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Nitric acid measurements in connection with corrosion studies

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Abstract

Atmospheric nitric acid does not only contribute to acidification and eutrophication but causes also deterioration of many materials. Material belonging to our cultural heritage is irreplaceable and its lifetime can depend on the corrosion rate. Nowadays, only very few long-term measurements of nitric acid concentration in Europe and elsewhere have been published so far. Due to the fact that atmospheric corrosion is a long-term effect, the relevant research does not necessarily require monitoring of nitric acid on a daily basis. Moreover, power supply is often not available at sites where it is of interest to study the corrosion rate of objects belonging to our cultural heritage. Besides, such measurements must not disturb the impression of the objects. In this context, the diffusive sampling technique provides average concentrations over long-term periods at a low cost. In addition, the samplers used are noiseless, comparatively small in size, and thus, their ambient exposure can be made inconspicuously and with discretion. The present paper is focussed on an intensive corrosion study, which was performed at 11 rural and 23 urban sites in Europe and one rural site in Canada during 2002/2003. For the above-mentioned reasons, the diffusive sampler's technique was employed for the nitric acid monitoring, where the diffusive samplers were first tested against the denuder technique and bi-monthly measurements of nitric acid were thus obtained. The bi-monthly concentrations varied from 0.05 to 4.3 $\mu g\,m^{-3}$ and the annual averages from 0.16 to 2.0 $\mu g\,m^{-3}$. The observations collected, depicted a summertime maximum and a wintertime minimum in the nitric acid concentrations, except at the northern rural sites, where a maximum in the winter was observed. Furthermore, the observed nitric acid concentrations in Southern Europe were higher than in Northern Europe. In a few places, close to the sites of urban measurements, rural measurements of nitric acid were also performed. The obtained nitric acid concentrations were higher in the cities, especially during the period of maximum concentrations.

Keywords: HNO_3; Diffusive sampling; Urban; Rural; Europe

1. Introduction

The acidification of soils, groundwater, lakes and the atmospheric corrosion of materials, including our cultural heritage, are partly caused by acidic gases such as SO_2, HNO_3 and HCl. In Europe mainly the concentration of SO_2 has been monitored.

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The observations show that SO_2 emissions in Sweden have decreased since the early 1970s, while in many European countries this decrease started late in the 1980s, when the first sulphur protocol was in force.

As to the NO_x, the first protocol was in force in 1991. In Sweden the HNO_3 and NO_2 concentrations have not decreased as much as the SO_2 concentration. It should be noted that HNO_3 was measured using the denuder technique in 1981/82 (Ferm et al., 1984) and has been routinely monitored using a filter pack, since 1993. The observations show that the NO_2 concentration has decreased a factor of 1.8 since 1982, when the NO_2 measurements started at the background sites in Sweden, while the SO_2 concentration decrease a factor of 10 during the same time. The HNO_3 concentration has been fairly constant since the filter pack measurements started and now exceeds the SO_2 concentration on a molar basis. The trends are shown for a background station on the Swedish West Coast in Fig. 1. The concentrations of the particulate products have not decreased as much as their gaseous precursors. The particulate sulphate concentration has decreased a factor of 2.2 since 1982 and particulate nitrate has in fact increased by 50% since 1993. The total (gas + particulate) nitrate concentrations was measured using a single impregnated filter between 1986 and 1993. No obvious trend in the total nitrate concentration can be observed between 1986 and 2003. No article on HNO_3 trend in urban air has been found in the literature. Perrino and Putaud (2003) have, however, published results from Montelibretti, which is a rural site but situated only 30 km downwind of Rome. They found ca. 40% decreasing concentration between 1994 and 2001.

