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# Constructing the European aerosol nitrate concentration field from quality analysed data

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## Abstract

We report on the construction of the aerosol nitrate concentration field in Europe from an interpolation of data. The first step was an active search for and a subsequent quality assessment of the (long term) data for this semi-volatile component, which is subject to a range of artefacts during sampling. Therefore first an overview of (filter) sampling methods in use in Europe and the associated sampling artefacts are presented. Denuder filter pack combinations have very minor artefacts and data obtained with this technique are therefore used as the starting point. Because of the paucity of data from these devices, values obtained with simple filter sampling were also considered after a critical analysis. We found that the largest artefact associated with inert filters (IF) (Teflon and Quartz) is evaporation of ammonium nitrate. Hence, concentrations obtained with the use of IF are lower values. Next, data from “total nitrate” filters were evaluated. Such filters collect both aerosol nitrate and nitric acid gas and the contribution of the gaseous compound was corrected for. The distances over which nitrate concentrations correlate was then analysed and it was found that in the winter half-year the correlation length was sufficiently long to warrant interpolation of the point data. The nitrate concentration field as obtained from interpolation of nitrate data in the period 1994–1997 was validated with intermediate point data from shorter lasting campaigns. The field has a large area of high nitrate concentrations ranging from southern England over continental western Europe into Poland, with concentrations of nitrate exceeding  $5 \mu\text{g m}^{-3}$ . Strong arguments are provided that the nitrate is predominantly present in the fine aerosol fraction (PM<sub>2.5</sub>). To the north nitrate concentrations range from  $2.5 \mu\text{g m}^{-3}$  in southern Sweden to  $<0.5 \mu\text{g m}^{-3}$  in mid-Scandinavia. To the east and west of the central European maximum the nitrate concentration trails off in a more gradual way. It was inferred that the concentration of nitrate in winter in Europe north of the Alps, with the exception of France from which country no data could be found, is 60% or more of that of sulphate. It should further be mentioned that in the Po-Valley ammonium nitrate levels are as high as those in western Europe. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Nitrate field; Sampling artefacts; Critical evaluation

## 1. Introduction

Nitrate could be an important component of the mass of the fine particles, PM<sub>2.5</sub>, in Europe (Heintzenberg et al., 1998; Kuhlbusch et al., 1999; EMEP, 1998; Chung, 2000). The reason for a growing interest in PM<sub>2.5</sub> is the discussion on a regulatory guideline for the maximum concentration of this parameter in the EU.

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The importance of the various components, and thus of nitrate, for the health hazard associated with PM<sub>2.5</sub> has yet to be established; for the time being regulation only considers total aerosol mass and nitrate is possibly an important contributor to this mass. However, the region in Europe where this applies has not been identified. Nitrate is also an acidifying component and a nutrient and the extent of the nitrate field is thus also of interest for the environmental topic of acid deposition and eutrofication.

Apart from the mentioned issues, fine aerosol particles play a major role in climate change, by reflecting solar radiation. In the central IPCC report on this effect (IPCC, 1996) only sulphate and carbon are considered, but in the Netherlands nitrate appears to be as important as the indicated aerosol components (Khlystov, 1998; ten Brink et al., 1997). For other locations in Europe no data are available on the contribution of nitrate to the light-reflecting aerosol. Recently, modelling studies of the global nitrate field were made by Adams et al. (1999) and Jeuken (2000) and the influence on reflection of solar radiation by Van Dorland et al. (1997) and Adams et al. (2001). These indicate a rather small contribution by nitrate on a global scale, but the results of the studies are highly uncertain due to the complexity of the formation mechanism and assumptions in the models. In addition, verification of the model results is seriously hampered by the lack of reliable data, specifically in Europe (Adams et al., 1999). The lack of reliable data was the incentive for the present study in which we made use of measured concentration data to construct the nitrate field in Europe.

At present, available long-term data are obtained with the standard 24 h sampling of aerosol by filtration and subsequent chemical analysis of the nitrate content. This is a straightforward procedure, however, the volatile character of ammonium nitrate and the reactivity of gaseous nitric acid make these filtration methods prone to artefacts (Slanina et al., 2001). The quality of the data is therefore unknown. Artefacts not only occur during sampling but are also observed during storage (Witz, 1985). In view of the artefact problem we will start the study with an overview of measurement methods in Europe, and the associated artefacts. It will be shown what the magnitude of the artefacts are and how they can be corrected for. The selection of data is based on this pre-evaluation. The specific corrections performed for the respective data are discussed in a special section after providing the general results first.

## 2. Filter types in use in Europe

Before we turn to a detailed overview we will briefly tabulate the artefacts occurring with the main filter types

in use in Europe and introduce the denuder filter (DF) pack technique in which the same type of filters are applied:

- (1) Inert material, Teflon and quartz: loss of ammonium nitrate by evaporation.
- (2) Impregnated material and nylon: deliberate collection of nitric acid but possibly also other gaseous nitrogen oxide derivatives.
- (3) Alkaline filters, cellulose (paper), cellulose-acetate: collection of nitric acid and possibly nitrous acid (HONO).

### 2.1. DF packs

The optimum method to collect the semi-volatile nitrate is to stabilise it after collection against evaporation, by impregnating filters with a reagent or to use a reactive type of filter. However, such substrates also collect gaseous nitric acid. Gas denuders are therefore applied to remove the interfering nitric acid. Over 20 years of experience have shown that these devices are very suitable for aerosol nitrate collection (e.g. Harrison and Kitto, 1990 and references therein). However, relatively little attention has been given to a possible interference by nitrous acid (HONO) which is easily absorbed by alkaline substrates and could subsequently be oxidised (Pakkanen et al., 1999). An own analysis of the extent of this effect, see Section 2.3 for details, shows that such an artefact is small. The long-term precision of the DF technique is 15% or better (Sickels et al., 1999).

In the Netherlands (RIVM network) a modified DF technique combination has been in use since 1989. Here a high-capacity active carbon denuder is employed to remove nitric acid and a cellulose filter for aerosol collection. It has been consistently shown that the method is equivalent with the (reference) DF pack method (Mennen et al., 1992; van Putten and Mennen, 1998; ten Brink et al., 2001).

