

## Reply to C. M. Laird, E. J. Zeller and G. A. M. Dreschhoff

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In their letter commenting on our recent paper "Relative contributions of tropospheric and stratospheric sources to nitrate in Antarctic snow", C. M. Laird, E. J. Zeller and G. A. M. Dreschhoff have launched a discussion that they should have launched several years ago when their findings began to be strongly questioned (Risbo et al., 1981; Herron, 1982a, b; Legrand and Delmas, 1984; Zanolini et al., 1985). These 5 publications have been systematically ignored in their own papers except in Laird's thesis (1986). This controversy had been clearly emphasized by Peel in his review paper of 1982 in *Nature*. The papers by Laird (1983) and Dreschhoff et al. (1983) published in the proceedings of a conference, do not contribute new data with regard to Parker et al. (1982) and to Laird et al. (1982), two papers published in journals with peer review. Laird, Zeller and Dreschhoff themselves, in their *Letter to the Editor* (first paragraph) cite Zeller and Parker (1981) and Laird et al. (1982) as basic references where their arguments are developed.

We recognize that a clerical error was unfortunately made in the transcription of Laird et al.'s (1982) Fig. 1. However, our discussion is based on the correct figure, the error having been committed at the time of the final drawing in our laboratory. It is true that this erroneous nitrate profile minimizes the impact of the 1972 SPE, as Laird et al. emphasize in their letter to the editor. However, our comments were not focused on this event in our 1986 paper, but rather on the 11-year solar cycle. Furthermore, this relatively "sharp peak" enters visibly within the limits of nature's own variability observed in the deposition of nitrate (Fig. 1, in Laird et al., 1982). In any case, in the  $\text{NO}_3$  concentration profile reported in

Fig. 3 (Laird, 1983), the years 1972 and 1973 are not at all exceptional.

Laird et al. emphasize that our South Pole time series stops at the end of the 1960s, just before the SPE of 1972, hinting that we would have analysed, but not reported, the following decade (the pit was sampled in 1977–1978) which in their opinion, is most crucial. Our choice of the 1959–1969 time period has been dictated by (1) the availability of the samples for the major ion program, the upper sequence having been used for other purposes, (2) the study of the years preceding and following the Agung volcanic eruption ( $1964 \pm 5$  years in Antarctica), and (3) the study of the well-marked 11-year solar cycle (1958–1969) with the highest sunspot number during this century (Eddy, 1977). A new data set covering more recent years was collected in 1983–1984 at the South Pole and the results will be reported in S. Kirchner's thesis to be presented at the beginning of next year.

We readily admit that the Maunder minimum is also a very important time period for investigating the possible impact of solar activity on the nitrate profiles. Parker et al. (1982) and Dreschhoff et al. (1983) published the results of the analysis of a 108 m South Pole firn core indeed showing relatively low ( $\times 0.3$ )  $\text{NO}_3$  concentrations for the years 1640–1715 (between  $\sim 30$ –40 m depth). Preliminary results (Kirchner and Delmas, 1987) exhibit no such pattern and a more complete analysis of the data will be reported soon. In their letter, Laird et al. note that "the Dome C nitrate profile does bear a resemblance to their South Pole and Vostok profiles". Our conclusion is much less optimistic: e.g., between  $\sim 1880$  and 1930, their profile (Parker et al., 1982) exhibits a decrease in the concen-

trations by a factor  $\sim 2$ , while our profile exhibits an increase of a factor 1.6. We have not conducted a Fourier analysis on the Dome C profile, since snow accumulation rates were much lower ( $3.2$  in comparison to  $8.5 \text{ g cm}^{-2} \text{ yr}^{-1}$ ) and much more highly variable at Dome C (Petit et al., 1982) than at the South Pole, rendering such an analysis hazardous. In any case, the profile reported in our Fig. 5 does not suggest any obvious periodicity in the nitrate concentrations.

Laird et al. claim that they have demonstrated the large variability of the snow and nitrate depositions at the South Pole with "frequent hiatuses in the ice sequence and pockets of anomalously high nitrate values". It is true that at the South Pole, a certain reworking of the surface layer can occur; nevertheless, their comment concerning the representativeness of the South Pole snow layer gives the reader a very erroneous idea concerning this question. Indeed from a detailed study of seasonal deuterium variations, Jouzel et al. (1983) proposed a year-by-year dating of the South Pole snow layers (back to 1880), demonstrating that the South Pole is probably the most adequate (undisturbed) location in Antarctica to study atmospheric chemistry changes over such decade periods. Laird et al. insinuate that our set of samples is not representative of the true conditions of snow deposition at the South Pole area. This affirmation is in no way supported by the examination of the corresponding isotope profile obtained by Jouzel et al. (1983) from a sampling collected just beside ours. Indeed, we can observe during the 1958–1969 time period that the deuterium variations were rather badly marked (in comparison with other time sequences), suggesting a certain reworking effect. In any case, we would have preferred to dispose of a sampling undisturbed sequence to study an atmospheric phenomenon. Laird et al. argue that they have analyzed 3 replicate columns to discuss the variability of the nitrate content, whereas we have only one profile at our disposal. In reply, we'd like to point out that we have thoroughly investigated the contamination problems (Legrand et al., 1984; see also Fig. 2 in our 1986 paper) and that consequently our data set is free from large analytical uncertainties. These contamination problems are clearly addressed in Dreschhoff et al. (1983), but their effects on the interpretation of the  $\text{NO}_3$  profiles are most prob-

