

# An analysis of the ionic composition of Irish precipitation and background air quality since 1980 based on samples collected at Valentia Observatory, Co. Kerry, Ireland

W. Bashir<sup>1,3</sup>, M. Ryan<sup>2</sup>, L. Burke<sup>2</sup>, F. McGovern<sup>3</sup> & B. Paull<sup>1</sup>

<sup>1</sup>National Centre for Sensor Research (NCSR),

School of Chemical Sciences, Dublin City University, Dublin, Ireland

<sup>2</sup>Met Éireann Headquarters, Dublin, Ireland

<sup>3</sup>Environmental Research Centre (ERC),

Environmental Protection Agency, Richview, Dublin, Ireland

## Abstract

This work has investigated the ionic composition of precipitation samples based on measuring  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4\text{-S}$ ,  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$  (mg/L) and the trends of  $\text{SO}_2\text{-S}$ ,  $\text{SO}_4\text{-S}$ , and  $\text{NO}_2\text{-N}$  ( $\mu\text{g}/\text{m}^3$ ) concentrations in air samples collected on a daily basis at Valentia Observatory, Cahirciveen, Co. Kerry, Ireland and analysed in the Met Éireann laboratory over the period 1980 - 2004.

The time series of annual average  $\text{SO}_2\text{-S}$  and  $\text{SO}_4\text{-S}$  concentrations ( $\mu\text{g}/\text{m}^3$ ) for the air data shows a distinct downward trend. The  $\text{NO}_2\text{-N}$  concentration ( $\mu\text{g}/\text{m}^3$ ) levels have remained relatively stable since measurements commenced in 1989. No such obvious trends are visible from the original precipitation data; however, by investigating the contribution of sea-salt sulphate to the total sulphate levels it is possible to conclude that the non-sea salt sulphate levels (i.e. anthropogenic contribution) have decreased since the measurements have commenced.

The location of the site on the south west coast results in exposure to the Atlantic Ocean and this results in considerable contribution of ions from the sea that is clearly shown from the wind sector analysis of the precipitation samples for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ . The air data shows that the highest concentrations for the  $\text{SO}_2\text{-S}$  and  $\text{SO}_4\text{-S}$  and  $\text{NO}_2\text{-N}$  are correlated with winds coming from an easterly and northeasterly direction (which is also confirmed from the non-sea salt sulphate levels for the precipitation results). The lowest concentrations were found for westerly directions. This has also been proven correct with the use of back trajectory analysis, which has allowed tracing the movement of air parcels using ECMWF analysis fields.

*Keywords:* background air concentration, precipitation, sulphur dioxide, sulphate, nitrogen dioxide, calcium, magnesium, sodium, sea-salt sulphate, anthropogenic sources.



## 1 Introduction

Atmospheric deposition is comprised of both dry and wet components. The dry component consists mostly of dust particles derived from both natural sources (e.g. soils, plant debris, volcanic emissions) and anthropogenic sources (e.g. fertilizers and other soil amendments, fly ash). Other materials contributing to the dry component include condensed aerosols and gases both adsorbed onto and deposited along with dust fall, or adsorbed directly by the materials of the earth's surface. Airborne particulates may have a marked effect upon the chemistry of wet precipitation, especially in areas downwind from major dust producing regions.

The wet component, or precipitation, consists of rain, drizzle, hail or snow and soluble constituents such as gaseous oxides of carbon, sulphur and nitrogen, which greatly enhance the acidity of precipitation by the formation of carbonic, sulphuric and nitric acids, respectively. The composition of rainwater is highly influenced by the history of air masses giving rise to precipitation i.e. what remains after transport from the continent, past deposition and recent over-ocean inputs. Precipitation composition, averaged over suitably long periods (seasons, years) is used as an indicator of atmospheric composition and its careful monitoring is essential to fully understand the extent of anthropogenic pollution [1].

