Atmospheric Environment 45 (2011) 873–882

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Temporal trends in sulphate concentrations at European sites and relationships to sulphur dioxide

Alan M. Jones, Roy M. Harrison*

School of Geography, Earth and Environmental Sciences, Division of Environmental Health & Risk Management, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

A R T I C L E I N F O

Article history:
Received 13 May 2010
Received in revised form
10 November 2010
Accepted 13 November 2010

Keywords:
Sulphate trends
Sulphur dioxide
Abatement
Non-linearity

A B S T R A C T

Temporal trends in sulphate data taken from UK networks from the period 2001–2008 have been examined, together with trends in relevant precursor gases. In general, trends in sulphate are small, and the data sets are not of sufficient length to determine the direction of trend with confidence. Since relatively short periods of high or low concentration near to the start or finish of the period have a disproportionate influence, the choice of period over which the trend is calculated is crucial to the outcome. All six sites showed a significant reducing trend in sulphur dioxide, while ammonia data appear to be affected by sampling problems and site relocations and clear trends are not apparent. Data relating annual mean airborne concentrations of sulphur dioxide and sulphate from several countries can be related through a relationship of the form: $\chi\,[SO_4^{2-}] = a \cdot \chi\,[SO_2]^b + c$ in which a, b and c are constants and χ represents concentrations. While constant b remains the same for different countries, a and c can change in ways that appear to relate to either the distance from major SO_2 sources, or the oxidising capacity of the atmosphere. Using the relationship between SO_4^{2-} and SO_2 derived from UK sites allows estimation of the reduction in sulphur dioxide emissions affecting UK sites needed to reduce sulphate concentrations by 1 μg m^{-3}. This is 55% and 49% for Harwell and North Kensington respectively.

1. Introduction

In the period prior to 2000 substantial reductions were observed in atmospheric concentrations of particulate matter under 10 μm aerodynamic diameter (PM_{10}) (AQEG, 2005), and in sulphur dioxide (SO_2) and oxides of nitrogen (NO_2) the gaseous precursors of particulate sulphate (SO_4^{2-}) and nitrate (NO_3^-) which make up a considerable proportion of the total PM_{10}. The reduction in SO_2 concentrations has been particularly notable, in the order of 60–90% over two decades in Europe (Lövblad et al., 2004), although the reduction of particulate sulphate concentrations has been less rapid. In more recent years, it has been observed in the United Kingdom (UK) that PM_{10} concentrations are not falling in line with expectations (Harrison et al., 2008). The reduction in the concentration of sulphate also appears to have ceased in recent years (Lawrence et al., 2008). While the concentrations of NO_x and SO_2 are still declining, the rate of reduction appears to be less than in previous years (AQEG, 2007; Hayman et al., 2007).

In the past three decades in Europe, and more recently in the United States, there have been substantial reductions in SO_2 emissions (Vestreng et al., 2007; Sickles and Shadwick, 2007a). The reductions in emissions of SO_2 and NO_x from sources in the UK and the first 15 member countries of the European Union (EU-15), from 1970 to 1980 respectively, are shown in Fig. S1 (see Supplementary information). Between 1970 and 2007 SO_2 emissions from land based sources in the UK reduced from 6365 to 591 kt yr^{-1}, while NO_x emissions fell from 2945 to 1486 kt yr^{-1} over the same period. Within the EU-15 between 1980 and 2007 SO_2 emissions fell from 25,999 to 4131 kt yr^{-1}, while NO_x emissions were reduced from 11,843 to 8757 kt yr^{-1}. Data is taken from the UK National Atmospheric Emissions Inventory (NAEI), and European Monitoring and Evaluation Programme (EMEP) databases. The trends in emissions from the UK and EU-15 are similar with UK emissions making up approximately 20% of the EU-15 emissions. Emissions of SO_2 and NO_x from international marine and air transport sources associated with the UK make up a small, but increasing, proportion of the total emissions.