### 2.2. Inert filters

With filters made of the chemically inert materials Teflon and quartz, volatilisation of collected ammonium nitrate and reaction of nitric acid gas with collected alkaline aerosol particles are well-known artefacts. In southern California the loss of nitrate has been extensively studied (e.g. Hering and Cass, 1999 and references therein). It was found that the extent of the loss varies, which could not be related to simple parameters and thus a generalisation was not possible. However, we extracted from the data that at temperatures < 10°C, the loss is small. Especially this aspect is of interest for the much cooler climatic conditions in Europe.

A “positive” artefact is reaction of nitric acid with co-sampled alkaline aerosol. However, in the area for which we assessed the nitrate concentration field evaporation dominates adsorption, as is evidenced from a comparison of data obtained with inert filter (IF) and reference methods (Putaud et al., 2001; Pakkanen et al., 1999; Behlen, 1996). Therefore it is almost certain that nitrate data obtained with IF are lower values. Especially during summer ambient nitrate concentrations can be largely underestimated (Putaud et al., 2001; Pakkanen et al., 1999; Hering and Cass, 1999).

### 2.3. Total nitrate

Impregnated filters, filter packs and nylon filters are often referred to as “total nitrate” (TN) filters, since they sample both aerosol nitrate and gaseous nitric acid. In a filter pack, the first filter collects the aerosol while the second traps the volatilised nitrate and ambient nitric acid. Nitric acid is quantitatively collected in the range of concentrations occurring in Europe (Matsumoto and Okita, 1998). The nitrate reported is the total nitrate of the two filters combined. The long-term precision of the sampling procedure is better than 15% (EMEP, 1998; Harrison and Kitto, 1990; Pakkanen et al., 1999).

A potential artefact is the absorption of nitrous acid and subsequent oxidation to nitrate. This artefact is negligible when NaCl is used for impregnation, since it does not absorb HONO (Matsumoto and Okita, 1998; Pakkanen et al., 1999). When this artefact would be important more alkaline impregnated filters should contain substantially more total nitrate than DF packs. This has not been observed for a series of different total filters in campaigns of Ferm et al. (1988), Krieg (1997b) and EMEP (1998). Analysis of the data from Perrino et al. (2001) shows that interference on NaF coatings is negligible. We thus conclude that the HONO absorption artefact is negligibly small.

### 2.4. Cellulose filters

At a number of sites cellulose (paper) filters are used. Recently, it has been shown that ammonium nitrate is fully retained on such filters (ten Brink et al., 2001), even at such elevated temperatures at which evaporation should have been complete. The adsorption of nitrous acid was negligibly small. Cellulose filters quantitatively adsorb nitric acid: Appel et al. (1979) and Spicer and Schumacher (1979) in the US and Mehlmann (1986) in Germany show that the capacity for retaining nitric acid is much higher than the amounts sampled in Europe. Summarising, cellulose filters act as TN filters and because of absence of preparation the precision in the nitrate values is most probably even better than that for the TN filter data given above. When a cellulose filter is

used as the front-filter in a filter pack very little nitrate is expected on the back-up filter and more importantly the data from this second filter cannot be used to assess the nitric acid concentration.

## 3. Data acquisition and criteria for selection and correction

### 3.1. Site selection and time span

The aim of the present study is to construct the (average) nitrate concentration field in Europe. For a climatological average at least a 10-year record would be required, and only in the Netherlands such a long data set exists. For the other sites the records are of a shorter duration. For consistency, data from the same period of 4 years (1994–1997) were used, provided that the data completeness was 66% or better.

We used some data from other years to check for consistency. Among these data are our own DF results from the period 1987–1994, reported here for the first time. Most of the other DF data were made available by the institutes approached. Data were, obviously, also taken from the public EMEP database. For the research on the spatial and temporal correlation of the nitrate concentration at the various sites use was made of the (yet unpublished) data provided by RIVM for the Netherlands and NERI for Denmark, for which we are particularly grateful. The number of data for a site in the southern UK (Colchester) was insufficient. However, in the years prior to the design period data were gathered in the area (Harrison and Allen, 1990) which fully support the values obtained in the design period. Therefore the Colchester data were included.

Data stemming from measuring locations which are more than 400 m above the surrounding plain were not considered here, because these are above the boundary layer in winter and thus not representative for the regional surface concentration, see e.g. Arends et al. (1997). It should be realised that artefacts, specifically a loss of nitrate by volatilisation, can occur during storage of the filter prior to analysis (Witz, 1985). Precautions to avoid losses are often not being made in monitoring programs: we only used data in the present study, which came from filters that were properly handled. The sites that meet these requirements are tabulated in Table 1 and shown in Fig. 1.

It appears that at only one location in southern Europe (Montelibretti near Rome, Italy) a long-term nitrate record, acquired with a DF system, exists. However, apart from this site only one other site with a long-time record is present in southern Europe. Therefore the southern limit of the area in which we made an analysis of data was at 47.5°N. A similar reasoning confines the area between 10°W and 30°E.

Table 1  
Overview of the average annual nitrate concentrations at the indicated sites and for the winter season (October–March) only

