respectively to a mean SO_2 oxidation time of 7 days, an aerosol mean residence time of 12 days and in-cloud mean scavenging time of 18 days.

This is the first attempt to determine the *in situ* tropospheric SO_2 oxidation rate constant using cosmogenic ^{35}S, and as such it is subject to the uncertainties inherent in novel measurements and oversimplifications. We do, however, have some independent information on the values of P and k in this region. In 1977 and 1978, Turekian *et al.*[14] determined the deposition flux of ^{7}Be (half-life 54 days) in New Haven (again at Kline Geology Laboratory) and obtained a value of 1.88 d.p.m. per cm^2 per month. The effective 'production' ratio of $^{7}Be/^{35}S$, as determined from bucket collections, was ~85 (activity ratio), which is close to the value estimated from Lal and Peters[15] and Lal[16]. The apparent agreement may be deceptive, however, as dry deposition of SO_2 was presumably not included in the bucket collections, and the determinations of ^{35}S and ^{7}Be were made at different times and by different collection methods. The ^{35}S measurements were made on individual storms, whereas the ^{7}Be data were obtained on monthly integrated samples collected in a continuously exposed collector. An independent value for k was determined for the eastern United States[17] from ^{210}Pb and ^{137}Cs fluxes measured in soils and atmospheric concentrations, the long-term time-averaged mean was $k \approx 0.2 \pm 0.1$ (2σ) per day, corresponding to a mean aerosol residence time of $\sim 5 \pm 2.5$ (2σ) days. Our value of 12 days is somewhat larger than this; the difference may be due to the short-term nature of our observations.

The mean oxidation time of 7 days at the time and location of our experiment is within the range of values predicted for homogeneous reactions[18] and markedly longer than the value based on ^{38}S systematics. The value of about six hours reported by Junkerman and Roedel[10,19] using ^{38}S is probably due either to hot-atom processes, as suggested by Calvert *et al.*[11] or, in our opinion, to surface boundary effects dominated by dry deposition of $^{38}SO_2$ on surfaces.

If the time constants for oxidation, in-cloud scavenging and aerosol deposition of ^{35}S are applicable to terrestrial sulphur, as implied by the similarity of the $^{35}S/S$ ratio of gaseous and particulate sulphur, then air in the boundary layer has efficiently mixed the ^{35}S from above and the terrestrial sulphur horizontally supplied from sources in the boundary layer, at least over a timescale of three days. For the specific time and place, New Haven in August 1990, the values of mean oxidation time and mean aerosol residence time obtained in this work may thus be valid for all sources of SO_2 entering the boundary layer. We expect these time constants to differ both with climate and location. Our method may provide a way of measuring the variation with position and time with a suitable deployment of collectors.

The role of dry deposition in removing SO_2 could also be determined by comparing the ^{35}S fluxes from bucket collections of precipitation with those from integrated vegetative and soil profiles, the difference between these yielding the ^{35}S flux to the ground surface by dry deposition. We are at present undertaking such a study. □

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Influence of biomass burning on equatorial African rains

Hélène Cachier & Joëlle Ducret

Centre des Faibles Radioactivités, CNRS-CEA, Avenue de la terrasse, 91198 Gif-sur-Yvette, France

BIOMASS burning affects the African continent all year round[1–4]. In the dry season there are widespread savannah fires, and there are always some domestic and agricultural fires. Here we present measurement of particulate black carbon, which is an unambiguous indicator of combustion, in rain waters collected at a remote site in the Northern Congo. We find that the rains contain pollutants from biomass burning, and are particularly affected during the Northern Hemisphere dry season. Our results show that biomass-burning smoke particles may act as cloud condensation nuclei, and might thereby play a part in cloud formation and hence precipitation in the tropics[3].

