An overview of possible processes able to account for the occurrence of nitro-PAHs in Antarctic particulate matter

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AN OVERVIEW OF POSSIBLE PROCESSES ABLE TO ACCOUNT FOR THE OCCURRENCE OF NITRO-PAHs IN ANTARCTIC PARTICULATE MATTER

Claudio Minero, Valter Maurino, Daniele Borghesi, Ezio Pelizzetti, Davide Vione*

Dipartimento di Chimica Analitica, Università di Torino, Via Pietro Giuria 5, 10125 Torino, Italy. *www.environmentalchemistry.unito.it*

* Corresponding author:

Davide Vione

Dipartimento di Chimica Analitica

Università di Torino

Via Pietro Giuria, 5

10125 Torino, Italy

Phone: (39)-0116707874

Fax: (39)-0116707615

e-mail: *davide.vione@unito.it*

Abstract

This paper gives an overview of the processes that can account for the occurrence of mononitro-PAHs (1-nitronaphthalene –1NN–, 2-nitronaphthalene –2NN–, 9-nitroanthracene) in the Antarctic particulate matter. Long-range transport of these compounds from the continents to the Antarctica seems an unlikely possibility given the photolability of 1NN and 2NN. The alternative possibility is that nitration takes place *in situ*. The nitration of naphthalene is very likely to occur in the gas phase, because the parent compound is too volatile to be present in particulate matter, even at the low temperatures of the Antarctic summer near the coast. In contrast, the volatility of anthracene is sufficiently low under such conditions to allow this compound to be present in particles at a significant concentration. The field data on nitronaphthalene ratios, together with an evaluation of their removal rates, indicate that the gas-phase nitration of naphthalene is more likely to be initiated by $^{\bullet}NO_3 + {^{\bullet}}NO_2$ (yielding 1NN:2NN $\approx$ 2.5:1) than by $^{\bullet}OH + {^{\bullet}}NO_2$ (yielding 1NN:2NN $\approx$ 1:1). Nitronaphthalenes, less volatile than the parent compound, can then be found in particulate matter. In contrast, the occurrence of 9-nitroanthracene could be consistent with an electrophilic, condensed-phase nitration process.

Keywords: Gas-phase nitration; Nitration in particles; Nitronaphthalene; 9-Nitroanthracene.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their nitroderivatives (nitro-PAHs) are compounds of concern for their possible impact on human health and the environment [1-4]. They are present in significant concentration in urban areas but have been detected also in remote locations, suggesting a likely world-wide distribution [5,6]. Nitro-PAHs can be formed upon atmospheric nitration of the parent PAHs, and different processes are possible under atmospheric conditions: gas-phase daytime nitration by $^{\bullet}OH + {^{\bullet}}NO_2$, gas-phase night-time nitration by $^{\bullet}NO_3 + {^{\bullet}}NO_2$, and condensed-phase nitration processes (in the presence of HNO_3, nitrogen dioxide, nitrate, and nitrite) [5,7-12]. Our research group has detected for the first time the nitro-PAHs in Antarctic particulate matter during the austral summer, thus giving additional evidence of their global distribution [13]. The presence of these compounds can be accounted for by either transport from the continents or *in situ* formation. However, the identified nitro-PAHs (in particular 1- and 2-nitronaphthalene, which undergo very fast photolysis in the atmosphere, making long-range transport very unlikely [14]) suggest the presence of an efficient formation process *in situ*. Furthermore the concentration values of nitro- and dinitronaphthalenes, with a high relative amount of the dinitroisomers, seem incompatible with the direct nitroderivative emission upon combustion processes [13].

