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SHORT CONTRIBUTION

$^{15}N/^{14}N$ ratios of NO_x from vehicle engines and coal-fired power stations

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ABSTRACT

Preliminary data are presented for the $^{15}N/^{14}N$ ratios of the two main sources of anthropogenic NO_x. Contrary to expectation, the $\delta^{15}N$ values of NO_x emitted from vehicle exhausts (-13 to -2‰) and coal-fired boilers ($+6$ to $+13$‰) are different from the isotopic composition of the nitrogen in their fuel + air mixtures (~ 0‰). These differences may reflect variable effects of kinetic isotopic fractionation in the formation (vehicles) and destruction (boilers) of NO, and have important consequences for the use of nitrogen isotopes in atmospheric studies.

1. Introduction

Because nitrogen compounds play such an important role in the chemistry and pollution of the atmosphere, several studies have been directed towards an examination of their $^{15}N/^{14}N$ ratios (Hoering, 1957; Moore, 1977; Freyer, 1978; Heaton, 1986, 1987). The interpretations of these studies, however, require information on the isotopic composition of the NO_x gases (NO and NO_2), for which very few data are available.

The major sources for the anthropogenic emission of NO_x are vehicles and coal-fired power stations. The nitrogen in their fuel + air combustion mixtures is either atmospheric N_2 (in vehicles) or atmospheric N_2 plus coal-nitrogen (in power stations). In both cases, this source nitrogen has a $\delta^{15}N$ value which is equal to or close to 0‰: $\delta^{15}N = 0$‰ for atmospheric N_2, $\delta^{15}N$ = typically -2 to $+3$‰ for coals (see footnote to Table 1 for definition of $\delta^{15}N$). It has therefore been assumed that the NO_x gases formed by oxidation of this nitrogen will also have $\delta^{15}N$ close to 0‰ (Freyer, 1978; Heaton, 1987). Whilst a $\delta^{15}N$ value close to 0‰ for the anthropogenic emissions of NO_x was partially supported by two earlier measurements of vehicle exhausts ($\delta^{15}N = -1.8$ and $+3.7$‰ (Moore, 1977; Freyer, 1978)), subsequent analyses of vehicle NO_x suggested a wider range ($\delta^{15}N = -13$ to -2‰, and a single analysis of NO_x from a power station yielded $\delta^{15}N = +5$‰ (Heaton, 1987)). I therefore present $^{15}N/^{14}N$ ratio data for NO_x from a further four vehicle exhausts and four power station emissions, and suggest possible mechanisms whereby the major sources of anthropogenic NO_x may have $\delta^{15}N$ values which are not close to 0‰. The new data are discussed in conjunction with the earlier data presented, but not discussed, in Heaton (1987).

2. Analytical method and precision

Gases were sampled from the exhaust pipes of test-bed and road vehicle engines at Pretoria (altitude = 1300 m, no catalytic convertors) and from downstream of the electrostatic precipitators of coal-fired boilers generating steam for electric power stations on the Transvaal Highveld

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(altitude = 1600 m). In each case, the gases were collected in one or more 17 l glass or 70 l polythene containers to which a solution of $NaOH + H_2O_2$ was then added. The sealed containers were left to stand, with occasional shaking, for 5–10 days. After destruction of H_2O_2 by boiling, the $NO_3^- + NO_2^-$ derived from NO_x was quantitatively converted to N_2 gas using the conventional Devarda's alloy and Rittenberg reaction steps (Heaton and Collett, 1985). Manometric measurement of the yield of N_2 allowed calculation of the concentration of NO_x. The $^{15}N/^{14}N$ ratios of the gas, determined on a VG SIRA 24 mass spectrometer, are expressed relative to that of atmospheric N_2 in the usual $\delta^{15}N$ (‰) notation (footnote to Table 1).

The reproducibility, based on the analysis of solutions from different containers filled at the same source, was ±1‰ in $\delta^{15}N$ and ±30 ppm in concentration. In contrast, when duplicate analyses were performed on splits of a solution from a particular container, the reproducibility was ±0.5‰ (and ±10 ppm in concentration), which is closer to the ±0.2‰ precision normally attainable for the analysis of NO_3^- solutions (Heaton and Collett, 1985).

