Reports

Soot Carbon and Excess Fine Potassium: Long-Range Transport of Combustion-Derived Aerosols

Abstract. *During a cruise from Hamburg to Montevideo, aerosol samples representing air masses from Europe, the Sahara, tropical Africa, South America, and open oceanic regions were collected. They showed significant amounts of soot carbon over large areas of the remote Atlantic, often similar to concentrations in rural continental areas. Back-trajectories and the ratios of soot carbon to total fine (less than 1.7 micrometers in diameter) carbon and of excess fine potassium (the portion not attributable to soil dust or sea salt) to soot carbon indicate that biomass burning in tropical regions is an important source of soot carbon to the world atmosphere. The ratio of excess potassium to soot carbon in the fine fraction of aerosols is proposed as an indicator of the relative contributions of biomass and fossil-fuel burning to soot carbon aerosols. The ratio of soot carbon to fine carbon suggests that most of the particulate organic carbon over the Atlantic is of continental origin.*

The production of soot is uniquely linked to combustion processes, for example, residential heating, power generation, vehicular emissions, or biomass burning, and is therefore closely connected to man's activities. This report examines the abundance of soot carbon and total aerosol carbon along a transect across the Atlantic Ocean from Europe to South America in order to obtain a perspective on the global distribution of this pollutant in the remote atmosphere.

Carbon in the form of soot, organic matter, and carbonates is a major constituent of atmospheric aerosols (*1*). Soot carbon is the only aerosol component able to absorb a significant amount of visible light; almost all other components will only scatter visible light. A global increase of atmospheric soot concentrations thus leads to an increased retention of solar radiative energy within the atmosphere and therefore to a warming effect that would tend to reinforce the CO_2 greenhouse effect (*2*). The surface structure of soot makes it an efficient absorber for a variety of molecules. It can therefore act as a pollutant vector, adsorbing compounds (for example, polynuclear aromatic hydrocarbons) and transferring them into respirable aerosol that is retained in the human lung. Highly mutagenic compounds have been identified in diesel engine soot (*3*). Surface catalysis of the oxidation of SO_2 to sulfuric acid takes place in droplets containing soot particles (*4*) and contributes to atmospheric acidity.

Aerosol samples were collected on the forward mast of the R/V *Meteor* during a cruise from Hamburg to Montevideo. To prevent contamination of the samples with emissions from the ship's stack, the sampling was controlled by a system which monitored wind speed and direction as well as the concentration of Aitken nuclei. Two types of samplers were used, Battelle-type impactors and stacked filter units. The stacked filter unit consists of a filter holder in which a Nuclepore filter 47 mm in diameter (nominal pore size, 5 μm) is mounted in front of a Teflon filter (nominal pore size, 2 μm) (Ghia Corporation, Pleasanton, California). At the face velocity used (~ 14 cm/sec), the Nuclepore filter has a 50 percent cutoff at about 1.7 μm aerodynamic particle diameter (*5*), so that particles with smaller diameters are collected quantitatively on the Teflon filter (*6*).

Soot carbon was quantitated by the reflectance technique (*7*), which has been validated by a cross-calibration experiment (*8*). The filters were mounted on a microscope (Carl Zeiss, Oberkochen, West Germany) and illuminated at an angle of ~ 45° with light from a tungsten lamp. The intensity of reflected light was measured with a CdS photocell. The reflectance of the filter area covered with aerosol was compared with that of an unexposed area on the same filter. The C_{soot} concentration is proportional to the reflection absorbance. The method is calibrated by reference to filters loaded with known amounts of C_{soot} from the combustion of acetylene. The precision of this method is ±10 percent; the detection limit for carbon is 1.3 μg/cm^2, which at the sample volumes used corresponds to 20 to 40 ng/cm^3.

The samples were analyzed by proton-induced x-ray emission (PIXE) for 21 elements; only the results for potassium and calcium will be discussed here. Total carbon, nitrogen, and oxygen were determined on the Teflon filters by proton elastic-scattering analysis (PESA). The analytical procedures used have been described (*6, 9*). Calibration was performed by irradiation of thin gravimetric standard targets. The accuracy of these procedures is 10 to 30 percent, depending on the particular elements and their concentrations. All samples were collected and analyzed in duplicate.