Field data suggest the existence of one or more nitration processes in the Antarctic troposphere [13]. This paper is an attempt to use the available data concerning nitroaromatic formation to put

constraints on the possible processes leading to the nitro-PAHs in the Antarctic particulate matter. The results could give insight into the chemistry of the Antarctic troposphere, and the processes occurring in particulate matter in remote areas. The present work discusses literature data concerning the nitration of naphthalene and anthracene, and the phase partitioning of these compounds and of their nitroderivatives. The discussion is supported by novel experimental data concerning the transformation of 1- and 2-nitronaphthalene (1NN, 2NN) upon nitrate photolysis, and the formation of nitrogen dioxide upon irradiation of solid nitrate. The relevant experiments are described in the "Materials and methods" section.

The discussion here will be limited to the detected mononitro-PAHs, because insufficient data are presently available to account for the occurrence of the dinitronaphthalenes, also detected in the Antarctic samples [13].

2. Materials and methods

2.1. Reagents

$NaNO_3$ (purity grade 99.5%) and $NaH_2PO_4 \times H_2O$ (> 99%) were purchased from Merck, 1-nitronaphthalene (99%) and 2-nitronaphthalene (85%) from Aldrich, acetonitrile (supergradient HPLC grade) from Scharlau, N_2 (99.998%) and O_2 (99.6%) from SIAD. All reagents were used as received, without further purification.

2.2. Procedures and instrumentation

2.2.1. Liquid-phase experiments

The transformation of 1NN and 2NN was studied upon UVB irradiation of nitrate in aqueous solution. The solutions (5 mL) were introduced into Pyrex glass cells (4.0 cm diameter, 2.3 cm height), and magnetically stirred during irradiation. As radiation source a UVB Philips TL 01 lamp was used, with emission maximum at 313 nm, producing a photon flux of 1.3×10^{-7} Ein s^{-1} in the cells, actinometrically determined with the ferrioxalate method [15]. After irradiation the solutions were analysed by HPLC, using a Merck-Hitachi chromatograph equipped with a model L4200 UV-Vis detector, L6200 and L6000 pumps for high-pressure gradients, and a Rheodyne 7125 manual injector (loop volume 54 μL). Elution was carried out with a 50:50 mixture of acetonitrile and aqueous phosphate (0.020 M NaH_2PO_4, pH 4.5), at 1.0 mL min^{-1} flow rate. The column used was a Merck RP-C18 LiChrocart (length 125 mm, diameter 4 mm), packed with LiChrospher 100 RP-18 (particle diameter 5 μm). Under such conditions the retention times were: 1-nitronaphthalene (1NN) 8.0 min, 2-nitronaphthalene (2NN) 9.0 min, column dead time 0.9 min. Detection wavelength was 210 nm. Further experimental details are reported elsewhere [16,17].

2.2.2. Gas-solid experiments

The formation of nitrogen dioxide was studied upon irradiation of solid nitrate. Solid $NaNO_3$ was prepared by evaporation of 25 mL of a 0.8 M solution (total weight 1.7 g), so as to obtain a finely and homogeneously deposited solid on a Petri dish (11 cm diameter). Irradiation was carried out in a 70 L stainless-steel reaction chamber, especially designed to study gas-solid photoreactions. Details of the chamber are given elsewhere [18]. The atmosphere (N_2/O_2) inside the chamber was obtained by mixing the high-purity gases (provided by SIAD, Bergamo, Italy) by means of an Entech model 4560 SL dynamic diluter. The relative humidity was regulated upon injection of Milli-Q water inside the chamber. Irradiation was carried out with a Philips HPR 125 W HG mercury lamp. The radiation emission by the lamp on the Petri dish was about 9 W m^{-2} for λ between 290 and 400 nm, measured with a CO. FO. ME. GRA. (Milan, Italy) power meter. The sampling and analysis of nitrogen dioxide was carried out with an Horiba model APNA-360 Ambient Monitor NO_x analyser.

3. Results and Discussion

3.1. Nitronaphthalenes

This section contains a discussion of previous literature data, supported by experimental results obtained as described previously, with the purpose of accounting for the occurrence of mononitronaphthalenes in the particulate matter in the Antarctica.