| Station                 | Code | Country | Method | Year             |                  | Winter           |                  | Reference                |
|-------------------------|------|---------|--------|------------------|------------------|------------------|------------------|--------------------------|
|                         |      |         |        | TNO <sub>3</sub> | aNO <sub>3</sub> | TNO <sub>3</sub> | aNO <sub>3</sub> |                          |
| Kolummerwaard           | KO   | NL      | DF     | —                | 4.6              | —                | 4.9              | RIVM (1999)              |
| Bilthoven               | BI   | NL      | DF     | —                | 5.0              | —                | 5.4              | RIVM (1999)              |
| Vredepeel               | VR   | NL      | DF     | —                | 5.1              | —                | 4.4              | RIVM (1999)              |
| De Zilk                 | DZ   | NL      | DF     | —                | 4.2              | —                | 4.6              | RIVM (1999)              |
| Wieringerwerf           | WI   | NL      | DF     | —                | 4.8              | —                | 4.9              | RIVM (1999)              |
| Huijbergen              | HU   | NL      | DF     | —                | 4.0              | —                | 3.9              | RIVM (1999)              |
| Muncheberg <sup>a</sup> | MU   | DE      | DF     | —                | 3.2              | —                | 4.7              | Zimmerling et al. (2000) |
| Wallisellen             | WA   | CH      | DF     | —                | 4.7              | —                | 7.1              | Thöni et al. (2000)      |
| Colchester <sup>b</sup> | CO   | GB      | DF     | —                | 4.5              | —                | 4.6              | Chung (2000)             |
| Melpitz                 | ME   | DE      | IF     | —                | 4.1              | —                | 5.4              | This study               |
| Kocetice                | KO   | CZ      | IF     | —                | 2.8              | —                | 3.4              | EMEP (2000)              |
| Svratouch               | SV   | CZ      | IF     | —                | 2.1              | —                | 2.1              | EMEP (2000)              |
| Keldsnor                | KE   | DK      | TN     | 5.5              | 4.8              | 5.9              | 5.5              | Frohn et al. (1998)      |
| Anholt                  | AN   | DK      | TN     | 3.9              | 3.2              | 4.0              | 3.6              | Frohn et al. (1998)      |
| Tange                   | TA   | DK      | TN     | 4.4              | 3.7              | 4.8              | 4.4              | Frohn et al. (1998)      |
| Ulborg                  | UL   | DK      | TN     | 4.3              | 3.6              | 4.6              | 4.2              | Frohn et al. (1998)      |
| Fredriksborg            | FR   | DK      | TN     | 4.0              | 3.3              | 4.5              | 4.1              | Frohn et al. (1998)      |
| Payerne                 | PA   | CH      | TN     | 5.3              | 4.7              | 6.7              | 6.4              | EMEP (2000)              |
| Eskdalemuir             | ES   | GB      | TN     | 1.7              | 1.1              | 1.9              | 1.5              | EMEP (2000)              |
| High Muffles            | HM   | GB      | TN     | 3.2              | 2.6              | —                | —                | EMEP (2000)              |
| Leba                    | LE   | PL      | TN     | 3                | 2.4              | 3.7              | 3.3              | EMEP (2000)              |
| Diabla Gora             | DI   | PL      | TN     | 2.9              | 2.3              | 4.0              | 3.6              | EMEP (2000)              |
| Jarczew                 | JA   | PL      | TN     | 3.9              | 2.9              | 5.0              | 4.4              | EMEP (2000)              |
| Rucava                  | RU   | LV      | TN     | 3.3              | 2.7              | 3.7              | 3.3              | EMEP (2000)              |
| Birkenes                | BI   | NO      | TN     | 1.2              | 0.8              | 1.1              | 0.9              | EMEP (2000)              |
| Skreaddalen             | SK   | NO      | TN     | 1.0              | 0.6              | 0.7              | 0.5              | EMEP (2000)              |
| Osen                    | OS   | NO      | TN     | 0.6              | 0.2              | 0.6              | 0.4              | EMEP (2000)              |
| Vavihill                | VA   | SE      | TN     | 2.7              | 2.1              | 2.9              | 2.5              | EMEP (2000)              |
| Roervik                 | RO   | SE      | TN     | 2.7              | 2.1              | 2.8              | 2.4              | EMEP (2000)              |
| Aspvreten               | AS   | SE      | TN     | 1.2              | 0.6              | 1.3              | 0.9              | EMEP (2000)              |
| Uto                     | UT   | FI      | TN     | 1.8              | 1.2              | 1.8              | 1.4              | EMEP (2000)              |
| Virolahti               | VI   | FI      | TN     | 1.4              | 0.8              | 1.5              | 1.1              | EMEP (2000)              |

Averages over the period 1994–1997 unless otherwise indicated. The codes by which the locations are identified in the figures are given in the second column. Where appropriate “total nitrate” concentrations are tabulated, as well as the aerosol nitrate concentrations after correction for nitric acid.

Methods/filter-types are indicated as: DF = denuder filter pack; IF = inert filter; and TN = total nitrate method.

<sup>a</sup>Data for Muncheberg are for 1995–1998.

<sup>b</sup>Data from Colchester originate from a shorter time series, see text.

Within this domain long-term data, fulfilling the criteria mentioned above, could not be found in Belgium, France and the western part of Germany.

### 3.2. Correction of total nitrate data

As mentioned above, data on total nitrate have to be corrected by subtracting the amount of nitric acid to obtain values for aerosol nitrate proper. At some sites nitric acid concentrations are available for extended periods such that confidence in their average values is high. At other sites we used concentrations of nitric acid as measured at sites in the vicinity. In some regions extended data sets on nitric acid data are absent and

nitric acid concentrations had to be estimated. The method by which this was done and the corrections are discussed in detail below. In Table 1 the concentrations of aerosol nitrate, obtained after correction for nitric acid, are being tabulated along with those of the (uncorrected) total nitrate.

## 4. Construction of the nitrate concentration field

### 4.1. Data points

The average nitrate concentrations at the sites selected here are shown in Fig. 1. These are compiled from data