The analysis of such dry and wet deposition is part of the monitoring of background air quality and precipitation carried out at the Valentia Observatory, Cahirciveen, Co. Kerry, Ireland since 1980. Met Éireann, the Irish Meteorological Service, owns Valentia Observatory. The Met Éireann Valentia Observatory positioned at 51,56 N, 10,15 W, altitude 9 m above sea level, was established as an EMEP monitoring site in 1980.

The Valentia data provides a relatively long-term perspective on variation of ambient sulphur dioxide (SO<sub>2</sub>-S), sulphate (SO<sub>4</sub>-S) and nitrogen dioxide (NO<sub>2</sub>-N) levels at the western boundary of Europe and also allows trends from the precipitation data to be identified.

## 2 Experimental section

### 2.1 Sampling and analysis of sulphur dioxide and sulphate in air

The filter pack method has been commonly used by EMEP sites for air sampling. These filter packs have been assembled with filters, one untreated and one impregnated filter. This is referred to as a 2-stage filter pack. The first filter in the air stream is an aerosol filter for collecting sulphate. This is followed by an alkaline impregnated filter, which is treated with 300 µl of 1.0 M KOH in 10% glycerol and 90% methanol. This collects sulphur dioxide and other volatile acidic substances. One filter pack is required for each day including a blank [2].

The filter pack is exposed to the environment for 24 hours and then returned to Met Éireann for analysis in the laboratory at the end of the week. The filter packs are disassembled and the filters are placed in separate beakers. The



extraction of sulphate from the aerosol filter requires 20 mls of deionized water being added to the beaker and is left for 24 hours. For the alkaline filter, 20 mls of 0.3% H<sub>2</sub>O<sub>2</sub> is added to the beaker and is left for 24 hours. Final analysis of the samples is by ion chromatography. Between 1980 – 2004 over 8000 air samples have been analysed in the Met Éireann laboratory.

## 2.2 Sampling and analysis of nitrogen dioxide in air

This is based upon the absorption of nitrogen dioxide on a sodium iodide impregnated glass-sinters. The impregnation solution consists of 9 g NaI and 1 g NaOH in 90 g methanol or ethanol. 500 µl impregnation solution is added to carefully cleaned glass sinters, one for each day. After exposure for 24 hours the extraction from the glass filter is performed with deionized water, which is then followed by analysis using the Griess method [2].

## 2.3 Sampling and analysis of precipitation samples

A bulk sampler is used for the collection of these samples. The precipitation sample is collected at 10 am after exposure for 24 hours at Valentia Observatory. The volume and pH of sample is measured on site. At the end of the week the samples are transported to Met Éireann laboratory where the analysis of the samples occurs by ion chromatography.

# 3 Sulphur dioxide in the air samples

The annual average SO<sub>2</sub>-S concentration (µg/m<sup>3</sup>) from the air samples is shown in Figure 1. Each annual average is based upon the number of samples analysed and accepted under the EMEP flagging regulations. A clear downward trend is evident from this data. The analysis suggests that annual average levels have decreased from approximately 0.78 µg/m<sup>3</sup> in 1981 to less than 0.19 µg/m<sup>3</sup> in 2004. This represents an approximate 75% reduction over the measurement period. These levels would be expected to decrease as local emissions are reduced. This observation therefore confirms the success of local emissions reductions actions.

## 3.1 Sulphate in the air samples

The annual average SO<sub>4</sub>-S concentration (µg/m<sup>3</sup>) is shown in Figure 2. As was the case for SO<sub>2</sub>-S, a clear trend towards lower levels is evident for the annual average data. A reduction of approximately 50% between 1981 and 2004 levels (0.69-0.37 µg/m<sup>3</sup>) was recorded. This decrease is not as large as that observed for SO<sub>2</sub>-S. A number of factors including the contribution of sea-salt sulphate at this site may have contributed to the observed levels. However sulphate, which is largely formed in the atmosphere through oxidation of sulphur dioxide, may be transported over long distances. This means that a range of anthropogenic sources, including North American sources, may have contributed to these observations.



