matters arising

Non-biogenic fixed nitrogen in Antarctic surface waters

PARKER ET AL.¹ have reported measurements of the fixed nitrogen content of Antarctic ice core samples, and calculate an annual input to the Antarctic ice sheet of 27×10^6 kg(N). Following Wilson and House², Parker *et al.*¹ suggest auroral activity as one possible source of this fixed nitrogen.

Auroral activity may produce $\sim 4 \times$ 10° kg (N) per yr during sunspot maximum (I assume 100 h of IBC Class II aurora per yr, extending over both polar caps, of total area 7×10^7 km² (ref. 3), a production of one ion pair per 35 eV energy input, and 1.3 NO molecules produced per ion pair⁴). This auroral nitrogen fixation occurs in the 70-90 km altitude range, and I do not consider it likely that a large fraction of the nitrogen fixed here will reach the surface because the photochemical lifetime of NO above 40-50 km is significantly shorter than the mean transport time down to this altitude (several days compared with a few weeks). At altitudes below 40 km or so NO has a very long photochemical lifetime, of the order of years, comparable to the mean transport time for an inert tracer to move from these altitudes down to sea level. This long transport time implies a uniform worldwide distribution, and the Antarctic represents approximately 3% of the total surface area of the Earth, so that in the absence of photochemical destruction the auroral source would deposit $\sim 8 \times$ 10^8 kg(N) per yr on Antarctica. I estimate (but cannot prove without a detailed calculation) that photochemical destruction may reduce this by perhaps two orders of magnitude on account of the ratio of photochemical to transport times in the lower mesosphere.

However, galactic cosmic ray ionisation produces $\sim 2 \times 10^7$ kg(N) per yr in NO molecules over each polar cap, principally at altitudes between 10 and 20 km. Formation of nitric acid and subsequent precipitation scavenging provides a mechanism for bringing this fixed nitrogen to the ground. Admittedly, the polar caps in this context extend well beyond the Antarctic continent³, but the atmospheric associated circulation with the meteorological polar cell will bring much of this material down to the ground near Antarctica. Galactic cosmic ray ionisation has a maximum at sunspot minimum, so that 11-yr modulation of variation by a factor of two would be expected.

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Institute for Defense Analyses, 400 Army-Navy Drive, Arlington, Virginia 22202

Artingion, Virginiu 22202

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PARKER ET AL. recently claimed that inorganic nitrogen-laden ice originating on the Antarctic continent might provide a major contribution to the nitrogen budget for the epipelagic zone of the Southern Ocean located south of the Antarctic convergence¹. They calculated annual inputs via continental ice for NO3-N and NH₄-N of 2.73×10⁴ tonnes and 1.88×10^4 tonnes, respectively. Assuming an average concentration for surface NO₃-N of 2.7 μ g l⁻¹ and an upper mixed laver volume of $50 \text{ m} \times 14 \times 10^6 \text{ km}^2 =$ 7×10^{17} l, they estimated the total NO₃-N in the upper mixed layer at 19×10^5 tonnes, and concluded that 7% of this total is injected annually by the melting of Antarctic continental ice.

This estimated input of non-biogenic fixed NO₃-N, 2.73×10^4 tonnes $\div 19 \times 10^5$ tonnes, is mathematically equivalent to about 1% of the estimated total NO₃-N in the upper mixed reservoir, however, rather than 7% as reported by Parker et $al.^{1}$. While it might be argued that an input of non-biogenic fixed NO₃-N which is 1% of the epipelagic reservoir standing total should not be dismissed from budget calculations, I suggest that the total NO₃-N in the reservoir has been underestimated in the calculation of Parker et al., and that the input of NO₃-N from continental ice is more nearly equivalent to about 0.02% of the upper mixed layer total and can be ignored.

The estimate made by Parker et al. of 2.7 μ g l⁻¹ (range 0.02-21.4 μ g l⁻¹) for mean NO₃-N concentration of Antarctic circumpolar surface water was derived from summary data tabulated as part of the Antarctic Map Folio series². A comparison with the source nutrient data for this series^{3,4} and with a second tabulation of the same data⁵, however, demonstrates that the units of nutrient concentration were incorrectly given in the Folio series as $\mu g l^{-1}$ when they, in fact, represent μ g-atm l⁻¹ concentrations. Assuming a mean surface NO₃-N concentration of $12 \,\mu g$ -atm l⁻¹ (168 µg NO_3-NI^{-1}) then, the amount of NO_3-N in the epipelagic Antarctic region can be recalculated at 7×10^{17} l × 168 µg l⁻¹÷ $10^{12} \,\mu \text{g tonne}^{-1} = 1.18 \times 10^8 \text{ tonnes.}$ The estimated annual input of NO₃-N from

continental ice¹ is thus 0.02%, or a minor component of the estimated reservoir standing total.

Parker et al. did not undertake a similar calculation for the relative contribution of non-biogenic fixed NH₄-N derived from continental ice, as little information on epipelagic NH4-N levels in the Southern Ocean is available in the literature¹. Recently, I measured water column NH4-N concentrations at 16 oceanographic stations in the Ross Sea and south of the Antarctic convergence, NH₄-N was assayed by a modified Solorzano phenolhypochlorite method⁶ aboard USCGC Glacier during December 1977-January 1978. Water samples taken in 5-1 Niskin bottles were filtered through $0.45 \,\mu m$ GF/A filters, fixed with phenol alcohol, refrigerated, and analysed within 24-48 h of collection, using a 10-cm path length in a Bausch & Lomb model 710 spectrophotometer. Surface NH₄-N concentrations in ice-free areas averaged 0.1 μ g-atm l⁻¹ (range < 0.1-0.3), with higher concentrations of NH₄-N in subsurface maxima⁷. Subsurface NH₄-N maxima generally occurred deeper than 50 m, and I here assume that $0.1 \,\mu\text{g-atm}\,l^{-1}$ is representative of NH₄-N concentrations in the upper mixed layer. Using Parker et al.'s estimate of 7×10^{17} l for volume of the upper mixed layer¹, I calculate a reservoir total for NH₄-N of 7×10^{16} µg-atm, or 1.2×10^6 tonnes. Thus, the estimated annual input of non-biogenic fixed NH⁴-N from continental ice¹ is mathematically equivalent to about 2% of my estimated reservoir total.

While the input of NH₄-N derived from continental ice, as a percentage of its reservoir total, is proportionally larger than the input of NO₃-N derived from continental ice as a percentage of its reservoir total, the former is apparently much less than the biogenic input of NH₄-N. For example, a conservative estimate is that 500 million tonnes of krill (Euphausia superba) are produced annually in the Southern Ocean^{8,9}. Ammonia is the primary nitrogenous waste of planktonic crustacea¹⁰⁻¹⁴, and shipboard measurements of NH_4 -N excretion by individual Antarctic euphausiids⁷ suggest that this amount of krill alone might excrete approximately $1.1 \times 10^{16} \,\mu g$ -atm NH₄-N d^{-1}

Daily NH₄-N excretion by krill, then, may represent about 8 times the annual non-biogenic input of NH₄-N from continental ice¹, or about 16% of my estimated epipelagic reservoir NH₄-N total. If one assumes that krill, which live primarily in epipelagic Antarctic waters as adults^{8,9,15}, excrete their NH₄-N wastes exclusively there, it follows that NH₄-N in