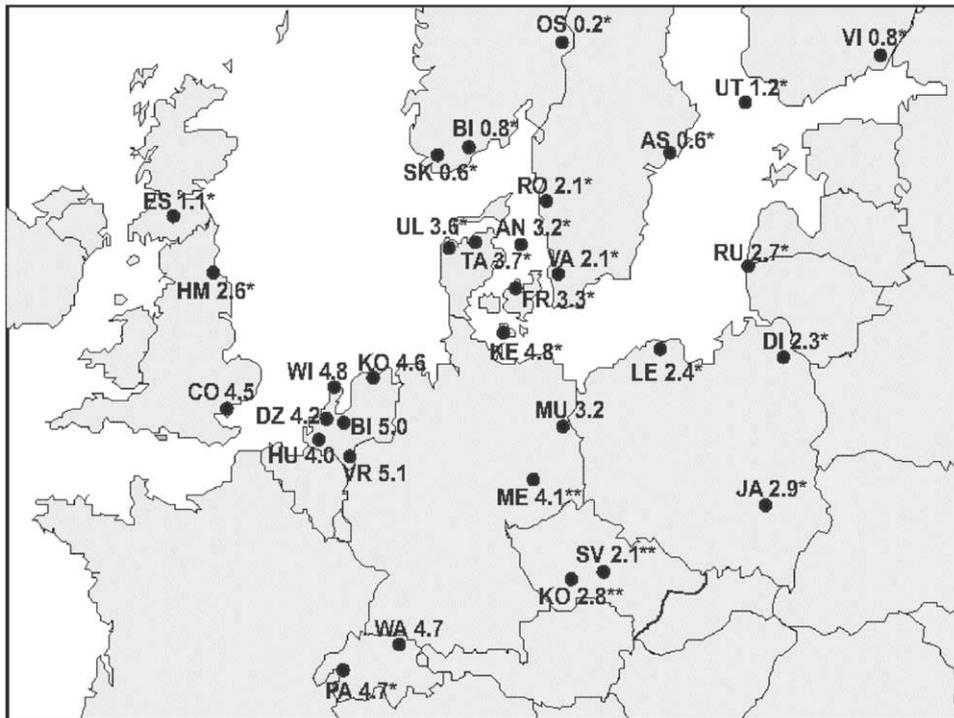


Fig. 1. Geographical location of the sites indicated with the codes as listed in Table 1. Also presented the annual average nitrate concentrations ( $\mu\text{g m}^{-3}$ ) (\* data corrected for nitric acid, \*\* data acquired with inert particle filters).

in the time period from 1994 to 1997 (Table 1). The data are for a rather short time span in a climatological sense and thus only semi-quantitative conclusions are in place. Concentrations in the Netherlands, of 5 and of  $4 \mu\text{g m}^{-3}$  in Germany and Switzerland, respectively, are not significantly different. Similar values come from the shorter data record in Colchester, southern England. The values at Melpitz and the Czech Republic are minimum values because IF were used.

#### 4.2. Spatial representativity

Construction of the nitrate concentration field from point data seems warranted when the distance over which the concentrations correlate is sufficiently large. Arends et al. (1997) found, for the dense network in Belgium, that the spatial correlation for *sulphate* is very high even over distances as large as complete countries. In analogy we use the sites in the Netherlands and Denmark to determine the correlation length for nitrate. The correlation length is defined as the distance between two points over which 50% of the temporal variance is explained by that at the second point, e.g. the correlation coefficient is 0.7. It is then assumed that the correlation and absolute concentrations at points in-between the two are correlated higher.

In Fig. 2 the weekly mean nitrate concentrations for six Dutch stations are presented for the year 1994. In the summer the correlation coefficient ranges between 0.54 and 0.92 (on basis of data from 1994 to 1999). The best correlation between the stations occurs in the winter half-year. In that period the correlation coefficient ranges from 0.67 to 0.95 and between the various stations with the highest correlation for the nearest pair of sites (see Table 2). The maximum distance between the sites is over 200 km. In Denmark, correlations with similar coefficients as those in the Netherlands were found for the winter season. Kolummerwaard, the most northerly Dutch station, is within the correlation range of Keldsnor, the most southerly station in Denmark at a distance of ca. 350 km.

There is also a good correlation between Munchenberg and the Dutch sites in winter. In Fig. 3 the weekly averaged concentrations in 1997 are compared with those in the Netherlands. In winter the correlation between the sites is reasonable ( $0.51 < r < 0.61$ ). The correlation between Melpitz and Keldsnor and Melpitz and the Dutch sites over distances of ca. 350 and up to 550 km, respectively, is also good (see Table 2 and Fig. 3). It should be noted that the nitrate concentrations in eastern Germany correlate well both in a relative sense and also in an absolute sense especially in the periods with high concentrations. In summer the

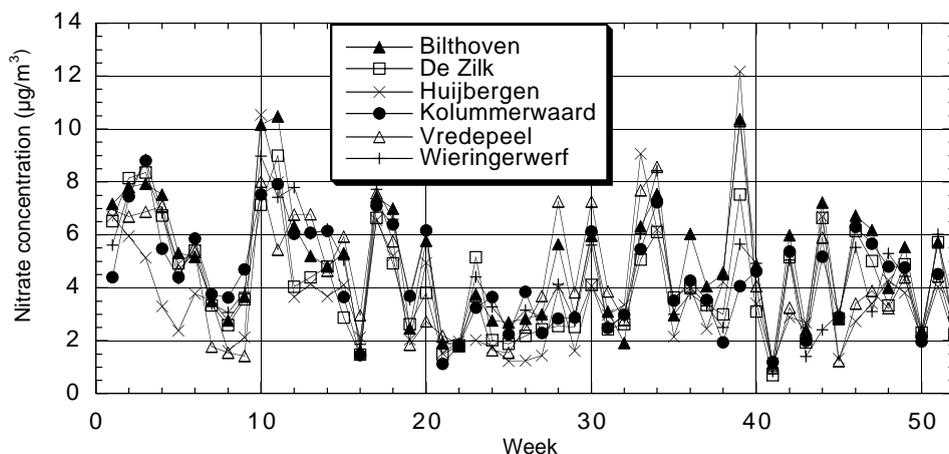


Fig. 2. Weekly mean nitrate concentrations in 1997 at six monitoring stations in the Netherlands.