Forty-six rain samples were collected over one year (June 1988–June 1989) at Enyele (2°5 N, 18° E) in the primary forest of Northern Congo. The equatorial forest, which is embedded between two large and populated savannah areas located north and south of the equator, is likely to be influenced by the biomass burning practices. Our sampling site is located in the dense part of the remaining virgin forest of Africa and almost unaffected by local human activities. It has an equatorial climate, with abundant rainfall all year round. A whole year's sampling of rain in this region can be considered to register the annually repeated influence of anthropogenic activities in both the northern and southern savannah regions of the African continent. Precipitation was collected as it occurred by an automatic rain collector. Rain water was then rapidly filtered on pre-cleaned glass-fibre filters. We determined total carbon (C_t) and black carbon (C_b) contents from halves of the same filter, following an analytical protocol previously reported for aerosols[2,5].

As shown in Fig. 1, black carbon is present in all samples, which unambiguously indicates that combustion inputs influence equatorial rains all year round. In tropical areas, the main combustion activity is likely to be the burning of biomass[1,6]. The overwhelming influence of vegetation combustion on tropical rains in Africa has already been suggested by Lacaux *et al.*[7,8] who measured low pH values in rains collected in the Ivory Coast and Congo, mainly due to high contents of NO_3^- ions which they attributed primarily to biomass burning inputs. In our rain samples too, the pH is low, with a mean value of ~4.4 (B. Lefeivre and J. P. Lacaux, personal communication), which is similar to values reported in different tropical or equatorial regions[7–10]. Mean values obtained for black and total carbon contents are 73 and 292 $\mu g\, C\, l^{-1}$ respectively (Table 1). The few data available from previous work suggest that the particulate carbon content of our rain samples is similar to those found in temperate source regions[11,12], although our sampling site is a hundred kilometres from the savannah source regions. This result indicates the importance of the particulate inputs from biomass burning and their long-range transport over the African continent. Figure 1 also stresses the predominance of the organic mode, which accounts for ~75% of the total carbon concentration found in the particulate phase in the rains. We

recall our previous studies on tropical carbonaceous aerosols[13,14], indicating that the biomass burning processes produce an organic-rich aerosol, which probably reflects poorly oxygenated combustions. Thus, the chief part of the particulate organic content in rains could also originate from the burning of the biomass. The concentrations of total and black carbon peak simultaneously, which reinforces the hypothesis of a common origin for the two carbonaceous components (C_b and C_o, which is assumed to be $C_t - C_b$) of the rain particles.

Consideration of the large-scale circulation pattern repetitively prevailing over Africa throughout the year can provide information on possible atmospheric inputs from biomass burning at our study site. In Africa, seasons are determined by the displacement of two discontinuity surfaces, separating hot, dry continental air masses from cooler and more humid maritime ones[15-17]: the intertropical convergence zone (ITCZ) is formed by the convergence of Sahelian and equatorial ocean air masses; the other is the interoceanic confluence (IOC) which separates air coming from the Southern Atlantic from that of the Indian Ocean. The extreme positions of these frontiers occur in January and July, which corresponds to the heart of the dry season in the Northern Hemisphere and Southern Hemisphere respectively. These positions are shown in Fig. 2*a*. During the dry season, biomass burning is at a maximum. For the savannahs of the Northern Hemisphere, the dry season is established once the ITCZ has moved south of these regions. A few weeks after the beginning of the dry season, savannah fires are widespread and last about a month. The sweeping of the ITCZ thus induces a latitudinal shift of the regions affected by savannah bushfires. It may be considered that the duration of the fire season in the whole African savannah region of the Northern Hemisphere is 3-4 months[1], centred on January. At the same time, the shifting of the IOC generates the sequence of seasons in the Southern Hemisphere, the regions having the dry season being those then located southeast of the IOC. The burning season peaks in July and lasts 4-5 months[1].

But the ground location of these convergence zones alone is not sufficient to explain the presence of biomass-burning pollutants at Enyele. At ground level, the sampling site always seems to be in the atlantic monsoon regime and therefore not affected by atmospheric fluxes coming from the savannah regions (Fig. 2*a*). The influence of biomass burning in rains at Enyele can be seen, however, by considering the vertical profiles of the ITCZ[15,16] and the IOC[16], which both show a shift with altitude. Figure 2*b* shows that areas directly affected by continental inputs during the dry season are much greater than previously suggested. In particular, during certain periods of the year, the forested equatorial regions of Central Africa, where the extreme locations of the convergence zones are observed, may be influenced by high-layer air masses that are built up in the savannah regions. These considerations indicate that because of the favourable geographical position of the sampling site and the alternation of savannah regions that are in the dry season, rains falling over Enyele are influenced during much of the year by severe savannah fires, raging either in the Northern or in the Southern Hemisphere.