1-Nitronaphthalene (1NN) and 2-nitronaphthalene (2NN) are the most abundant nitro-PAHs found in the Antarctic particulate matter. Their concentration values range from 2 to 200 fg m^{-3}. The concentration ratio between 1NN and 2NN varied from about 1:1 to 2:1 according to the sample [13]. The detection of nitronaphthalenes in particles is an interesting result, because these compounds are usually present in the gas phase under typical temperate climate [14]. In the Antarctica, however, the low temperature of the atmosphere favours the occurrence of these compounds in the airborne particulate matter. The fact that 1NN and 2NN are the most abundant nitro-PAHs in Antarctic particles can be accounted for by two factors: *(i)* they are the most abundant nitro-PAHs also at temperate latitudes, just in this case they are not found in particulate matter; *(ii)* the parent PAHs may possibly derive from transport from the continents, which might favour the molecules with the highest vapour pressure, such as naphthalene [13]. Long-range transport of 1NN and 2NN from the continents to the Antarctica seems rather unlikely, because the atmospheric lifetime of these compounds under temperate conditions is only 1-2 hours due to photolysis [14].

To gain insight into the process leading to nitronaphthalene formation, some indications concerning the partitioning of naphthalene and derivatives between atmospheric phases would be of use. The vapour pressure of the solid would be a useful indicator of partitioning, but unfortunately the

available data do not cover the desired temperature range for the compounds under study. Sufficiently extended data exist for the Henry's Law coefficient k_H [20], which measures the partitioning of a given compound between the gas and the aqueous phase. The coefficient k_H is actually useful for the evaluation of partitioning between the aqueous phase, not particulate matter, and the gas phase, but in the absence of other indicators it can be adopted as a first approximation. The Henry's Law coefficient is the ratio between the concentration of the compound in the aqueous phase (in mol L^{-1}) and its partial pressure in the gas phase (in atm). The coefficient k_H varies with temperature according to the following law [20]:

$$k_H = k_H^{\otimes} \cdot exp\left[\frac{-d\ln k_H}{d(1/T)} \cdot \left(\frac{1}{T^{\otimes}} - \frac{1}{T}\right)\right] \qquad (1)$$

where $k_H^{\otimes}$ is the Henry's Law coefficient at the temperature $T^{\otimes}$, T the temperature in Kelvin, and d $\ln k_H$ / d (1/T) is the temperature dependence (in Kelvin). In the case of naphthalene, assuming $T^{\otimes}$ = 298.15 K, it is $k_H^{\otimes} \approx 2$ mol L^{-1} atm^{-1} and d $\ln k_H$ / d (1/T) = 3600 K [20]. It would mean that, for naphthalene, $k_H \approx 6$ at 273.15 K (0 °C). These data indicate that naphthalene is far too volatile to be present in significant amount in particulate matter, even at the low temperatures of the Antarctic summer. Indeed, compounds that can be found at reasonable levels in particles have k_H values of about 100 or more [20]. The nitration of naphthalene is thus likely to occur in the gas phase, followed by deposition of the nitronaphthalenes into particulate matter. Note that deposition can take place both in the air and, during sampling, from the incoming air into the particles already collected on the filter.

By contrast, occurrence in particles would be possible for anthracene ($k_H^{\otimes} \approx 30$ mol L^{-1} atm^{-1}, d $\ln k_H$ / d (1/T) = 4000 K, resulting in $k_H \approx 100$ at 273 K), pyrene ($k_H^{\otimes} \approx 80$ mol L^{-1} atm^{-1}, d $\ln k_H$ / d (1/T) not available), and fluoranthene ($k_H^{\otimes} = 110$ mol L^{-1} atm^{-1}, d $\ln k_H$ / d (1/T) = 6990 K, giving $k_H \approx 950$ at 273 K) [20].