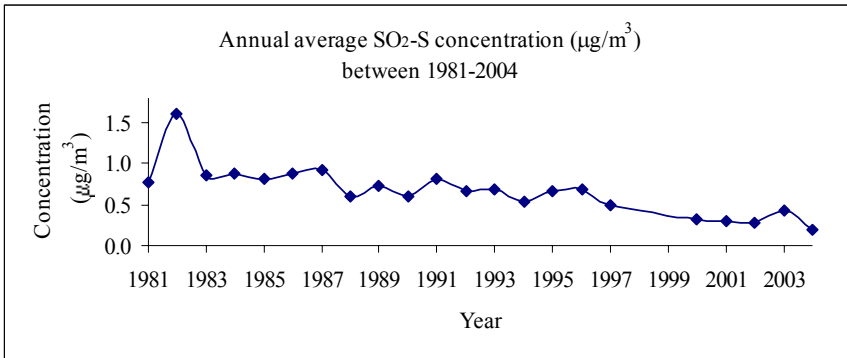


Figure 1: The annual average SO<sub>2</sub>-S concentrations (µg/m<sup>3</sup>) found in air samples collected at Valentia Observatory.

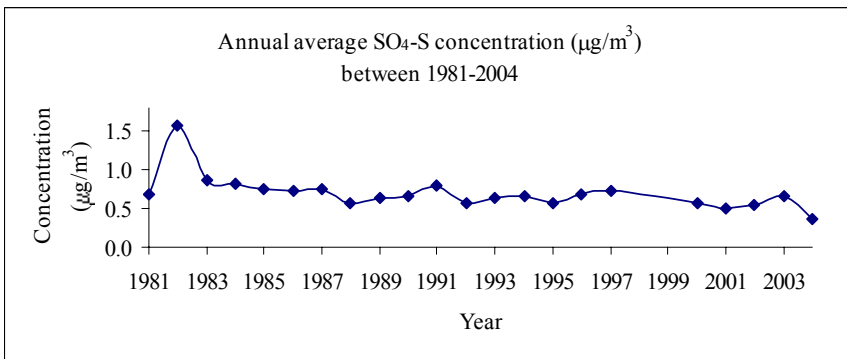


Figure 2: The annual average SO<sub>4</sub>-S concentrations (µg/m<sup>3</sup>) found in air samples collected at Valentia Observatory.

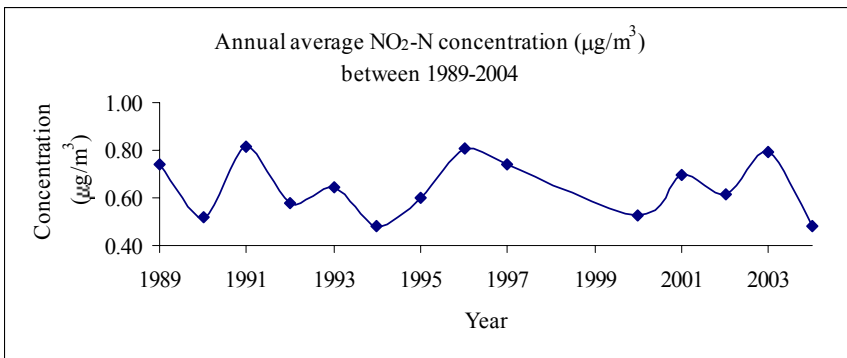


Figure 3: The annual average NO<sub>2</sub>-N concentrations (µg/m<sup>3</sup>) found in air samples collected at Valentia Observatory.



### 3.2 Nitrogen dioxide in the air samples

The annual average  $\text{NO}_2\text{-N}$  concentration ( $\mu\text{g}/\text{m}^3$ ) is shown in Figure 3. The levels have remained relatively stable throughout the measurement period, which commenced in 1989 and probably reflect the difficulties that exist in addressing emissions of oxides of nitrogen from combustion sources. The data set is therefore less extensive than that for  $\text{SO}_2\text{-S}$  and  $\text{SO}_4\text{-S}$ . However, an annual wintertime peak is apparent in the monthly data.