The cruise track of the R/V *Meteor* is shown in Fig. 1. Sampling period 1 was in the port of Hamburg before leaving the dock. Periods 2 and 3 were under the influence of air masses that traversed England and parts of northeastern Europe but which, because of high wind velocities, had not accumulated very high concentrations of pollutants. The vessel entered the open North Atlantic during period 4, which was characterized by cold maritime air masses of Arctic origin. During periods 5 and 6, the ship traversed an area dominated by a large high-pressure area in the region of the Azores. An intense haze layer resulting from Sahara dust aerosols was evident during these periods, especially around sunset. Period 7 was under the influence of the northeastern trades, with 48-hour trajectories extending to the coast of North Africa. The ship entered the region of the Intertropical Convergence Zone (ITCZ) at about 11°N during period 8. The ITCZ was poorly defined both in terms of its meteorological expression as observed from the vessel and in terms of its representation on weather charts during the observation period. Trace gas measurements during the cruise (CH_4, H_2, CO, and mercury) showed pronounced gradients occurring near 11°N (*10*), an indication that the transition between Northern and Southern Hemisphere air masses occurred at this latitude. Back-trajectories during period 8 show air-mass origins in tropical North Africa during the first part of this sampling interval, followed by the arrival of air masses from tropical and equatorial South America. Air from tropical South America dominated period 9; toward the end of this period the transition to purely marine air of the southeastern trades took place. During a significant portion of period 10 the vessel was within sight of the Brazilian coast during strong to

the K/Ca ratio increases steeply with decreasing particle size (during periods 1 through 3, 8 through 10, 12, and 13). I interpret this as resulting from the presence of a submicrometer particle population rich in potassium in addition to the presence of some potassium from the fine fractions of the sea salt and soil dust aerosols. No comparable fractionation between potassium and calcium has been seen in either pure sea salt aerosols, for example, those from Cape Grim, Tasmania (*11*) or soil dust–derived aerosols (for example, periods 5 through 7 from this data set). This argument is further supported by the data from the fine fraction of the stacked filter units (Fig. 2) which show potassium and calcium values near those for seawater and crustal proportions for oceanic periods 4 and 11 and for the Sahara dust–dominated periods 5, 6, and 7. To estimate the amount of K_{excess}, I have multiplied the calcium concentration by the best-fit K/Ca ratio (0.75) and subtracted this value from the K_{fine} concentrations. Comparison of these K_{excess} data with the C_{soot} values shows an impressive similarity in their distributions (Fig. 2). This result suggests that both sets of values result from combustion processes. (Soot carbon production is uniquely related to combustion.) This correlation also eliminates any possibility that the presence of C_{soot} on the filters could be due to contamination from the ship's stack, since the K/C_{soot} ratio in particulates from fuel oil combustion should be on the order of 10^{-5} (*17*), whereas the observed ratio was near 10^{-1}.

Despite the obvious temporal coherence between soot and excess potassium, the K_{excess}/C_{soot} ratio varies through almost one order of magnitude in the sample set. It is, however, relatively constant within a given type of air-mass origin (Fig. 1): 0.05 to 0.06 for the air masses originating in northern Europe, 0.10 to 0.16 for the Sahara plume, and 0.26 to 0.36 for the air from the tropical regions of Africa and South America (Fig. 2). I attribute the high amounts of K_{excess} relative to C_{soot} for the tropical regions to the prevalence of biomass burning in these regions accompanied by a release of K_{fine}. The K_{excess}/C_{soot} ratios in the air masses of tropical origin are close to the values measured on aerosols dominated by brush-fire emissions collected in Brazil (0.21 to 0.46) and on the island of Fernando de Noronha off the coast of Brazil (0.30 to 0.41) during the same season as the *Meteor* cruise (*18*).

