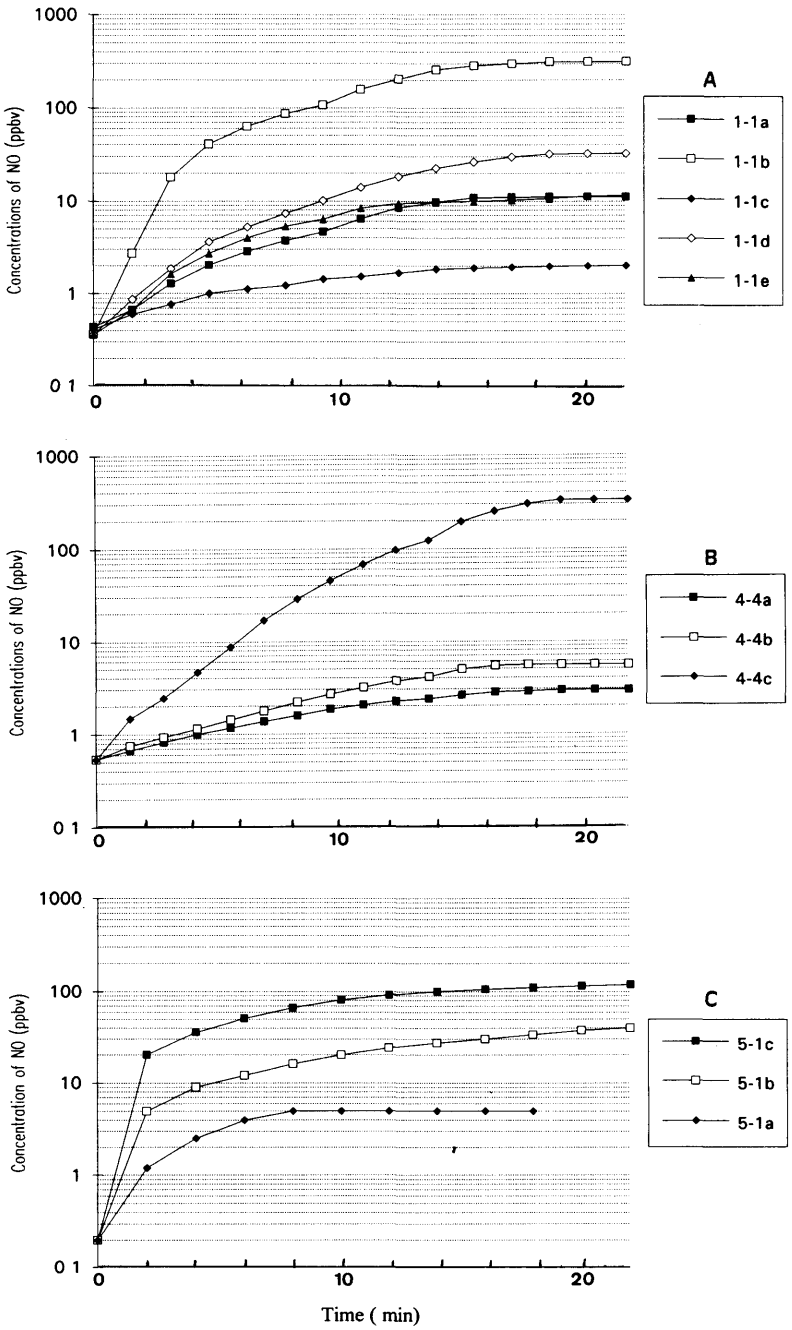

Fig. 2. Evolutions of nitric oxide concentration within the dynamic chamber corresponding to natural and treated soils referenced in Table 1. A: soil 1–1: influence of nitrites and lime, B: soil 4–4: influence of nitrate and nitrite, C: soil 5–1: influence of urea.