### 3.3 Sea-salt sulphate contribution in the air samples

The analysis of the  $\text{SO}_4\text{-S}$  air data is somewhat hampered by the absence of analysis of the contribution from sea-salt to these levels. Sea-salt ions such as  $\text{Na}^+$  are now part of the regular EMEP chemical analysis since 2004. Figure 4 shows the total sulphate and non sea-salt sulphate (anthropogenic) levels during 2004. The lowest anthropogenic concentrations were observed from the westerly directions and the highest from the easterly.

Trends in the  $\text{NO}_2\text{-N}$  data were less defined.

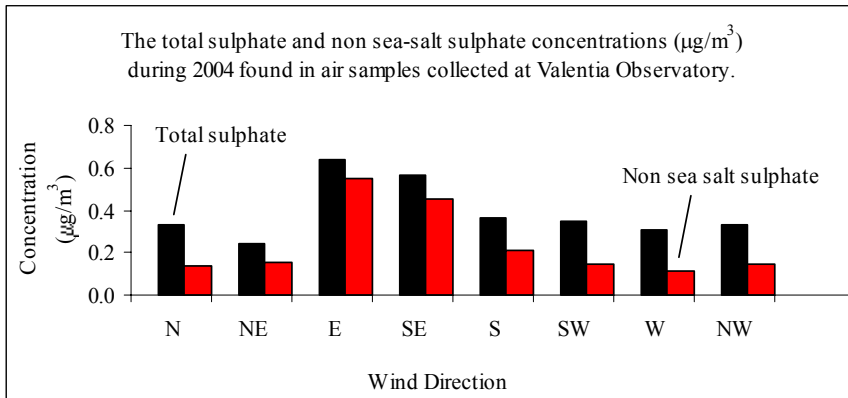


Figure 4: The total sulphate and non sea-salt sulphate concentrations ( $\mu\text{g}/\text{m}^3$ ) during 2004 found in air samples collected at Valentia Observatory.

## 4 Wind direction based analysis

The daily concentration data were sectorised according to the daily average wind direction. Average concentrations of  $\text{SO}_2\text{-S}$ ,  $\text{SO}_4\text{-S}$  and  $\text{NO}_2\text{-N}$  data for six wind local sectors are shown in Figures 5, 6 and 7 respectively. The figures clearly show that the highest concentrations were recorded for east and northeasterly directions. The lowest concentrations were found for westerly directions.

The difference in concentrations between east and westerly data is clearest for the  $\text{SO}_2\text{-S}$  and  $\text{NO}_2\text{-N}$  data. The difference in concentration is not as large for  $\text{SO}_4\text{-S}$ . As was outlined in the previous section, this can in part be attributed to

the contribution from sea-salt in air coming from the west over the open ocean. This contribution is reduced during easterly conditions.

It is apparent from the full data set that reduction in ambient levels occurred for all wind directions. The concentrations measured in samples from westerly air display a small but significant reduction over the measurement period. Long-range transport of sulphur dioxide from North America is not considered to a significant influence on the measurements. Natural oceanic sources such as seasonal emissions from phytoplankton are also not expected to display such a decline. Therefore, this observation is considered to reflect decreased sulphur dioxide levels in re-circulated air from largely local sources. However, further examination of this feature is required.

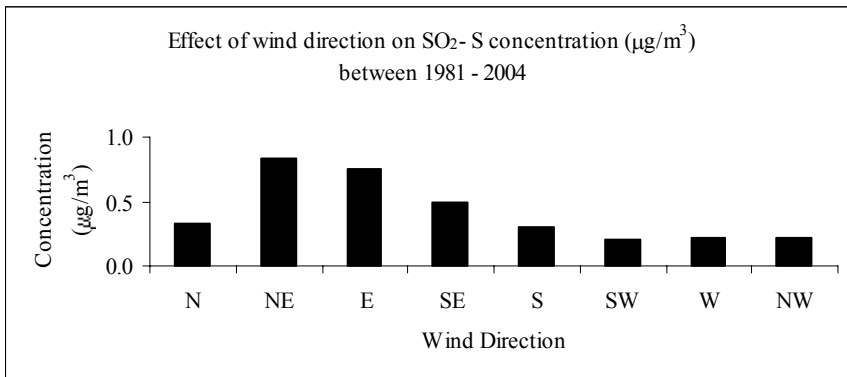


Figure 5: The effect of wind direction on SO<sub>2</sub>-S concentrations (µg/m<sup>3</sup>) found in air samples collected at Valentia Observatory.