On the other hand, the combustion of fossil fuels, especially of petroleum products, seems to generate little K_{excess}. Data from most coal-fired power plants show K/Ca values near or below the crustal ratio (*19, 20*); K_{fine} enrichment is rarely seen in such emissions (*15*). Therefore, the most likely sources for the K_{excess} observed in the air masses of European origin are firewood burning [the consumption of firewood is greater in Europe than in North America, especially if eastern Europe is included (*21*)] and waste incineration. The latter process has been suggested as a source of K_{excess} on the basis of studies in the Washington, D.C., region (*22*). Since a significant number of the combustion sources in industrialized regions produce C_{soot} but no significant amounts of K_{excess} (diesel and gasoline engines, oil-fired and coal-fired power plants), we must expect lower K/C_{soot} ratios from industrialized areas. This is in agreement both with the data from this study and with observations made in the United States (ratios from 0.025 to 0.09) (*23, 24*). If one assumes that biomass combustion (firewood, waste incineration, agricultural burning) is the only source of K_{excess} even in industrialized countries and that this source is characterized by a K_{excess}/C_{soot} ratio of ~ 0.3 as observed in the tropical air masses in this study, then the ratios observed from Europe and North America would correspond to a contribution of 10 to 30 percent from biomass burning to the total C_{soot} in industrialized regions. This value coincides with the lower range of the estimates obtained on the basis of ^{14}C measurements of atmospheric aerosols (*13*) and source balances (*1*). Ultimately, the K_{excess}/C_{soot} ratio may prove an important tracer in the source identification of pollutant aerosols. An important case in point is the Arctic haze, in which a considerable amount of C_{soot} has been observed (*25*). On the basis of K_{fine} and calcium concentration data, it may be possible to attribute the source of this haze to Europe or to Asia, which has an extremely high rate of biomass combustion (*21*).

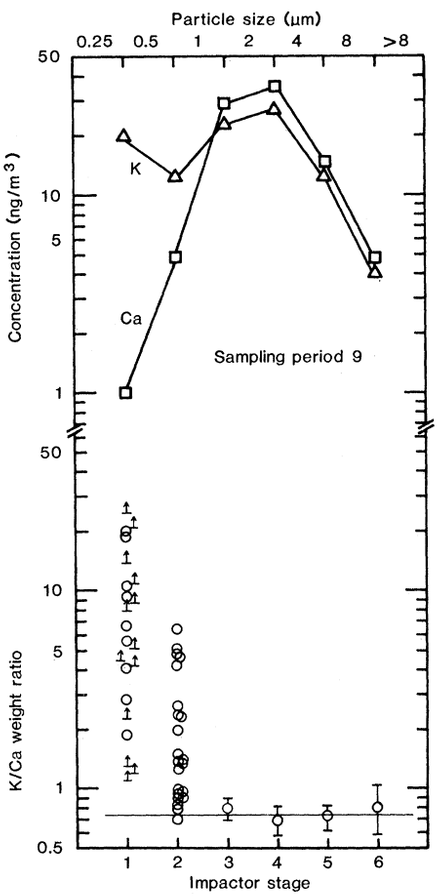


Fig. 3. Size distribution of potassium and calcium in aerosols collected by Battelle-type impactors during *Meteor* cruise 56/1, period 9. The impactors are made from electrically conductive, injection-molded plastic (PIXE International Corporation, Tallahassee, Florida). They were operated at flow rates of about 1 liter/min and have the following size cutoffs for stages 0 through 6: < 0.25, 0.25 to 0.5, 0.5 to 1, 1 to 2, 2 to 4, 4 to 8, and > 8 μm aerodynamic diameter. Stage 0 consists of a Nuclepore backup filter with a > 80 percent collection efficiency over a broad size range with a minimum efficiency for particles 0.03 μm in diameter. No potassium or calcium was detectable on stage 0. The particles were impacted on Mylar surfaces coated with Vaseline (stages 2 through 6) or paraffin (stage 1) to prevent particle bounce-off. The K/Ca ratio for the different size fractions is shown in the form of individual points (or lower limits when calcium was not detectable) for stages 1 and 2. For the larger particle diameters, the mean and standard deviations (N = 24) are given, as the points would have plotted too close together. The best fit for the K/Ca ratio for all values on stages 3 through 6 is indicated as a horizontal line (K/Ca = 0.75).