Among the known gas-phase nitration processes, that involving $^{\bullet}OH$ + $^{\bullet}NO_2$ gives 1NN and 2NN with equal but low yield (0.3% each), while $^{\bullet}NO_3$ + $^{\bullet}NO_2$ give 1NN with 17% and 2NN with 7% yield [14]. Concentration data of nitronaphthalenes in the Antarctic particulate matter indicate that 1NN:2NN = 1-2 [13], consistent with both processes, although the $^{\bullet}NO_3$ + $^{\bullet}NO_2$ one has a far higher yield. The concentration data have however to be corrected for the partitioning and degradation of the nitronaphthalenes. Henry's law coefficient data for 1NN and 2NN are unfortunately not available, but some indication may come from compounds with similar structure. 1-Methylnaphthalene has $k_H^{\otimes}$ = 2.7 and 2-methylnaphthalene $k_H^{\otimes}$ = 2.0 mol L^{-1} atm^{-1}. Furthermore, the different nitrotoluene isomers have very similar $k_H^{\otimes}$ values: 17 mol L^{-1} atm^{-1} for 2-nitrotoluene, 14 for 3-nitrotoluene, and 16 for 4-nitrotoluene [20]. The values of the Henry's law coefficient are quite different for 2- and 4-nitrophenol [20,21], but in this case the effect is due to an intra-molecular hydrogen bonding that makes 2-nitrophenol much more hydrophobic than 4-

nitrophenol. Hydrogen bonding being absent in the case of the nitronaphthalenes, limited difference can be expected between the $k_H^{\otimes}$ values of 1NN and 2NN. This suggests that the two isomers are likely to undergo partitioning to a similar extent, and that their concentration ratios in particulate matter are representative of the whole atmospheric ratios. This also means that the possible sampling bias, connected with the deposition of gas-phase 1NN and 2NN into the particles already collected on the filter, would not modify much the concentration ratio of 1NN to 2NN. Accordingly, while the absolute concentration values of 1NN and 2NN in the particles could be modified, the presumably similar partitioning of 1NN and 2NN is little likely to modify much their concentration ratio, which is the focus of the present discussion.

Because of formation and transformation processes, compounds on particles can reach a steady-state concentration arising from the formation-transformation budget. As a first approximation, the steady-state condition for each nitronaphthalene isomer (NN) would be given by the following expression:

$$\frac{d[NN]}{dt} = 0 = R_{f,NN} - k_{d,NN} \cdot [NN] \tag{2}$$

where $R_{f,NN}$ is the nitronaphthalene formation rate, $k_{d,NN}$ the pseudo-first order degradation rate constant, and [NN] the steady-state concentration. In the steady-state approximation, the concentration ratio of 1NN and 2NN in particulate matter would be:

$$\frac{[1NN]}{[2NN]} = \frac{R_{f,1NN}}{R_{f,2NN}} \cdot \frac{k_{d,2NN}}{k_{d,1NN}} \tag{3}$$

In this case the ratio $R_{f,1NN} \, R_{f,2NN}^{-1}$ would allow the assessment of the process leading to nitronaphthalene formation, but an estimate of the ratio $k_{d,1NN} \, k_{d,2NN}^{-1}$ is also required.

Particle deposition, photolysis, and reactivity in the particles are the most likely removal processes for nitronaphthalenes in the Antarctic atmosphere. In the case of particle deposition, it would be $k_{d,1NN} = k_{d,2NN}$. About photolysis, the half-life times of 1NN and 2NN at temperate latitudes have been evaluated as 1.7 and 2.2 hours, respectively, ranking nitronaphthalenes among the most reactive compounds as far as the direct photolysis processes are concerned [14]. In the Antarctica the half-life times are likely to be longer due to the lower solar irradiation, but the relative ratios are unlikely to change very much. A further decrease of the reactivity can be expected as a consequence of the occurrence of 1NN and 2NN in particles. Particle-bound compounds are expected to undergo photolysis to a lesser extent compared to those occurring in the gas phase [14], but again there is no reason to expect a substantial change in the relative reactivity. As a consequence, in the case of direct photolysis it would be $k_{d,1NN} > k_{d,2NN}$ and, from equation (3), $[1NN] \times [2NN]^{-1} < R_{f,1NN} \times R_{f,2NN}^{-1}$.