Experiments on 70 l containers filled with pure N_2 plus small quantities of NO of known isotopic composition, using an analytical method identical to that employed for the NO_x samples, indicated an accuracy of ±1‰ in $\delta^{15}N$. Thus, whilst there is clearly room for improvement in the method used in collecting NO_x and converting it to $NO_3^- + NO_2^-$ in solution, I am confident that the $\delta^{15}N$ values reported here are correct to within about ±1‰. In view of the unexpected range of values, this is quite adequate for the purposes of this discussion.

3. Results and discussion

Vehicle engines running under heavy load yielded high NO_x concentrations with $\delta^{15}N = -2$‰ (Table 1), which is similar to the value of −1.8‰ reported by Freyer (1978). Under reduced load, however, the $\delta^{15}N$ values for vehicles decline to as low as −13‰. In contrast, all the NO_x samples from coal-fired boilers had positive $\delta^{15}N$ values between +6 to +13‰ (Table 1). Thus the two major sources of anthropogenic NO_x have quite distinct ranges of $\delta^{15}N$ values, and in many cases these values are different from 0‰.

Table 1. *$^{15}N/^{14}N$ ratios of vehicle engine and power station NO_x*

Source	NO$_x$	
	$\delta^{15}N$ (‰)[*1]	ppm (V)[*2]
Vehicle engines[*3]		
(type, speed, load)		
engine 1: 2500 rpm, 214 Nm	−2	—
engine 2: 1720 rpm, 210 Nm	−2	1550
engine 3: 2800 rpm, 165 Nm	−2	1960
engine 2: 2000 rpm, 154 Nm	−7	1000
engine 1: 3200 rpm, 40 Nm	−11	940
engine 4: 2000 rpm, idle	−7	190
engine 5: 1000 rpm, idle	−12	100
engine 6: 1000 rpm, idle	−13	130
Coal-fired power stations[*4]		
Kriel, boiler 5		
(coal $\delta^{15}N = +1.1$‰)	+13	350
Kriel, boiler 2		
(coal $\delta^{15}N = +1.2$‰)	+9	350
Dhuva, boiler 1		
(coal $\delta^{15}N = +1.0$‰)	+12	—
Kelvin, boiler 15	+8	260
Rooiwal, boiler 5	+6	280

[*1] $\delta^{15}N\ (‰) = \left(\frac{(^{15}N/^{14}N)_{\text{sample}}}{(^{15}N/^{14}N)_{\text{standard}}} - 1\right) \times 10^3$. The standard is atmospheric N_2.

[*2] NO_x concentrations for power stations are approximate.

[*3] Engine numbers: 1 = test-bed 1.6 l petrol; 2 and 3 = test-bed 3.9 l diesels; 4 = 1.4 l petrol; 5 and 6 = 3.0 l diesel.

[*4] Boiler types: Kriel = wall-fired, 500 MW; Dhuva = wall-fired, 600 MW; Kelvin = wall-fired, 48 MW; Rooiwal = tangentially-fired, 48 MW.

The mechanisms for the formation of NO_x in vehicles and power stations have been reviewed by a number of authors (Bowman, 1975; Heywood, 1976; Hayhurst and Vince, 1980; Wendt, 1980). The following discussion suggests, in a brief and highly simplistic fashion, possible isotopic "fractionation" processes which may account for the $\delta^{15}N$ values for NO_x shown in Table 1.

3.1. Vehicle engines

The nitrogen content of petrol and diesel fuels is negligible. Essentially all the NO_x is therefore derived by the production of "thermal NO" from atmospheric N_2 at high temperatures (>2000°C). Under conditions of chemical and isotopic equilibrium at high temperatures:

$$N_2 + O_2 \rightleftharpoons 2NO.$$

Theory predicts that the isotopic fractionation should be very small (Urey, 1947). The NO should therefore have a $\delta^{15}N$ value very similar to that of atmospheric N_2, i.e., close to 0‰.