Total carbon as determined by PESA on the fine particle fraction includes the C_{soot} component, organic carbon, and possibly some inorganic carbonates. In the fine fraction of most aerosols, little or no carbonate is present (*26*). Total C_{fine} decreased as the ship was moving off shore in the Northern Hemisphere and reached its lowest values in the Sahara plume (Fig. 2). The tropical air masses, characterized by high C_{soot}, also carried significant amounts of organic carbon. Increasing amounts of C_{fine} were again encountered during sampling periods 12 and 13. These observations suggest a continental origin for much of the particulate organic carbon present over the Atlantic, in agreement with the results of Chesselet *et al.* (*27*). This suggestion is supported by the C_{soot}/C_{fine} ratios, which for almost all the *Meteor* data (Fig. 2) fall within the range of 0.2 to 0.65 observed for fine particulates in the United States (*1, 23*). The *Meteor* data

moderate onshore winds; all trajectories point to the open tropical Atlantic. Period 11 showed similar air-mass origin, although the distance to shore was considerably greater. Trajectories are not available for period 13 and part of period 12; offshore winds were observed aboard ship during part of these sampling periods.

The air-mass origin is closely reflected in the chemical composition of the fine fraction of the atmospheric aerosol (Fig. 2). High concentrations of C_{soot}, comparable to those observed in rural continental areas (*1*), and high concentrations of fine potassium are seen in air masses of continental origin, even over the remote tropical Atlantic. The production of fine particulate potassium during biomass combustion has been consistently observed (*11–13*). It has also been suggested as a result of fossil-fuel combustion (*14–15*).

In order to determine the concentration of excess fine potassium in the Atlantic aerosols, I have investigated the relation between calcium and potassium as a function of particle size in the impactor samples collected during the same sampling periods (Fig. 3). The K/Ca ratio in seawater is 0.97; the crustal average is 0.71 (*16*). In the size fractions > 2 μm in diameter the observed ratios fell between the seawater and crustal values (within the precision of the analysis). Regression analysis gives a value of 0.75 for the K/Ca ratio in the coarse aerosol fractions for all data sets of the *Meteor* samples ($N = 93$, standard deviation = 0.11). No trend with particle size is evident within the coarse fraction, but for the size fractions < 2 μm in diameter