TABLE 1 Mean concentrations of total and black particulate carbon in rains

	C_b ($\mu g\ C\ l^{-1}$)	C_t ($\mu g\ C\ l^{-1}$)	C_b/C_t (%)
Seattle*	60		
Sweden*	100		
Paris region†	335±320	1,185±1,190	29±10
Enyele‡			
Whole year	73±59	292±162	24±10
November-March	155±59	477±173	33±6
Rest of the year	45±18	236±89	20±6

* Data from Ogren *et al.*[11].
† Data from Ducret and Cachier[12].
‡ This work collected June 1988-June 1989.

In Fig. 1, the group of rains collected during the dry season of the Northern Hemisphere (from November to March) is clearly separate from the others, with both particulate total and black carbon concentrations two or three times as great as during the rest of the year (Table 1). This feature is not affected by the variation of the seasonal amount of rainfall (mean amount of rain from November to March was 16 mm; for the other months it was 22 mm). Our results do not, however, clearly record the other main expected episode of biomass burning. That is, the start of the bushfire season in the Southern Hemisphere is not clearly reflected by an increase in the rain particulate concentrations. This may either be due to differences in the intensity and frequency of biomass burning in the African northern and southern savannahs (the northern countries supporting a larger population) or to the geographical position being more favourable for the efficient atmospheric transport of continental emissions from the northern regions. Another salient point of our data is the occurrence of a background combustion component in rain samples collected during periods when savannah bushfires are limited (October-November, April-May). This background of pollution cannot be attributed to local or even regional activities. It confirms the continuous influence throughout the year of biomass-burning emissions, primarily through domestic and agricultural fires (use of wood and charcoal for cooking, slash-and-burn fires), and the complexity of atmospheric transport and deposition patterns over this region of the African continent.

Preliminary calculations based on recent estimates of forested areas[1], rainfall in equatorial regions (2.2 m)[1], areas of burnt savannah[4] and fine aerosol emission factors in biomass combustions[2], and on our rain concentration data, indicate that ~15% of the 2 tg of black carbon released in the atmosphere of Africa, essentially by savannah fires, is removed by wet deposition over the whole humid African forest. The primary forest of Northern

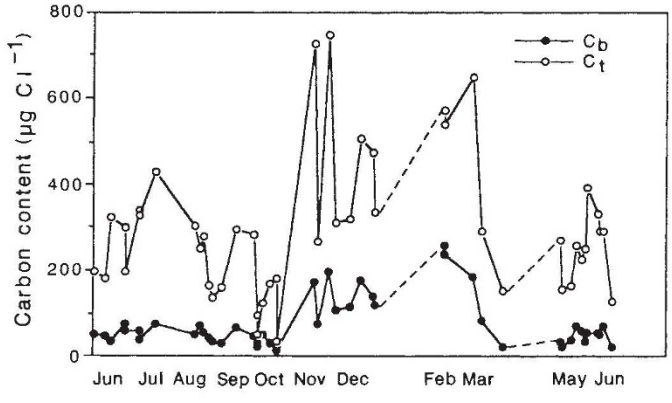

FIG. 1 Black carbon and total carbon contents of rains over the primary forest of Enyele (Northern Congo).