In many cases, however, the combustion mixture in a vehicle engine does not achieve equilibrium. The rate of NO formation is kinetically limited by the high energy required for rupturing the triple bond of the N_2 molecule:

$$N_2 + O \rightarrow NO + N. \qquad (1)$$

The rate of reaction for the lighter molecule ($^{14}N^{14}N$) will tend to be faster than that for the heavier molecule ($^{15}N^{14}N$). If the difference between these isotopic reaction rates is significant at high temperatures, then the NO will tend to have $^{15}N/^{14}N$ ratios lower than that of atmospheric N_2, i.e., negative $\delta^{15}N$ values.

The relative importance of equilibrium versus kinetic conditions will depend on the operation of the engine. Under heavy load, for example, a closer approach to equilibrium (and higher NO_x concentrations) is promoted by higher peak combustion temperatures and a longer reaction time (advance of spark ignition). This may explain why NO_x from engines under load has $\delta^{15}N$ values close to 0‰, reflecting a greater degree of equilibrium, whilst engines at idle have lower $\delta^{15}N$ values, reflecting the influence of kinetic isotope fractionation.

3.2. Power stations

In coal-fired power stations, where the combustion temperatures (about 1300–1400°C) are too low for the formation of significant amounts of thermal NO, most of the NO_x is derived from the coal as "fuel NO". Transvaal coals typically contain 1.4 to 1.8% nitrogen, and the $\delta^{15}N$ values for the coal used in firing the boilers sampled in this study were +1.0 to +1.2‰ (Table 1). This organic nitrogen is decomposed in the flame to form reactive compounds such as N, NH, HCN, etc. which, on reaction with oxygen-containing radicals, form NO. The reaction sequence is sufficiently rapid to be completed in the flame zone. If no isotopic fractionation occurs during its formation, the fuel NO should have an isotopic composition similar to that of the nitrogen in the coal.

After combustion, however, the NO concentration declines by reactions analagous to the reverse of reaction (1):

$$NO + N \rightarrow N_2 + O \qquad (-1)$$

for which, in contrast to reaction (1), the reaction rate is relatively rapid at post-combustion temperatures. If the rate of destruction of ^{14}NO is faster than that of ^{15}NO the remaining NO will become progressively enriched in ^{15}N. This could account for power station NO_x having positive $\delta^{15}N$ values (Table 1), higher than those of the fuel nitrogen.

4. Conclusions

It must be emphasised that the above discussion is simplistic, and serves only to indicate possible processes which might produce NO_x having $^{15}N/^{14}N$ ratios which are lower (in vehicles) or higher (in power stations) than the ratios of the nitrogen in their fuel + air mixtures. A full study of how the operating conditions of vehicle engines and coal-fired boilers influence the isotopic composition of NO_x is probably of more relevance to the combustion engineer.

Whichever processes are responsible, the data in this report cast doubt on the general validity of assuming that the $\delta^{15}N$ value of anthropogenic NO_x is close to 0‰. In an urban area it appears that the mean isotopic composition of the total emitted NO_x will probably depend on both the proportions of vehicles and power stations, and on their operating conditions.

Since there is no apparent overlap in the range of $\delta^{15}N$ values for NO_x from vehicles and power stations one must expect a difference between the average, "typical" value for each type of source. The characterization of a typical value for vehicle engines could be achieved by sampling test-bed engines run through representative driving cycles, and a similar approach might also be attempted for coal-fired boilers.

It appears from Table 1 that typical $\delta^{15}N$ values for vehicles and power stations may differ by as much as 10‰, and this points to the possibility of using $^{15}N/^{14}N$ ratio analyses as a means of tracing the source of atmospheric NO_x. The validity of such an application, however, would be very dependent on whether or not NO_x undergoes a significant change in its isotopic composition during the course of atmospheric chemical reactions after its emission.

Finally, it should be stressed that some sources of anthropogenic NO_x may have "unusual" isotopic compositions. The stack of a nitric acid plant in a fertilizer/explosives factory near Johannesburg, for example, emits 2800 ppm NO_x with $\delta^{15}N = -150‰$ (Heaton, 1987); a result of the type of isotopic fractionation processes described by Taylor and Spindel (1958). Whilst this type of source is small in terms of the total regional inventory of NO_x, it may have a measurable effect on the isotopic composition of the local NO_x.

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