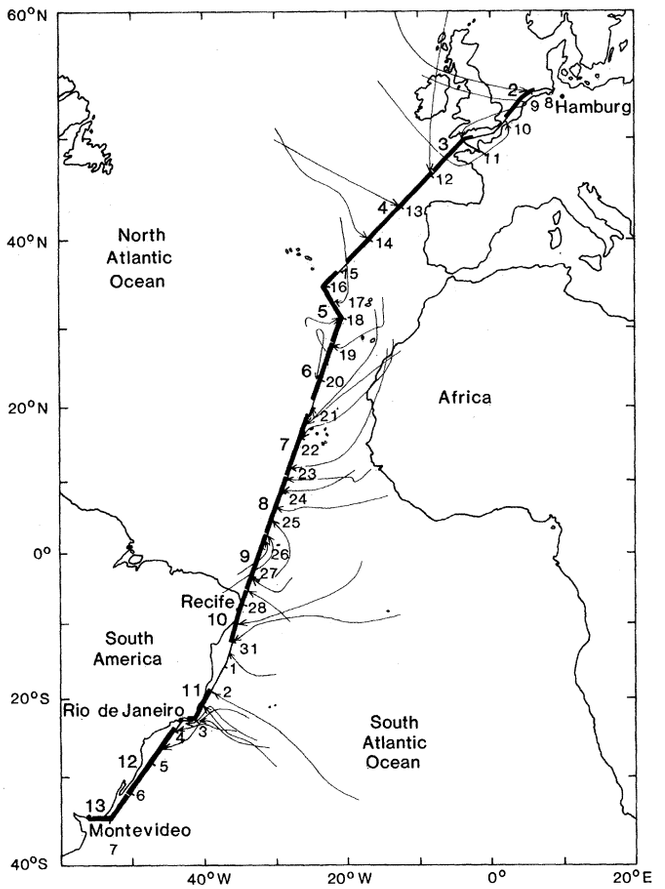
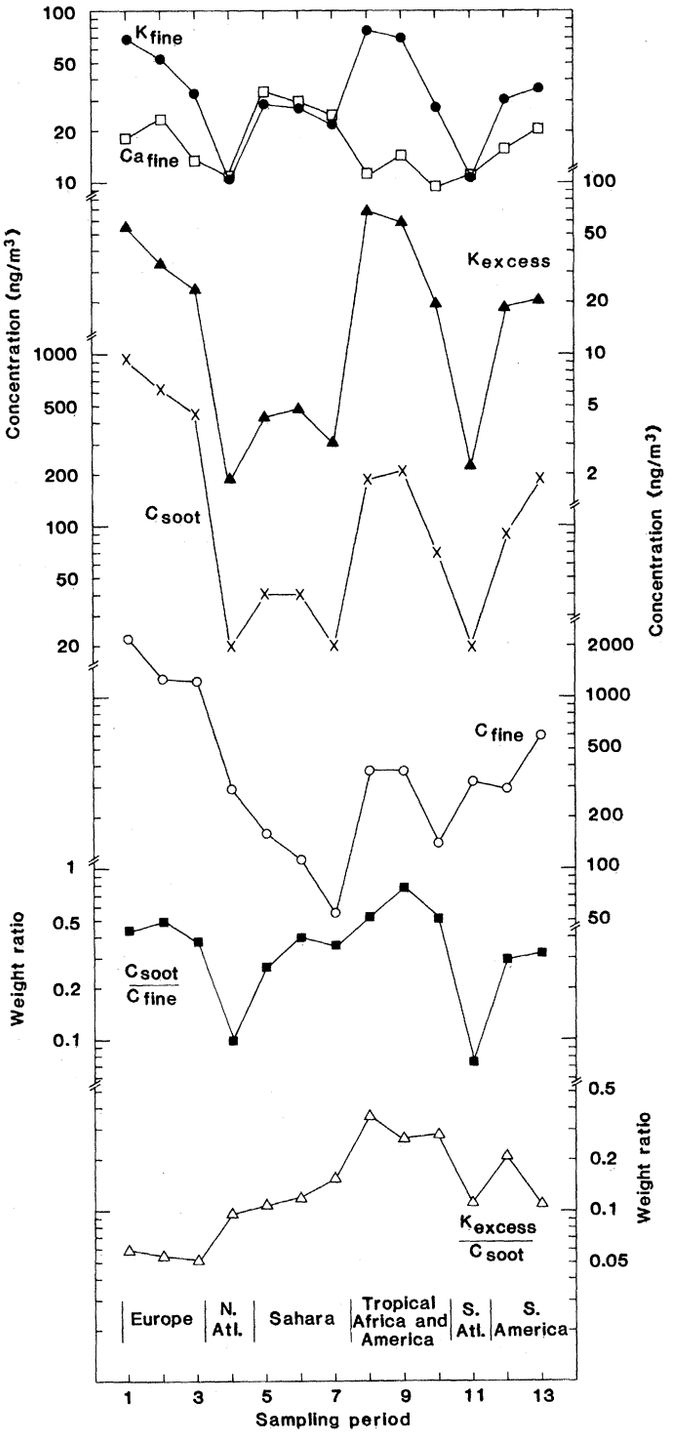


Fig. 1 (above). Track of cruise 56/1 of the R/V *Meteor* from Hamburg to Montevideo (7 October to 10 November 1980). The sampling periods are identified by the heavy lines; the period numbers are indicated to the left of the track. Noon positions with dates are marked to the right of the track; 48-hour isobaric air-mass backtrajectories (*30*) are indicated where available. Fig. 2 (right). Composition of the fine fraction (< 1.7 μm) of atmospheric aerosols collected during *Meteor* cruise 56/1. Concentrations are plotted against sampling periods shown in Fig. 1.



show a tendency for higher C_{soot}/C_{fine} ratios during the sampling periods dominated by biomass burning, in agreement with data from Townsville, Australia (*11, 28*), where I have observed values between 0.7 and 0.9 in aerosols which showed significant contributions from agricultural burning and brush fires.