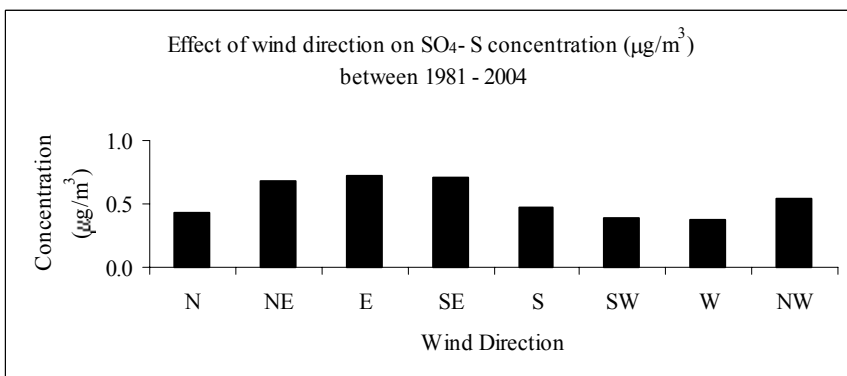


Figure 6: The effect of wind direction on SO<sub>4</sub>-S concentrations (µg/m<sup>3</sup>) found in air samples collected at Valentia Observatory.

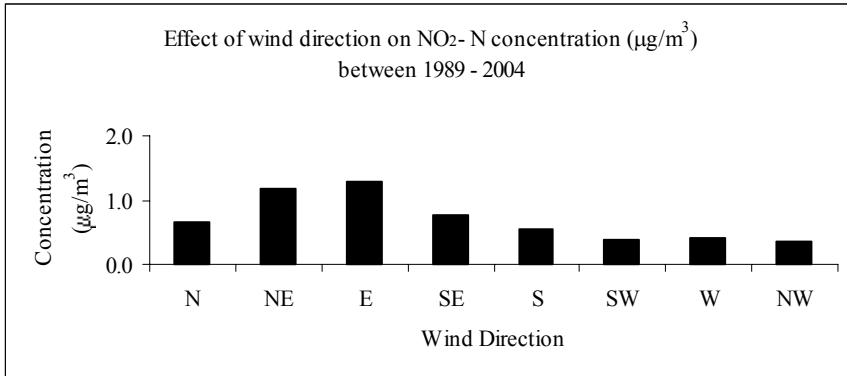


Figure 7: The effect of wind direction on NO<sub>2</sub>-N concentrations (µg/m<sup>3</sup>) found in air samples collected at Valentia Observatory.

## 5 Chemical trends in precipitation

The time series of weighted mean concentrations of SO<sub>4</sub>-S, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub>-N and NO<sub>3</sub>-N (mg/L) illustrated various trends. Elevated concentrations of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup> were observed during stormy sea conditions which would be expected, as the station is located on the south west coast of Ireland, which resulted in contributions of these ions from the seawater. SO<sub>4</sub>-S showed the greatest reduction from the linear regression based trend line.

## 6 Sea-salt sulphate contribution to the precipitation samples

With the precipitation data both sulphate and sodium has been measured since the early 1980s and it is therefore possible to investigate the contribution of sea-salt sulphate and hence calculate the non-sea salt sulphate levels i.e. anthropogenic levels. It is possible to conclude that indeed the anthropogenic contribution has decreased since the measurements have commenced as shown in figure 8. A similar decreasing trend in non sea-salt sulphate concentrations was also observed in other EMEP sites in the UK, such as Eskdalemuir, in Scotland.