Among the other possible reactions that can take place in the particles, the photolysis of nitrate is an important one [18,22-24], in particular when considering the case of the Antarctica as can be inferred from the deposition data of the anions in the snow [25,26]. In analogy with nitrate photolysis in solution one can write [24]:

$$NO_3^- + h\nu + H^+ \rightarrow {}^\bullet NO_2 + {}^\bullet OH \qquad (4)$$
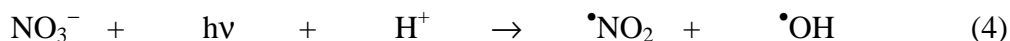
In the attempt to model nitronaphthalene degradation upon nitrate photolysis, we monitored the time evolution of 1NN and 2NN (initial concentration 10^{-5} M) upon UVB irradiation of 0.10 M NaNO$_3$. The corresponding curves are shown in Figure 1, indicating that under such conditions it is $k_{d,1NN} \approx 4\, k_{d,2NN}$.

An overview of the possible processes for the degradation of 1NN and 2NN indicates that $k_{d,1NN} \geq k_{d,2NN}$. Accordingly, from equation (3) it is $R_{f,1NN} \times R_{f,2NN}^{-1} \geq [1NN] \times [2NN]^{-1}$, where the observed ratio $[1NN] \times [2NN]^{-1}$ on particles is in the range 1-2. The ${}^\bullet OH + {}^\bullet NO_2$ process would yield $R_{f,1NN} \times R_{f,2NN}^{-1} \approx 1$, hardly compatible with field data, while in the case of ${}^\bullet NO_3 + {}^\bullet NO_2$ it would be $R_{f,1NN} \times R_{f,2NN}^{-1} \approx 2.5$, compatible with the condition $R_{f,1NN} \times R_{f,2NN}^{-1} \geq [1NN] \times [2NN]^{-1}$. Accordingly, the ${}^\bullet NO_3 + {}^\bullet NO_2$ pathway seems more likely to account for the occurrence of nitronaphthalenes in the Antarctic particulate matter. It is also more reasonable because of the higher yield (24% total nitronaphthalenes against 0.6% of the ${}^\bullet OH + {}^\bullet NO_2$ pathway [3]). The nitrate radical undergoes photolysis in the presence of sunlight [8], but its atmospheric lifetime is likely to be longer in the Antarctica than in temperate areas due to the lower irradiation intensity.
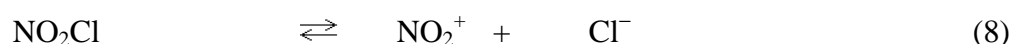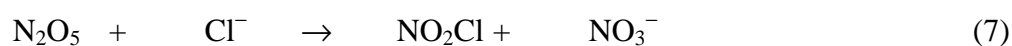
The occurrence of ${}^\bullet NO_2$ is required for the ${}^\bullet NO_3 + {}^\bullet NO_2$ pathway to be operational, also considering that ${}^\bullet NO_3$ is formed upon reaction between ${}^\bullet NO_2$ and ozone. An important source of nitrogen dioxide in the polar troposphere is represented by the irradiation of the snow layers, possibly because of the photolysis of nitrate [27,28]. The photolysis of aqueous nitrate yields nitrogen dioxide upon reaction (4). Figure 2 shows the time evolution of nitrogen oxides upon irradiation of solid NaNO$_3$ (1.7 g), finely dispersed on the surface of a Petri dish, under a simulated atmosphere (78% N$_2$ + 22% O$_2$) with 56% relative humidity, inside our gas-solid photoreactor. The main product of nitrate photolysis is nitrogen dioxide, while the small amount of nitric oxide is likely originated by photolysis of the nitrogen dioxide itself. The reported data show the possibility that nitrogen dioxide is generated upon photolysis of nitrate, also in the absence of an aqueous solution.