During the period of emission reduction, a disparity between the rates of reduction of airborne SO_2 and SO_4^{2-} concentrations has been noted by numerous authors. Lövblad et al. (2004) reported on the rate of reduction of SO_2 emissions, and the airborne concentrations of SO_2 and particulate SO_4^{2-} over 20 years in 16 European countries. They noted that while the SO_2 concentrations generally responded linearly to the reductions in SO_2 emissions over the

---

* Corresponding author. Tel.: +44 121 414 3494; fax: +44 121 414 3709.
E-mail address: r.m.harrison@bham.ac.uk (R.M. Harrison).

1352-2310/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2010.11.020

period, the reductions in SO_4^{2-} aerosol were generally much less. A number of other studies in Europe and North America have examined the relationship between SO_2 emission trends or the measured SO_2 trends and particulate SO_4^{2-} concentration trends (Ruoho-Airola et al., 2004a,b; Sickles, 1999; Fowler et al., 2005; Reid et al., 2001; Bashir et al., 2008; Karneli et al., 2009; Anttila and Tuovinen, 2010; Sickles and Shadwick, 2007a,b; Dutkiewicz et al., 2000; Mueller, 2003; Lawrence et al., 2008). Most confirm a non-linearity between particulate SO_4^{2-} and SO_2. One study by Dutkiewicz et al. (2000) found a linear relationship between SO_2 emissions and particulate SO_4^{2-} concentrations by allocating different weightings to the contributions of SO_2 emissions from different source areas. Malm et al. (2002) investigating the annual values of the 80th percentile of particulate SO_4^{2-} concentration, rather than the mean concentrations, found that they closely tracked the differing SO_2 emissions in four distinct regions of the United States.

The studies described above generally compare annual values of SO_2 and particulate SO_4^{2-} concentration, or means of the seasons of consecutive years (Mueller, 2003; Sickles and Shadwick, 2007a,b). The seasonal cycles of SO_2 and particulate SO_4^{2-} are usually different, with maximum SO_2 concentrations tending to occur during winter, and maximum particulate SO_4^{2-} concentrations most commonly occurring during the summer (Dutkiewicz et al., 2000; Sickles and Shadwick, 2007a,b; Berglen et al., 2007). However Bashir et al. (2008) reported higher total SO_4^{2-} concentrations during the winter at a site on the west coast of Ireland, and Spindler et al. (1999) also observed higher concentrations of SO_4^{2-} during the winter in Saxony. Cyrys et al. (1995) found higher SO_4^{2-} particle concentrations during winter in eastern Germany and the Czech Republic which they ascribed to greater emissions from coal combustion for heating and poorer atmospheric dispersion. Querol et al. (2009) ascribed high summer concentrations of SO_4^{2-} in the Mediterranean to enhanced photochemistry, reduced air mass movement or increased mixing depth allowing increased mixing with polluted air masses, or the possible greater contributions of secondary marine SO_4^{2-}, but also noted a secondary maximum in the SO_4^{2-} concentration during winter.

Various reasons have been suggested for the non-linearity between the trends of concentration of SO_2 and particulate SO_4^{2-}, which have been summarised by Reid et al. (2001) as:

- Different statistical approaches yielding different results;
- Spatial or temporal inhomogeneities;
- Different lengths of data record;
- Different atmospheric lifetimes of SO_2 and particulate SO_4^{2-};
- Obscuration of concentration differences by meteorological variability;
- Systematic changes in the concentrations of other atmospheric constituents or other sources.

Added to this are:

- A temporal increase in the deposition efficiency of SO_2 due to co-deposition with ammonia (Fowler et al., 2005);
- Oxidant limitation of the SO_2 conversion to SO_4^{2-} at higher concentrations (Vieno et al., 2010).