Table 2

Coefficients of correlation for nitrate at the indicated sites in the winter period (October–March), calculated from weekly averaged concentrations

| Stations | BI    | KO    | VR    | DZ    | HU    | WI    | AN    | FR    | UL    | TA    | KE    | MU    | ME    |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| BI       | 1.000 | 0.900 | 0.781 | 0.916 | 0.803 | 0.916 | 0.365 | 0.447 | 0.609 | 0.554 | 0.651 | 0.533 | 0.783 |
| KO       | 0.900 | 1.000 | 0.733 | 0.890 | 0.719 | 0.947 | 0.424 | 0.542 | 0.749 | 0.644 | 0.776 | 0.562 | 0.718 |
| VR       | 0.781 | 0.733 | 1.000 | 0.669 | 0.800 | 0.779 | 0.197 | 0.251 | 0.485 | 0.339 | 0.516 | 0.512 | 0.673 |
| DZ       | 0.916 | 0.890 | 0.669 | 1.000 | 0.738 | 0.913 | 0.386 | 0.533 | 0.653 | 0.629 | 0.669 | 0.558 | 0.736 |
| HU       | 0.803 | 0.719 | 0.800 | 0.738 | 1.000 | 0.764 | 0.119 | 0.198 | 0.417 | 0.311 | 0.461 | 0.568 | 0.699 |
| WI       | 0.916 | 0.947 | 0.779 | 0.913 | 0.764 | 1.000 | 0.355 | 0.446 | 0.729 | 0.598 | 0.702 | 0.613 | 0.724 |
| AN       | 0.365 | 0.424 | 0.197 | 0.386 | 0.119 | 0.355 | 1.000 | 0.807 | 0.747 | 0.841 | 0.748 | 0.162 | 0.354 |
| FR       | 0.447 | 0.542 | 0.251 | 0.533 | 0.198 | 0.446 | 0.807 | 1.000 | 0.738 | 0.829 | 0.799 | 0.340 | 0.491 |
| UL       | 0.609 | 0.749 | 0.485 | 0.653 | 0.417 | 0.729 | 0.747 | 0.738 | 1.000 | 0.920 | 0.814 | 0.465 | 0.639 |
| TA       | 0.554 | 0.644 | 0.339 | 0.629 | 0.311 | 0.598 | 0.841 | 0.829 | 0.920 | 1.000 | 0.831 | 0.390 | 0.537 |
| KE       | 0.651 | 0.776 | 0.516 | 0.669 | 0.461 | 0.702 | 0.748 | 0.799 | 0.814 | 0.831 | 1.000 | 0.431 | 0.771 |
| MU       | 0.533 | 0.562 | 0.512 | 0.558 | 0.568 | 0.613 | 0.162 | 0.340 | 0.465 | 0.390 | 0.431 | 1.000 | 0.923 |
| ME       | 0.783 | 0.718 | 0.673 | 0.736 | 0.699 | 0.724 | 0.354 | 0.491 | 0.639 | 0.537 | 0.771 | 0.923 | 1.000 |

correlation is small and not significant ( $0.19 < r < 0.42$ ) and the concentrations are also very different. The correlation of weekly averaged data between Melpitz and Munchenberg is also high.

In addition, data from campaigns were used to establish the correlations on a short-term basis. The values from the German site of Eilsum (Behlen, 1996) correlate well with those in the Netherlands on a day by day basis. Data in Halberstadt, correlated well with those in Melpitz and Leipzig, situated 140 km to the SE, see Fig. 4, with correlation coefficients close to 0.70. It is thus concluded that the distances over which nitrate concentrations correlate in Europe is large in the winter half-year, with estimated correlation lengths in the order of 400 km which are sufficiently long to warrant interpolation of the concentration between measuring locations. In addition the nitrate data are most reliable in this season.

#### 4.3. Construction of the nitrate concentration field in Europe

The nitrate concentration field for the winter half-year (October–March) was obtained by Delaunay triangulation and subsequent linear interpolation of the point data (see Fig. 5). A region with nitrate concentrations exceeding  $4 \mu\text{g m}^{-3}$  occurs from southern England over continental western Europe into Poland, with a maximum in Switzerland. Nitrate concentrations exceed  $3 \mu\text{g m}^{-3}$  in central eastern Europe. There is strong gradient from south to north in Scandinavia. To put these concentrations in perspective they are compared with those of sulphate presented in Fig. 6. It appears that in western Europe the nitrate concentration equals or exceeds that of sulphate. The nitrate to sulphate concentration ratio decreases to  $\sim 0.5$  in eastern Europe. The lowest ratios are found in northern Scandinavia.

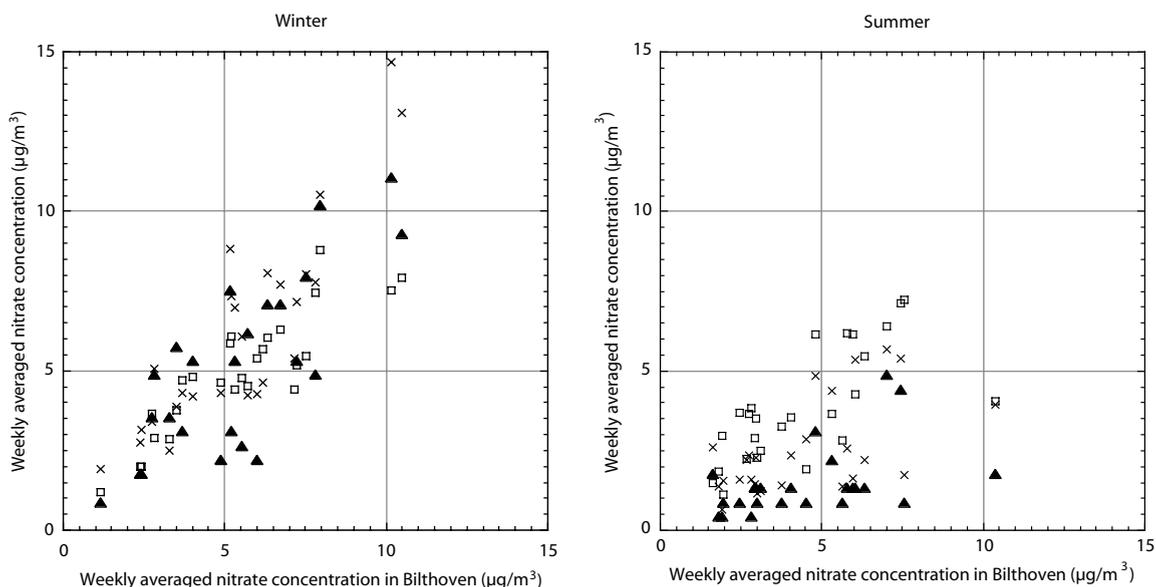


Fig. 3. Weekly averaged nitrate concentrations in Kolummerwaard (□), Melpitz (×) and Muncheberg (▲) as compared to those at Bilthoven during summer and winter 1997.