ably underestimated by these authors. For instance, we have obtained a fairly stable and low  $\text{NO}_3$  level ( $15 \pm 3 \text{ ng g}^{-1}$ ) for the entire Holocene time period at Vostok (Legrand et al., 1987), whereas Parker et al. (1982) found mean concentrations at the same location (deduced from the spline smoothing function) oscillating between 20 and  $55 \text{ ng g}^{-1}$ . Their method of discarding anomalously high values does not guarantee that the clean profile is free from analytical artefacts.

Another question is the common use made by Laird et al. of deposition fluxes instead of concentrations. When atmospheric concentration changes are studied, it seems clear that concentrations must be reported, if we consider that the concentrations in the precipitation are supposed to mimic the atmospheric concentrations. This is the base of atmospheric chemistry studies from precipitation analyses. It is clear that the air-snow correlation is more-or-less verified, according to additional phenomena during the scavenging or the dry deposition of atmospheric impurities (for  $\text{HNO}_3$  particularly, these processes are poorly understood). The variability of the  $\text{NO}_3$  fluxes depends not only on the amount of nitrate present in the snow, but also on the accumulation rates of snow which are also highly variable. The power spectrum found by Dreschhoff et al. (1983) would be linked to the precipitation rate and not to the precipitation nitrate concentration changes. This problem could be solved by such an analysis performed on both concentrations and deposition fluxes.

Laird et al. comment on our interpretation of Fig. 4 by using an argument ("a tropospheric source, whether it be from the oceans or from lightning will be the same over Antarctica") which is, in our opinion, not correct, since (1) the production of  $\text{NO}_3$  by lightning occurs throughout the troposphere whereas sea salt particles are produced at sea level, and (2) sea salt is in the form of particles whereas  $\text{HNO}_3$  is a gas. A good illustration of these different behaviours of atmospheric impurities may be found in the results obtained for Na and excess sulfate concentrations (mainly produced by oxidation of S compounds emitted from the sea surface) in the same samples. We found no direct relationship between the deposition of these 2 species (Legrand, 1985; Legrand and Delmas, 1985). Anyway the increase in nitrate concentration

poleward is not continuous, as attested by low concentrations found at Dome C and Vostok.

In the free troposphere, lightning-produced  $\text{HNO}_3$  is not removed rapidly by precipitation and is available for long-range transport. The importance of lightning as a source of  $\text{HNO}_3$  in remote areas is now widely recognized and quantified. As regards the ratio of the relative contributions of troposphere and stratosphere sources to Antarctic  $\text{NO}_x$  as calculated by Hameed et al. (1981), we point out that the 5:1 figure reported by Laird et al. represents the source ratio (stratosphere:troposphere), whereas the 1:1 ratio we have considered reflects the actual contribution at 90°S, taking into account sources, sinks and transport. Moreover the 1:1 ratio was calculated assuming a strong latitudinal dependence on the  $\text{NO}_x$  downward flux from the stratosphere (in favor of the high latitudes), a dependence which is a matter for serious discussion (see not only Sanak et al. (1985) but also Raisbeck et al. (1981)). Finally Ko et al. (1986) using a 2-D model, demonstrate that lightning sources contribute significantly to the tropical  $\text{NO}_x$  budget in the lower stratosphere. This is the result of the diabatic circulation which provides this layer with  $\text{NO}_x$ -rich air from the tropical mid-troposphere, which then allows these  $\text{NO}_x$  to be transported poleward. Consequently, we maintain our conclusion regarding the relative importance of the lightning with respect to the stratosphere sources.

We have chosen a production rate of 1.25 NO molecules per ion pair created, which can be considered as a lower limit. Laird et al. have chosen 2.5 NO molecules per ion pair as a better estimate. The resulting figures are reported in Fig. 7 of our 1986 paper and in Fig. 1 of Laird et al.'s *Letter to the Editor*. The comparison of the two figures leads to the conclusion that the phenomena occurring in the stratosphere only slightly modulate the stratospheric  $\text{NO}_x$  production after the 11-year solar cycle. On the other hand, larger variations may be introduced sporadically by SPEs. The only possibility for finding an 11-year solar cycle in Antarctic snow would be to appeal to the thermospheric (and/or mesospheric) production of NO by solar cosmic rays as Laird (1983) did. We commented on this source in Legrand and Delmas (1986), but discarded it on the basis of the Jackman et al. (1980) paper.

In conclusion, we have no reason to be against the finding of the 11-year solar cycle in Antarctic snow. On the contrary, this would give a new impetus to glaciochemical research. However, we estimate that Laird et al.'s measurements have, until now, provided no clear evidence of such an effect. Moreover our own data point to a contrasting conclusion. On the other hand, the impact of the solar modulation on the stratospheric  $\text{NO}_x$  sources is very difficult to assess by calculation only and the question of the relative importance of a thermospheric  $\text{NO}_x$  production is still open.

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