Reid et al. (2001) conclude that there is a limited understanding of the chemical and physical processes involved in particulate SO_4^{2-} formation. They reject the first three possibilities, because of the general agreement between different studies, and the efforts made to minimise variability within studies, although there is a need to make allowance for changes in analysis techniques (e.g. Ruoho-Airola et al., 2004b) during the period of certain data sets.

Because the lifetime of sulphur in the atmosphere can be several days, it is argued by Sickles and Shadwick (2007b) that the extent of conversion of SO_2 to SO_4^{2-} increases with distance, with SO_4^{2-} having a longer lifetime in the atmosphere than SO_2, resulting in SO_4^{2-} aerosol concentrations being more dependent upon SO_2 emissions a long distance upwind than on local sources (Karneli et al., 2009). Emission trends in the local and upwind areas may differ. Dutkiewicz et al. (2000) were able to find a linear relationship between particulate SO_4^{2-} concentrations and upwind SO_2 emissions by giving appropriate weightings to the contributions of different upwind source areas. Micallef and Colls (1999) regressed particulate SO_4^{2-} concentrations against SO_2 concentrations for a number of predominantly rural United Kingdom sites, and concluded that the positive intercepts were representative of SO_4^{2-} from distant sources.

Reid et al. (2001) suggest that if the slower decline of SO_4^{2-} concentrations than SO_2 concentrations was due to an increase in the rate of conversion resulting from an increase in the oxidising power of the atmosphere, then increased ozone levels should also be observed, which they do not believe to be the case. They also suggest that the production of SO_4^{2-} is insensitive to ammonia concentrations and therefore any change in ammonia concentrations should have no effect. Some model studies (e.g. Pun et al., 2008) show sensitivity of sulphate to ammonia emissions, while others (e.g. Renner and Wolke, 2010) do not. However, atmospheric SO_4^{2-} is produced by the oxidation of SO_2 by both gaseous and aqueous-phase reactions (Dutkiewicz et al., 2000). The gas phase reaction of SO_2 with hydroxyl radical is not influenced by ammonia. However, in the presence of liquid water (e.g. cloud or fog), SO_2 dissolves forming bisulphite and sulphite ions

$$SO_2 + H_2O \leftrightarrow SO_2{\cdot}H_2O$$

$$SO_2.H_2O \leftrightarrow HSO_3^- + H^+$$

$$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$$

The equilibria are sensitive to pH, and HSO_3^- is the predominant species over the range pH 2–7. Oxidation of HSO_3^- leads to formation of sulphuric acid which in turn causes a reduction in pH, which limits the solubility of SO_2 and affects some oxidation processes. The main oxidation processes are with hydrogen peroxide, which is little affected by pH, but limited by the typically low concentrations of H_2O_2, or with ozone, which is far more abundant, but the reaction slows as pH reduces. Were it not for mass transfer limitations, this reaction would deplete SO_2 at $5 \times 10^3\%\ h^{-1}$ at pH 6, but only at $3 \times 10^{-2}\%\ h^{-1}$ at pH 3 in the presence of 50 ppb ozone (Harrison, 2001). The presence of ammonia is important, as it is a basic gas which neutralises sulphuric acid, maintaining a higher pH and hence rate of SO_2 oxidation. Choularton and Bower (2001) suggest that in the United Kingdom the vast majority of SO_4^{2-} is formed through aqueous-phase processes, but this is likely to be very seasonally dependent.

Fowler et al. (2005) have observed an increase in SO_2 deposition velocities (flux normalised by concentration) as SO_2 concentrations have fallen while ammonia concentrations have remained constant, as a result of co-deposition to wet plant surfaces. This could introduce a non-linearity between SO_2 emissions and airborne concentrations, which is evident when viewing 18 years of UK data, but not in the past ten years of data (Fig. 3.7 in ROTAP, 2009). Such trends will also have been influenced by a progressive change from low to high-level emissions.

The Airborne Particulate Concentrations and Numbers Network (APCNN) was established in the UK in late 2001 with two sites in