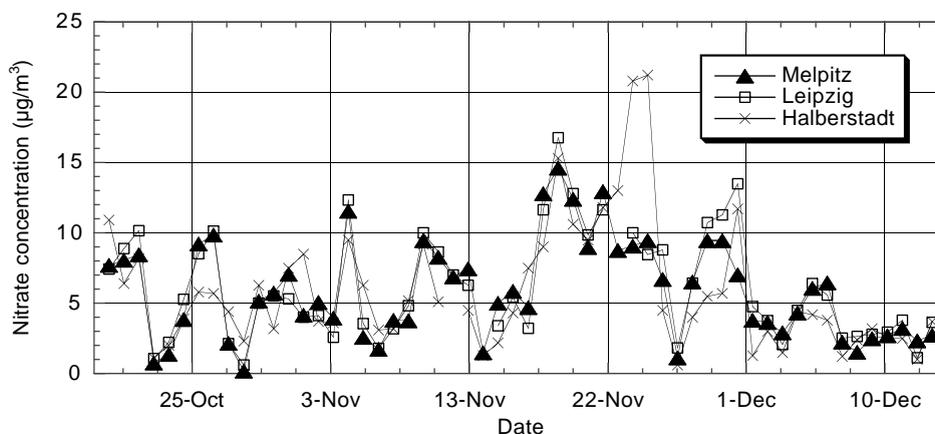


Fig. 4. Nitrate concentrations at the locations of Melpitz, Leipzig and Halberstadt during fall 1993.

The total budget of nitrate, defined as the horizontally integrated concentration in Europe north of the Alps, relative to that of sulphate is therefore close to 0.6.

## 5. General discussion

### 5.1. Concentration field

#### 5.1.1. Data quality

Data quality is highest in western Europe because of the use of the reference artefact-free DF samplers. The IF give minimum values in Melpitz and the Czech Republic. The uncertainty in the data inferred from total

nitrate needs a more detailed discussion. As an example the correction method for the total nitrate concentration measured at Payerne, Switzerland, is discussed, see also Table 3. In the table wintertime nitric acid, total nitrate and aerosol nitrate data are given. In addition, data from sites in the vicinity are provided. From these data the average nitric acid concentration in winter was estimated to be  $0.3 \mu\text{g m}^{-3}$ , which is the value subtracted from the average total nitrate concentration to obtain the value for aerosol nitrate as presented in Table 1 and Fig. 6. A doubling of the nitric acid correction would lead to a 5% decrease in the aerosol nitrate concentrations, which is insignificant compared to the measuring uncertainties.

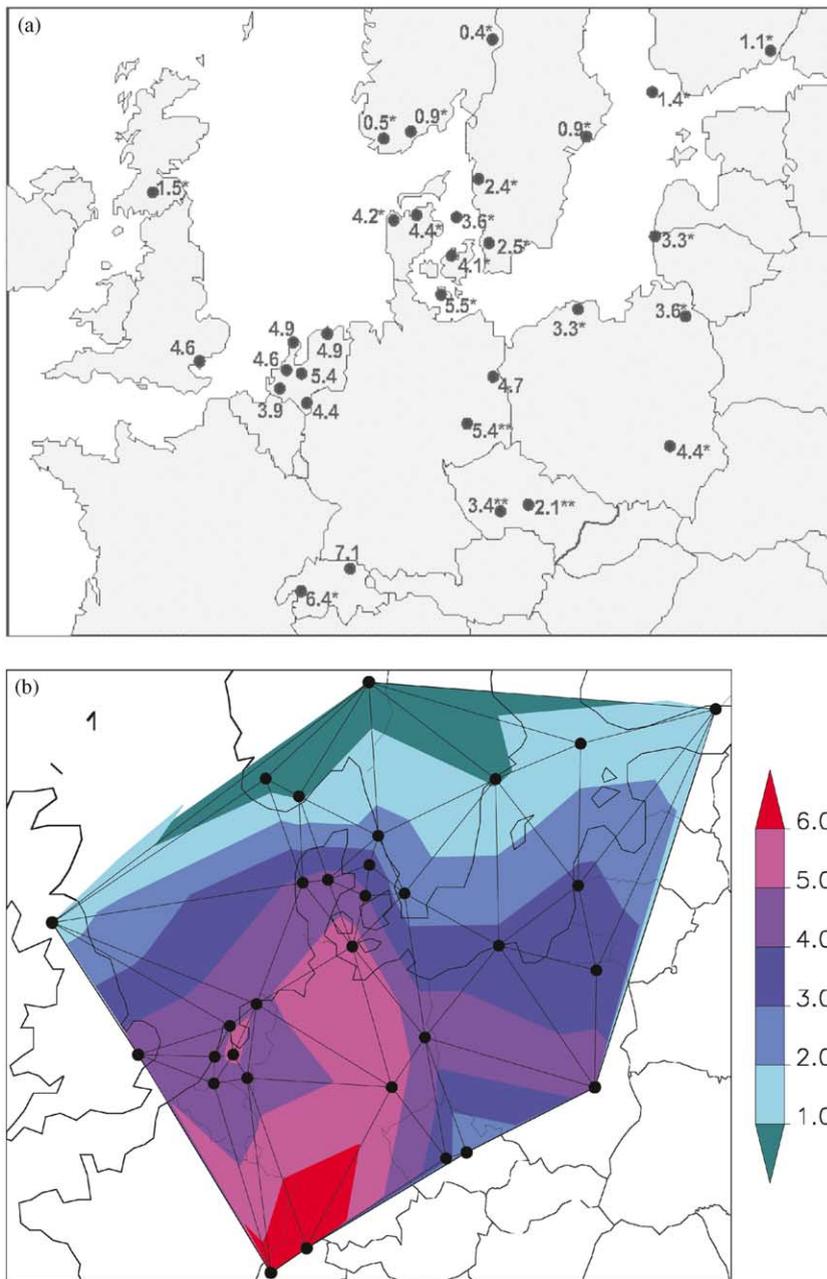


Fig. 5. (a) Nitrate concentration ( $\mu\text{g m}^{-3}$ ) during winter (October–March) (\* data corrected for nitric acid, \*\* data acquired with inert particle filters). (b) Nitrate field obtained by Delaunay triangulation and subsequent interpolation of the data.