Table 3. *Soil treatment experiments: influence of nitrite, nitrate, ammonia (urea), and nitrification inhibitors (nitrapyrin and acetylen) on nitric oxide release from soils of the Mayombe forest (area of the chamber 800 cm²)*

Forest soil and experiment reference	Treatment	NO flux $\times 10^9$ molecules $cm^{-2} s^{-1}$	Ratio: $\frac{\text{treated soil}}{\text{natural soil}}$
soil 1–1a	Natural soil 1–1	14.8	1
soil 1–1b	soil 1–1 treated with 0.01 g NO_2^-	1478	100
soil 1–1c	soil 1–1 treated with 0.01 g NO_2^- + lime	2.9	0.19
soil 1–1d	soil 1–1c 24 h after treatment	51.2	0.41
soil 1–1e	soil 1–1c 72 h after treatment	15.7	1.06
soil 4–4a	natural soil 4–4	14.8	1
soil 4–4b	soil 4–4 treated with 1 g NO_3^-	24.6	1.7
soil 4–4c	soil 4–4 treated with 1 g NO_3^- + 0.01 g NO_2^-	666	45
soil 5–1a	natural soil 5–1	2.56	1
soil 5–1b	soil 5–1 treated with 1 g urea	109.1	42
soil 5–1c	soil 5–1c 24 h after treatment	216.6	86
soil 4–3a	natural soil 4–3	33.3	1
soil 4–3d	soil 4–3 treated with nitrapyrine	3.45	0.1
soil 4–3e	soil 4–3 treated with acetylene	7.2	0.21

4.2.2. Influence of pH. The addition of soda lime to the surface treated by nitrites leads to an immediate increase in pH from 4.4 to 5.3. This enhancement is sufficient to bring down the NO release to values 4 × lower than that of natural soil (Fig. 2A, 1–1d). The buffer capacity of the soil then lowers the pH so that, 24 h later, the NO release increases again, up to values three times higher than the natural flux (51.2×10^9 molecules $cm^{-2} s^{-1}$, Table 3). Three days after treatment, the nitrites added being almost completely volatilized, the emission drops back to the normal level (15.7×10^9 molecules $cm^{-2} s^{-1}$). The neutralization of soil pH being favourable to the biological activity, particularly to nitrification, the suppression of the NO emission by liming, clearly shows the chemical origin of the process. Addition of nitrite and lime to natural soils were repeated on 5 plots in the same area with quite reproducible results. The origin of the nitrous acid undergoing auto-decomposition was then to be determined: nitrification or denitrification?

4.2.3. Origin and control of nitrite production. Nitrite formation in soil may come from ammonium oxidation under aerobic conditions, or from nitrate reduction under anaerobic conditions (nitrate respiration). The addition of nitrate to the soil to simulate a natural process is justified because anaerobic conditions can appear during the rainy season when throughfalls bring down nitrates to ground surface. After addition of nitrates, the NO flux was multiplied by 8 in February 1992 (22.8 versus 2.7×10^9 molecules $cm^{-2} s^{-1}$) in the middle of the wet season, by 2 in June 1991 (Fig. 2B, 4–4b), and by 1.2 (not significant) in July 1991 during the dry season. This result highlights the influence of anaerobic conditions confirmed by the absence of N_2O emissions during the dry season (July). It is noticeable that the addition of 100 kg[N-NO_3^-] ha^{-1} has considerably less effect than that of 1 kg[N-NO_2^-] ha^{-1} (Fig. 2B, 4–4c) although nitrate reduction, which is a biological process (nitrate respiration), is easier than nitrite reduction. This constitutes another argument in favor of the auto-decomposition of nitrites.

Under aerobic conditions, the production of nitrites depends on ammonium oxidation by nitrite bacteria. The oxidation of ammonium in nitrite by the monoxygenase is inhibited by nitrapyrine and

acetylene. The effects of these enzymatic inhibitors are spectacular (Table 2). The natural flux is reduced by a factor of 10 under the effects of nitrapyrine, and by 5 under those of acetylene. The formation of NO is therefore linked to NH_4 oxidation either directly or undirectly through decomposition of the HNO_2 produced. This ammonium oxidation depends on the presence of nitrite bacteria and also on the amount of available NH_4. To verify the role of this last factor, urea, whose hydrolysis is very fast in soils at elevated temperature, was added to the soil (Fig. 1C). The input of urea leads to a rapid increase in the flux of NO (multiplied by 42, 1 h after treatment, Table 2) and 24 h after treatment the flux continues to increase (mutiplied by 62) due to the completion of urea hydrolysis. It seems, therefore that the nitrite production is controled by ammonification and not by the presence of ammonium monoxygenase. The availability of ammonium nitrogen would be at a maximum at the end of the rainy season if we refer to fluxes measurements carried out on natural soils in different seasons (Table 2).

5. Conclusions

Soils of the tropical forests of central Africa appear to be a source of nitric and nitrous oxide as already observed in similar media, especially in the Amazon region. Average fluxes measured on natural soils (10^{10} and 2×10^{10} molecules cm^{-2} s^{-1} for NO and N_2O respectively) are close to the values found in Brazil.