Periods 4 and 11 were characterized by the virtual absence of C_{soot}, but not by extremely low total carbon concentrations, and consequently show the lowest C_{soot}/C_{fine} ratios (Fig. 2). At Cape Grim, Tasmania, I observed comparable amounts of organic carbon (140 to 310 ng/m^3) in marine air without a detectable soot component (< 20 ng/m^3) (*11*). In all these cases, there is almost no continental aerosol component detectable in the fine or large fractions. Total iron concentrations for periods 4 and 11 were 7.1 and 1.6 ng/m^3, respectively; at Cape Grim, iron was not detectable. It is not clear if this organic carbon represents truly marine organic matter, as has been suggested by Eichmann *et al.* (*29*), or the product of gas-to-particle conversion of long-lived vapor-phase organic precursors of continental origin, as has been suggested by Chesselet *et al.* (*27*).

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An Ictidosaur Fossil from North America

Abstract. *Teeth of a North American ictidosaur,* Pachygenelus milleri, *n. sp., found in the Upper Triassic Dockum Group of Texas, indicate that it is very similar to* Pachygenelus monus *of South Africa and* Chaliminia musteloides *of South America. The presence of a Gondwana element in the Northern Hemisphere attests to the ease of dispersal of the Late Triassic vertebrates through Pangea. Ictidosaurs are small, highly advanced, carnivorous cynodonts that display a mosaic of reptilian and mammalian features in the masticatory apparatus. They were contemporaneous with early mammals and probably closely related to them.*

The history of mammalian origins from cynodont reptiles toward the end of the Triassic is slowly unfolding. Recent mammals and reptiles are easily distinguished by the differences of anatomical, physiological, reproductive, and adaptive features, but in the reptile-mammal transition documented by the Late Triassic fossils, the distinction is not clear-cut. First, diagnostic mammalian features of soft anatomy are lacking from fossils; second, the fossil record of early mammals is very fragmentary—many taxa are known only from tiny teeth and jaws; third, many advanced cynodonts already possessed a large suite of mammalian features (such as secondary palate, enlarged dentary with coronoid process, reduced postdentary bones, complex cheek teeth with precise occlusion and limited replacement, and double occipital condyles) which make the class boundary more difficult. The presence of a squamosal-dentary articulation forming part or all of the joint between the skull and lower jaw is now used as the most practical diagnostic criterion for the class Mammalia (*1*).

This distinction in the jaw articulation was found to be inadequate, however. At least some cynodonts, such as ictidosaurs (*2*) and *Probainognathus* (*3*), have a dentary-squamosal contact, which makes them mammals by strict application of this criterion. Yet their complex lower jaws and single auditory ossicle in the middle ear are clearly still reptilian. Opinion has long been divided as to whether ictidosaurs are reptiles or mammals. Two features shared only by mammals and ictidosaurs among synapsids are prismatic enamel in the dentition (*4*) and overall small size. This is why the ictidosaurs are of special interests to evolutionists.

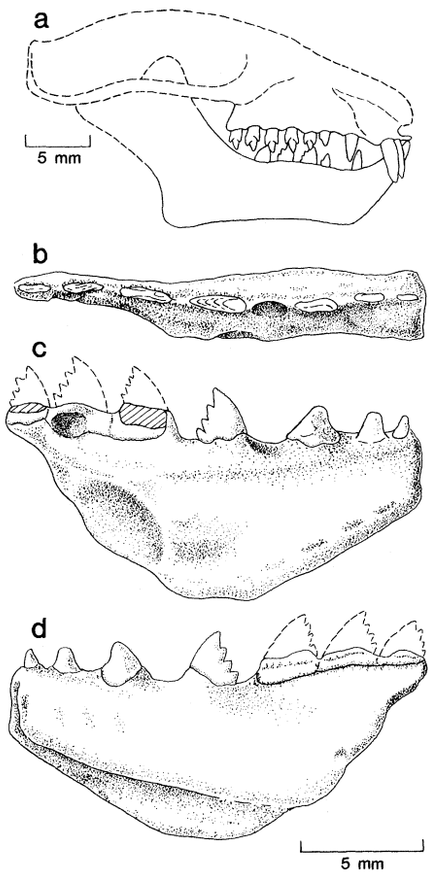

Fig. 1. (a) Right lateral view of the skull of *Pachygenelus monus* (*10*); (b) occlusal, (c) labial, and (d) lingual views of the right dentary of *Pachygenelus milleri*, n. sp. (TTU P 9020).