For Denmark the correction was based on data from EMEP (1998) and Andersen and Hilbert (1993). In Denmark the nitric acid concentration is small compared to the total nitrate concentration and even a doubling of the nitric acid correction would lead to a mere 10% change in aerosol nitrate.

In southern Sweden and along the coast of the Baltic Sea few nitric acid data are available and total nitrate

data were corrected assuming a nitric acid concentration of  $0.4 \mu\text{g m}^{-3}$ . This value was obtained by averaging the available wintertime nitric acid data in this region in the range of  $0.1\text{--}0.7 \mu\text{g m}^{-3}$  (Behlen, 1996; Foltescu et al., 1996; EMEP, 1998; Plate, 2000). Using the highest value in this range results in an uncertainty of only 10% in the aerosol nitrate concentrations. Further to the north in Scandinavia the correction becomes more uncertain,

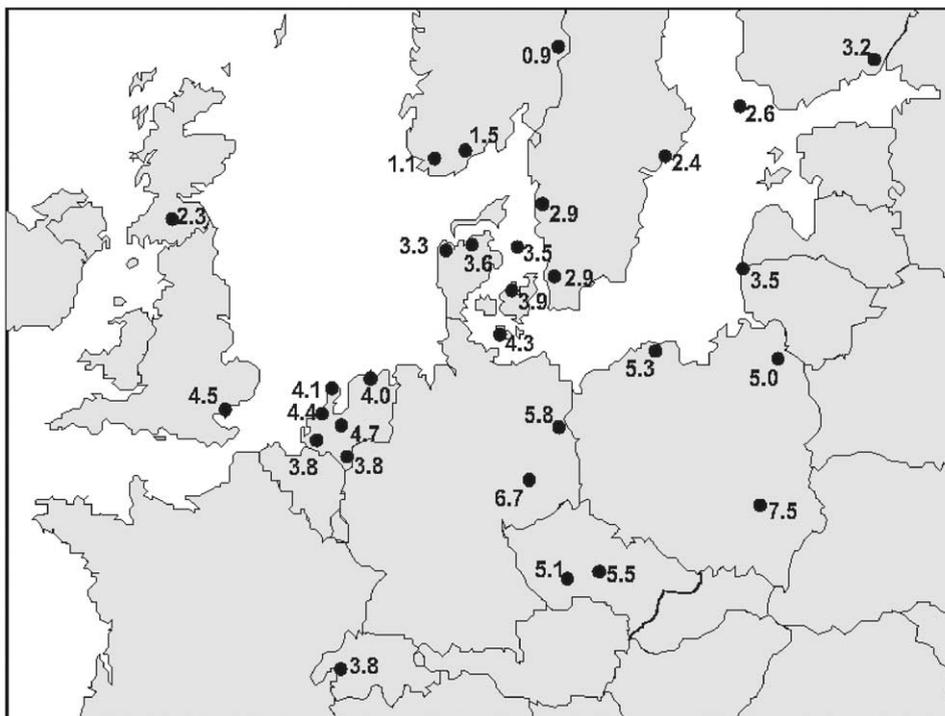


Fig. 6. Sulphate concentration ( $\mu\text{g m}^{-3}$ ) during winter (October–March) at the sites where nitrate data also were available.

Table 3

Total nitrate concentrations as measured in campaigns and the concentrations of nitric acid gas and aerosol nitrate at Payerne (PA), Switzerland, and at sites in the vicinity

| Site        | Period    | N   | TNO <sub>3</sub> | HNO <sub>3</sub> | aNO <sub>3</sub> | Reference                    |
|-------------|-----------|-----|------------------|------------------|------------------|------------------------------|
| Payerne     | Dec 1993  | 21  | 5.0              | 0.2              | 4.8              | Krieg (1997b)                |
| Payerne     | Jan 1995  | 20  | 6.4              | 0.3              | 6.1              | Krieg (1997b)                |
| Payerne     | Oct 1995  | 21  | 7.6              | 0.3              | 7.3              | Krieg (1997b)                |
| Wallisellen | 1995–1997 | 518 | 7.3              | 0.2              | 7.1              | Thöni et al. (2000)          |
| Wallisellen | 1999      | 177 | 6.9              | 0.2              | 6.7              | Thöni et al. (2000)          |
| Basel       | 1998      | 182 | 6.9              | 0.2              | 6.7              | Thöni and Leuenberger (1999) |
| Schupfheim  | 1996      | 168 | 5.9              | 0.2              | 5.7              | Krieg (1997a)                |
| Payerne     | 1994–1997 | 686 | 6.7              | 0.3              | 6.4              |                              |

Data are for the winter (January–March and October–December) of the year indicated or for the period specified. In the lowest row the average wintertime total nitrate for the period 1994–1997 is given. The tabulated average nitric acid concentration, extrapolated from the indicated campaigns, was used to correct the total nitrate to the tabulated aerosol nitrate concentration in the last column.

since nitric acid data are absent. However, the absolute values are low so that the real aerosol nitrate concentrations are very low anyhow. An overview of nitric acid data is given in an extended report (Schaap et al., 2001)

For Jarczew (Poland) we assumed a concentration of nitric acid of  $0.6 \mu\text{g m}^{-3}$  HNO<sub>3</sub>, as a conservative maximum that is high compared to the corrections at the other sites. This correction would lead to an uncertainty of 20% in aerosol nitrate. In Poland

(Jarczew, Leba, Diabla Gora) there is an additional complication in that the aerosol nitrate concentration obtained here could be 20% high, since total nitrate as determined with the local method was systematically 20% higher than the calibrated reference filter pack (EMEP, 1999). In summary, the corrections for nitric acid in the given areas in winter are (negligibly) small.

The corrections for the annual average data points given in Section 4 were made using the same method as

for the winter data discussed above. However, annual data are more uncertain because of a higher uncertainty in the summer values. The reason is that IF are subject to severe evaporation losses due to the lower stability of ammonium nitrate in summer (see above). Additionally, at higher temperatures the concentrations of nitric acid relative to aerosol nitrate are higher (Zimmerling et al., 2000; Thöni et al., 2000), which leads by necessity to a larger uncertainty in the correction of this component in the total nitrate data.