NO emission from acid soils of the Mayombe forest seems to be partly linked to the chemodenitrification (chemical decomposition of nitrites). All the favourable conditions for this phenomenon to occur are to be found: very low pH, abundance of clay, and reduced metals (Wullstein and Gilmour, 1964; 1966; Nelson and Bremner, 1970). In fact, the reaction induced is instantaneously suppressed by liming, the residual flux being 4 × less than the natural one although the increase in pH is known to favor the biological activity (nitrification and denitrification). Nitrous acid is a key compound in the nitrogen cycle as it appears during nitrification as well as during denitrification (Van Cleemput and Baert, 1984). In the soils studied its formation is linked to nitrification all the year round and also, possibly, to denitrification during the rainy season in relation with local anaerobic conditions and nitrate input by throughfall. Nevertheless, the dominant source of nitrites is certainly the oxidation of ammonium. The activity of ammonium monoxygenase is not limiting as the input of ammonia nitrogen leads to a strong enhancement of the flux of nitric oxide. On the basis of this results it is possible to put forward a conceptual model of nitrogen oxide emission from the Mayombe forest soils (Fig. 3).

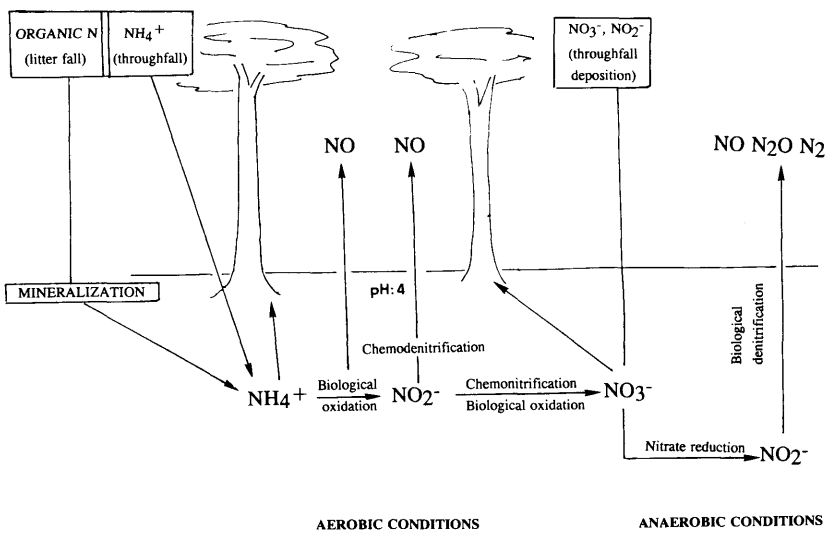

Fig. 3. Conceptual model of the nitrogen cycle in soils of the Mayombe forest.

The relative importance of emissions is linked to the high mineralization activity of these soils, in spite of a very low pH. This condition can be found in grasslands and in certain broad-leaved tree forests (Colbourn et al., 1987; Slemr and Seiler, 1991; Delany et al., 1986; Williams et al., 1988), but not in coniferous forests (Johansson, 1984; Delmas, unpublished data). An interesting issue of the results deals with a possible enhancement of anthropogenic NO emissions, due to extensive use of ammonium fertilizers on acidic lateritic soils in industrial plantations in tropical regions.

6. Acknowledgements

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7. Appendix

Flux measurement techniques of nitric oxide

Flux measurements of NO by dynamic chamber is a widely used technique because it is quite simple to operate, it can be used at any time of the day and whatever the vegetation cover. However, this technique presents several disadvantages, the most important being the exclusion of natural air turbulence. When the flux is calculated from the slope of the increase of concentration within the chamber the value obtained represents a net flux which takes into account emission and absorption at the surface. Moreover, the slope at the origin is often difficult to use because of the interference of NO with ozone within the chamber before O_3 destruction is complete. The ventilation of the chamber is also a problem. The ventilation should have been regulated in order to reproduce natural turbulence. This was not done during our experiments.

For NO, as for most trace gases, the net flux into the atmosphere is the resultant of emission and absorption processes. Calculation of emission flux and deposition velocity are obtained by the resolution of the continuity equation in the soil-chamber system.

$$dC/dt = D(C_0 - C)/V + J_0/h - LC/h$$

where:

C is the concentration in the chamber (molecules cm^3),
C_0 the concentration in ambient air,
D the air flow through the chamber ($cm^3\ s^{-1}$),
V the volume of the chamber (cm^3),
h the height of the chamber (cm),
J_0 the emission flux (molecules $cm^{-2}\ s^{-1}$),
L the absorption velocity ($cm\ s^{-1}$).