Very few measurements of ambient HNO_3 levels have been reported in Europe. Within EMEP only five countries (9 of ca. 170 stations) are reporting HNO_3 concentrations (year 2000). Probably, this is partly due to cumbersome measurement technique. Results deduced from occasionally acquired observations in the frame of several HNO_3 measurement campaigns have

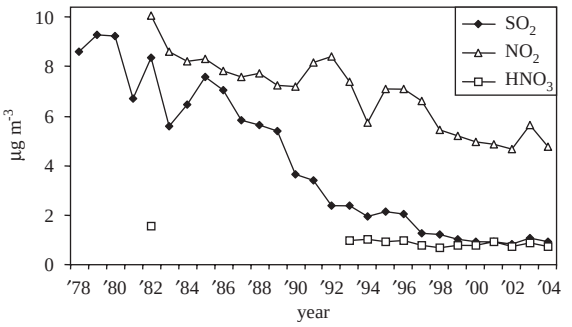

Fig. 1. SO_2, NO_2 and HNO_3 concentrations at Råö on the Swedish West Coast. Measurements from IVL, EMEP program financed by Swedish EPA.

already been published (Grennfelt, 1980; Harrison and Pio, 1983; Kitto and Harrison, 1992; Mehlmann and Warneck, 1995; Parmar et al., 2001; Janhäll et al., 2003). However, only a few in-field campaigns with longer measurement periods (one year or longer) have been published. Ferm et al. (1984) used a denuder with an impregnated filter behind to measure HNO_3 and particulate NO_3^- at a rural site on the Swedish West Coast. They obtained concentrations of 1.6 and 2.6 $\mu g\,m^{-3}$, respectively. Mészáros and Horváth (1984) used a filter pack to measure HNO_3 and particulate NO_3^- at a rural site in central Hungary. They obtained average concentrations of 3.7 and 3.9 $\mu g\,m^{-3}$, respectively. Cadle (1985) used a denuder difference technique in a suburb of Detroit. He found annual averages of 1.7 and 2.5 $\mu g\,m^{-3}$, respectively. Hoek et al. (1996) used annular denuders with a preceding Teflon-coated glass impactor for removing coarse particles, in the Netherlands. They have published numbers for one semi-rural and one rural site. The rural site had highest concentration (0.7 and 5.7 $\mu g\,m^{-3}$, respectively). Pio et al. (1996) used a denuder at Areão, a coastal rural site in Portugal. They sampled particulate NO_3^- separately using a high volume sampler. They obtained concentrations of 0.36 and 1.8 $\mu g\,m^{-3}$, respectively, Danalatos and Glavas (1999) used a denuder and a separate filter sampler in a suburb of Patras in Greece. They obtained concentrations around 2.6 and 1.1 $\mu g\,m^{-3}$, respectively. Bari et al. (2003) used a denuder at Manhattan and Bronx in New York City, but did not analyse particulate NO_3^-. They obtained HNO_3 concentrations of 1.6 $\mu g\,m^{-3}$ (Manhattan) and 1.0 $\mu g\,m^{-3}$ (Bronx).

The decreasing sulphur dioxide levels in most parts of Europe and the increasing automobile traffic, causing elevated levels of nitrogen compounds, ozone and particulate matter, have created a new multi-pollutant situation. In this context, Varotsos et al. (2005) applied the detrended fluctuation analysis to the surface NO_2, O_3, and aerosol particle measurements made in Athens during 1987–2003, showed that the temporal evolution of air pollution exhibits a long memory effect. In particular, this analysis revealed persistent long-range power-law correlations from about 4 h to 9 months for PM_{10} in Athens, and for lag times from about 4 h to 2 weeks for $PM_{2.5}$ fluctuations in a 6-month data set collected in East Baltimore.

The effect on corrosion induced from this new multi-pollutant composition of air in Europe has been studied in the frame of an EU-project entitled MULTI-ASSESS (http://www.corr-institute.se/MULTI-ASSESS, Kucera et al., 2005). The main purpose of the project was to develop dose-response functions for prediction and prevention of damage to cultural heritage and to establish air concentration limit values for the protection of different materials. The dose-response functions and the concentration limit values will be published elsewhere.