3.2. 9-Nitroanthracene

Differently from the case of nitronaphthalenes, only one nitrated isomer of anthracene (9-nitroanthracene, hereafter 9NA) has been detected in the Antarctic particulate matter. Furthermore, the concentration values are much lower compared to 1NN and 2NN, and included in the range 5-30 fg m^{-3}. This is possibly due to a decreasing occurrence of the parent compounds with increasing molecular weight, perhaps indicating that the less volatile compounds are less likely to undergo

transport to the Antarctica [19]. Phase partitioning data ($k_H^\otimes \approx 30$ mol L^{-1} atm^{-1}, $k_H \approx 100$ at 273 K), under conditions representative of the Antarctic summer climate, indicate that condensed-phase nitration processes are not unreasonable for anthracene. Moreover, 9NA is unlikely to be formed via gas-phase processes [14].

9NA has been detected in diesel exhaust, where it is likely to be formed upon high-temperature electrophilic nitration [14]. 9NA is also a product of electrophilic nitration in the atmosphere [29]. In the environment, electrophilic nitration processes can take place in the presence of HNO$_3$, N$_2$O$_5$, and NO$_2$Cl [30,31]:

$$HNO_3 + H^+ \rightarrow NO_2^+ + H_2O \qquad (5)$$
$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^- \qquad (6)$$
$$N_2O_5 + Cl^- \rightarrow NO_2Cl + NO_3^- \qquad (7)$$
$$NO_2Cl \rightleftharpoons NO_2^+ + Cl^- \qquad (8)$$

Electrophilic nitration in particulate matter is a reasonable possibility considering that the Antarctic aerosol is often acidic due to the presence of sulphuric acid, produced by oxidation of biologically generated dimethylsulphide [32,33]. The possibility of electrophilic nitration would be supported by the sporadic detection of 1-nitropyrene in some of the samples of Antarctic particulate matter [13]. 1-Nitropyrene is formed upon electrophilic nitration of pyrene [7], which can undergo partitioning to airborne particulate matter in the Antarctic summer climate ($k_H^\otimes \approx 80$ mol L^{-1} atm^{-1}). The sporadic detection of 1-nitropyrene can be accounted for by its concentration values, considerably lower than those of 9NA [13].

4. Environmental significance

This paper presents an overview of the possible nitration processes that can account for the occurrence of mononitro-PAHs in Antarctic particulate matter. The concentration data of these compounds, and the presence of the photochemically labile 1NN and 2NN in quite high concentration, constitute an argument in favour of the local origin of the Antarctic nitro-PAHs. In contrast, long-range transport from the continents seems unlikely [13]. The understanding of the nitration processes could give insight into the local atmospheric chemistry. The nitration of naphthalene is likely to take place in the gas phase, because this compound would undergo negligible partitioning to particles even at the low temperatures of the Antarctic summer. Among the gas-phase nitration processes, that initiated by $^\bullet NO_3$ seems more likely when considering the relative concentration values of 1NN and 2NN, and their possible phase partitioning and degradation processes. Such a pathway would require a source of nitrogen dioxide, which in the Antarctica could be the photolysis of solid nitrate, as suggested by our gas-solid photoreactor runs (Figure 2) and by field data [25-27].

The occurrence of 9NA might be compatible with a nitration process taking place in the particles. The nitration process could be electrophilic, which would also explain the occasional detection of 1-nitropyrene in the Antarctic particulate matter.