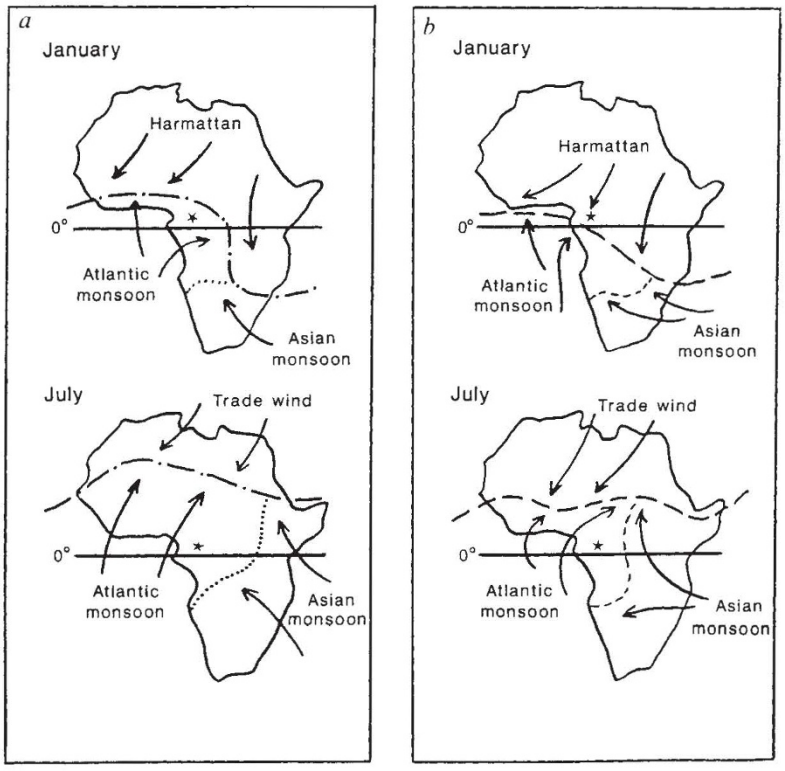

FIG. 2 *a*, Ground location of the two discontinuity surfaces ITCZ (— · —) and IOC (· · · · ·) in January and in July. *b*, Position of ITCZ (— —) and IOC (- - - -) at pressure level of 850 mbar for the same period. ★, location of the sampling site.

Congo itself could receive more than 10% of these inputs.

Previous work[13,14] has indicated that the fluctuations of the relative abundance of black carbon (expressed as C_b/C_t) recorded in the aerosols could be related to different combustion processes, depending on the type of vegetation being burnt and on the physical parameters of the fire. An important result was the noticeable increase of the black carbon content in aerosols generated by well oxygenated large-scale bushfires. Applying such an approach to our rain sample results shows that the apparent covariation of the total and the black carbon contents hides important fluctuations of the C_b/C_t ratio, which ranges between 10 and 57%. Such variations of the black carbon content in rains might indicate differences in the biomass-burning sources, as already seen for aerosols. From the C_b/C_t ratio it can also be seen that the group of rain samples collected from November to March (the dry season in the Northern Hemisphere), is separate from the others, with a mean value of 35% which is significantly different from that obtained for the other samples (mean value of 20%). This result suggests that during this period, the main combustion sources influencing the rains are different from those affecting rains during the rest of the year. The higher C_b/C_t ratios in these November–March samples could reflect inputs of products emitted by more oxygenated fires, namely the large-scale savannah fires of the Northern Hemisphere.

It must be emphasized that the black carbon fraction is more abundant in our rain samples (mean $C_b/C_t = 24\%$) than in the tropical aerosol samples in source regions (mean $C_b/C_t = 12\%$)[13,14]. This apparent discrepancy suggests that a considerable fraction of the organic aerosol dissolves in the hydrometeors, enhancing the relative importance of black carbon in the particulate phase. It may be hypothesized that the hydrophilic behaviour of carbonaceous aerosols from biomass burning is due to the coating of particles by water-soluble material. This coating could be gained rapidly in the biomass-burning plume because of the combination of two main factors: the surface properties of the carbonaceous particles which are efficient absorbants of gases, and the enrichment of the plume in mineral (such as HNO_3 and NH_3) and gaseous organic species. As the biomass-burning aerosols are mainly submicrometre-sized particles, they are potential nuclei for cloud condensation[3,18]. The partial disappearance of organics from the particulate phase in rain waters may indicate that the carbonaceous particles are incorporated in the hydrometeors, and it could be a key step in enabling these aerosols to act as cloud condensation nuclei. If so, our rain concentration data indicate that the important production of particles by biomass combustion could alter the radiative balance and the precipitation regimes in the Tropics. Finally, the question of whether the partial dissolution of organic aerosols produced by biomass burning contributes to the dissolved organic carbon load and the organic acidity of the present or previous rains deserves further investigation. □

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