After a quasi linear increase, the concentration inside the chamber reaches a steady state with $dC/dt = 0$ (see examples on Fig. 1). Emission fluxes of NO can be calculated from the same measurement, in two different ways, either using the linear part of NO variation inside the chamber, or with the equilibrium concentration (C_{eq}).

In the first case the flux is given by:

$$J_0 = (dC[NO]/dt)(VN/SRT \times 10^9),$$

where the deposition velocity is not taken into account, i.e., J_0 is a net flux and in the second case:

$$J_0 = [D/S(C_{eq} - C_0) + LC_{eq}]\ N/RT \times 10^9,$$

$C(t)$ and C_0 in ppbv,
$N = 6.02 \times 10^{23}$ (Avogadro number),
$L = 0.04\ cm\ s^{-1}$, $S = 800\ cm^2$, $V = 15\ l$, $D = 20\ cm^3\ s^{-1}$,
$R = 0.082\ l\ atm\ mole^{-1}\ K^{-1}$, T(K),
J_0 in molecules $cm^{-2}\ s^{-1}$.

In the second case, the deposition velocity has to be considered. An average value was determined for the soils of the Mayombe forest by means of a method based on two static chambers connected in series. This method gives two equilibrium states allowing independent calculation of absolute emission flux and deposition velocity. This technique is applicable only when emission fluxes are the same in the two chambers. It is comparable to the

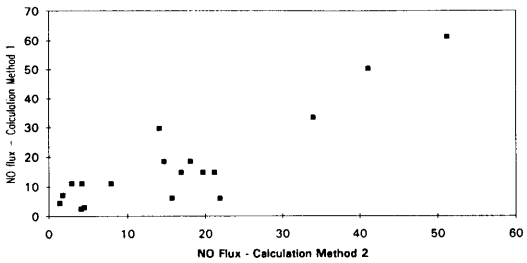

Fig. 4. Comparison of NO fluxes (10^9 molecules $cm^{-2}\,s^{-1}$) calculated from the same measurements by two methods: method 1: slope of the curve at the origin; method 2: calculation from equilibrium concentration in the chamber taking into account a deposition velocity of 0.04 cm s^{-1}.

one developed by Kaplan et al. (1988) which was based on the variations of air flow through the chamber obtained with an auxiliary pump. The average value of NO deposition velocity on the Mayombe forest soil, 0.04 cm s^{-1}, was the same than that obtained on the Amazon forest soils. This value is used in flux calculation based on equilibrium concentrations.

Fluxes obtained by the two calculation methods are fitted in Fig. 4, they agree quite well; however a rather large scattering of points is observed for the lowest values. In this case a linear part in NO variation inside the chamber is not always easy to find whereas the equilibrium concentration is well defined. On the contrary for high fluxes, especially on treated soils, the equilibrium concentration cannot be reached due to saturation of the instrument (200 ppbv). NO fluxes reported in this paper are the values calculated by the first method for fluxes higher than 20×10^9 molecules $cm^{-2}\,s^{-1}$ and by the second method for the lowest fluxes.

The destruction of NO by ozone in the chamber is limited in this case because ozone concentration at ground level inside the forest never exceeds 4 ppbv, the increase in NO concentration starts immediately after the chamber is set up on the frame (Fig. 1). Laboratory experiments were carried out to determine the influence of turbulence in the chamber. Chamber ventilation increases O_3 and NO_2 deposition but also NO emission. For low fluxes, enhancements of about 80% can be observed. The artificial increase in the friction velocity in the chamber reducing the surface boundary layer, is certainly the cause of this enhancement of the flux. It seems that ventilation induces an error on flux measurements at least with the type of chamber used. We did not use ventilated chambers to avoid this artificial flux enhancement, in the absence of measurements of surface resistance in the chamber (Galbally and Roy, 1978). Air mixing and turbulence in the chambers are only assured by the air circulation of the pump of the chemiluminscence instrument whose air flow is 1 l min^{-1}. The fluxes measured may therefore be underestimated by a factor of 2 in the case of low fluxes; however, it must be noticed that in the forest, at ground level, natural air circulation and turbulence are very low.

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