#### 5.1.2. Check of the consistency of the field with data from campaigns

The field as constructed in the previous chapter was checked with data at sites inside the field domain (see also Schaap et al., 2001); these data are either from short-term campaigns or from longer term data from earlier years. Short-term values from sites in eastern Germany and at the north coast of Germany range from 4.8 to 5.9  $\mu\text{g m}^{-3}$  (Behlen, 1996; Plate, 2000) and sites in the Ruhr area give similar concentrations (Kuhlbusch et al., 1999). These values are in agreement with the concentration projected in the field (Fig. 6). Additional data obtained in Basel and Schupfheim (CH) also compare well with the projected data (Thöni and Leuenberger, 1999; Krieg, 1997a).

For data from other time periods than the design period only qualitative conclusions are in place. In Wolkersdorf, Austria, the average aerosol nitrate concentration in the winter of 1990/1991 obtained with a DF method was 6.2  $\mu\text{g m}^{-3}$  (Puxbaum et al., 1993). In Erfurt (Germany), west of Leipzig an annual value of 3.7  $\mu\text{g m}^{-3}$  was obtained in 1991 (Brauer et al., 1995) which is similar to those projected in Section 4.1. In Sokolov (Czech Republic) the nitrate concentration in 1991 was 3.9  $\mu\text{g m}^{-3}$  (Brauer et al., 1995), which is substantially higher than that found with the Teflon filters at the Czech sites. This is indicative that the Teflon filters are subject to severe nitrate loss. The apparently larger nitrate loss from Teflon in the Czech Republic than those from the quartz filters near Leipzig are in line with observations by Eatough et al. (1988) and ten Brink et al. (2001) in intercomparison tests.

*Addendum.* Due to the lack of data in southern Europe the nitrate field could not be assessed there. However, for The Po region in northern Italy sufficient nitrate data are available to allow the conclusion that the area with high maximum nitrate concentrations during winter includes northern Italy (Krieg, 1994; EMEP, 1998; Putaud et al., 2001). Applying the same correction procedure for Ispra as for the sites north of the Alps with nitric acid data from Krieg (1997b) and EMEP (1998) winter time aerosol nitrate concentrations of 7.2  $\mu\text{g m}^{-3}$  are obtained with an associated uncertainty of 15%.

#### 5.2. Size fraction

The size of the particles in which nitrate is contained is of special environmental interest, as indicated in the introduction. In the Netherlands, measurements have been made with cascade-impactors in which the aerosol is size-fractionated into several size-classes. It appears that sampling artefacts in cascade impactors are rather small, see Hering and Cass (1999) or ten Brink et al. (1997). In measuring campaigns in almost every second year since 1979 it has been consistently found that the nitrate in the Netherlands (ten Brink et al., 1997) is preferentially present in the fine aerosol fraction (particles smaller than 2.5  $\mu\text{m}$ ). In the UK and at Melpitz the same applies (Heintzenberg et al., 1998; Colbeck, 2000). In Muncheberg only the fine aerosol was collected and hence, the high, nitrate concentrations tabulated pertain to fine aerosol nitrate.

Another more indirect indication that the nitrate is in the fine aerosol mode is its presence in the form of ammonium compound. In Europe, ammonium nitrate has consistently been observed in the fine aerosol fraction. The reason for this is that ammonium nitrate is formed in a heterogeneous reaction at the surface of existing aerosol which is concentrated in the fine aerosol (Seinfeld and Pandis, 1997). A dominant presence of ammonium nitrate is therefore taken as evidence that the nitrate is in the fine aerosol fraction. Nitrate is indeed mainly present as ammonium nitrate in the Netherlands, Denmark, Germany and Switzerland and thus most likely in the whole of western Europe. In Hungary the winter nitrate is also in the fine aerosol mode (Meszaros et al., 1997). Therefore, we expect that also in central Europe the nitrate in winter is present as fine nitrate and that the projected field can be interpreted accordingly.

#### 6. Conclusions and implications

In this study an attempt was made to construct the average nitrate concentration field for Europe for the period 1994–1997. For this purpose we actively searched for data. We show that sampling artefacts with the DF packs used in Europe is small and that data obtained with such devices can serve as reference data. It was shown that values data acquired with IF are lower values. Total nitrate concentrations were corrected for the contribution by nitric acid for which separate information was analysed.

To assess the spatial representativity we assessed the correlation length, which was found to be  $\sim 400$  km in winter. This finding warranted interpolation of data at stations at distances of that order or smaller. The field constructed in this way was successfully validated with data from measuring campaigns. It is found that in

winter large areas in Europe have nitrate concentrations exceeding  $4\ \mu\text{g m}^{-3}$ , with a possible maximum of  $7\ \mu\text{g m}^{-3}$  in Switzerland. In western Europe nitrate concentrations are equal to or even exceed those of sulphate, while sulphate concentrations are higher in eastern and northern Europe. Overall, in the sites north of the Alps the surface nitrate concentration budget is about 60% of that of sulphate.

It is shown that nitrate is in the fine aerosol mode (particles smaller than  $2.5\ \mu\text{m}$  in diameter). We identified a large area in Europe where the volatile ammonium nitrate contributes  $5\ \mu\text{g m}^{-3}$  or more to regional PM<sub>2.5</sub>. This is a large proportion of the proposed particulate standards for PM<sub>2.5</sub> in Europe:  $20\ \mu\text{g m}^{-3}$ . For regulatory purposes it is therefore important to sample PM with an appropriate method without (large) nitrate artefacts.

The presence of nitrate in the fine aerosol mode is of specific relevance for the reflection of radiation. The scattering of visible light gives rise to visibility impairment. Nitrate must therefore be a key component in regional haze in Europe, which has already been demonstrated to be the case in the Netherlands (Diederer et al., 1985; ten Brink et al., 1997). In addition, nitrate reflects solar radiation and the associated cooling could be similar in magnitude as that by sulphate over the area mentioned. Locally such an effect was already identified in the Netherlands (Khlystov, 1998).

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