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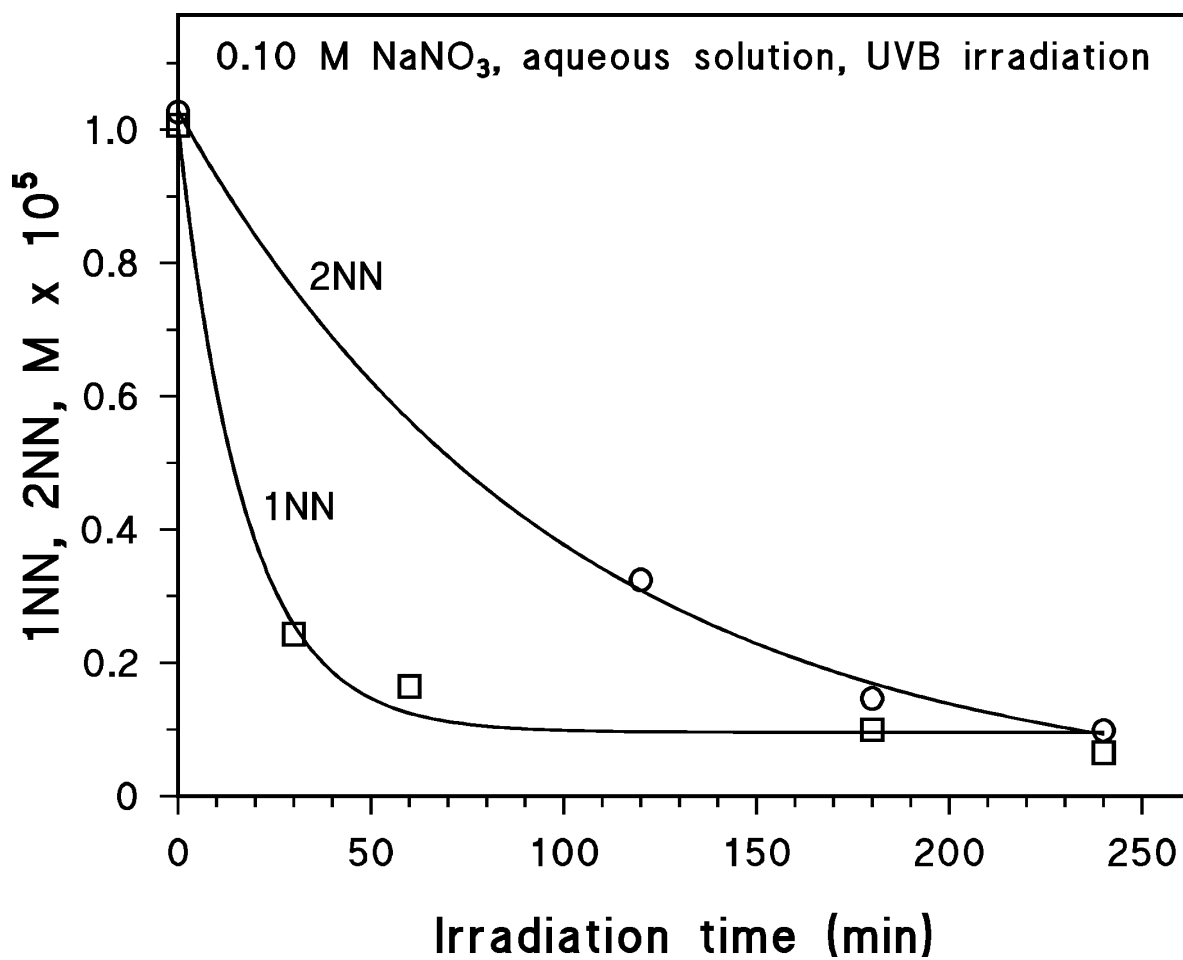**Figure 1.** Time evolution of 1NN and 2NN (initial concentration 1.0×10^{-5} M) in the presence of 0.10 M NaNO₃, UVB irradiation.
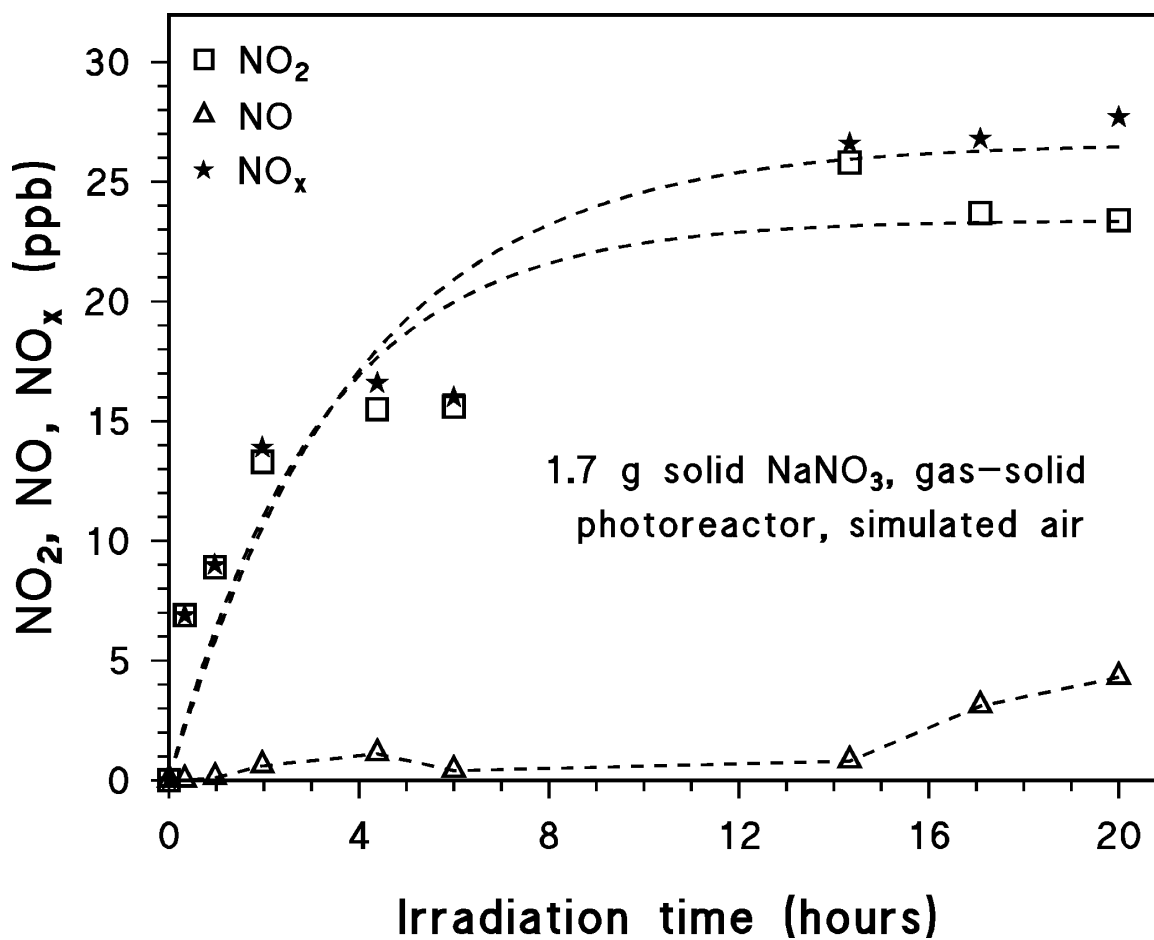
Figure 2. Time evolution of nitrogen dioxide, nitric oxide and total nitrogen oxides upon irradiation of solid NaNO₃ (1.7 g, finely dispersed on a Petri dish), under simulated air (78% N₂, 22% O₂) and 56% relative humidity, in the gas-solid photoreactor.