The air data, as mentioned previously, shows that the highest concentrations for the SO<sub>2</sub>-S and SO<sub>4</sub>-S and NO<sub>2</sub>-N are correlated with winds coming from an easterly and north easterly direction, which is also confirmed from the anthropogenic levels for the precipitation results as shown in figure 9. The lowest concentrations were found for westerly directions. This has also been proven correct with the use of back trajectory analysis, which has allowed tracing the movement of air parcels using ECMWF analysis fields.

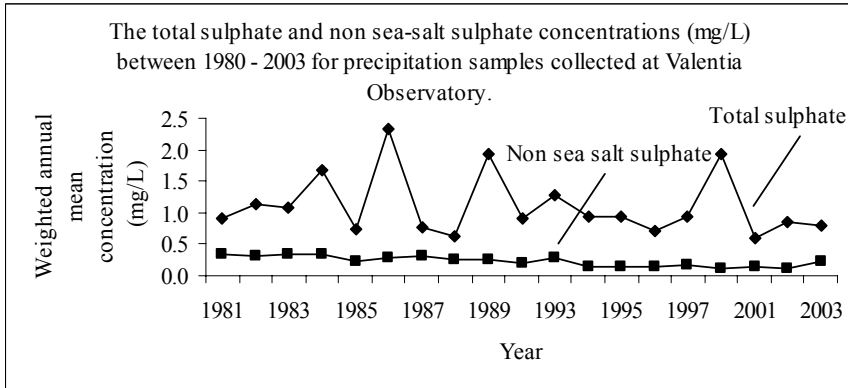


Figure 8: The total sulphate and non sea-salt sulphate concentrations (mg/L) between 1980–2003 for precipitation samples collected at Valentia Observatory.

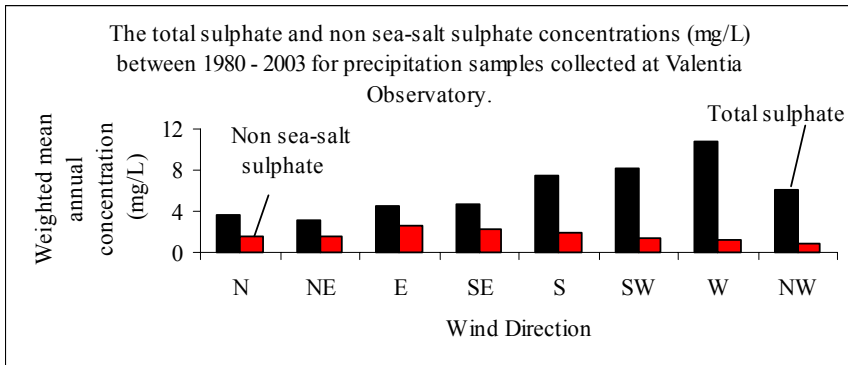


Figure 9: The total sulphate and non sea-salt sulphate concentrations (mg/L) between 1980–2003 for precipitation samples collected at Valentia Observatory.

## 7 Conclusions

The Valentia data constitutes a valuable record of atmospheric change since 1981 from a western European perspective. These data show the success of national and international actions to reduce emissions of sulphur species. This has resulted in a decrease in ambient levels  $SO_2$ -S and  $SO_4$ -S levels observed in Ireland. The main findings from the observational records are;

- $SO_2$ -S levels have decreased by approximately 75% since 1981.
- $SO_4$ -S levels have decreased by approximately 50%, however, the real rate of decrease may be masked by local influences





- The results for NO<sub>2</sub>-N are not yet as clear. No trend has been observed in the ambient levels, which have remained relatively stable since measurements commenced.
- The highest anthropogenic concentrations were correlated with winds coming from an easterly and northeasterly direction: the lowest concentrations were from the westerly directions. Both precipitation and air data investigations confirmed this.

## References

- [1] Seinfeld, J.H., Pandis, N.S., *Atmospheric Chemistry and Physics*, John Wiley and Sons, Inc. New York, Chicester, Weinheim, Brisbane, Singapore, Toronto, pp. 41 – 63.
- [2] EMEP manual for sampling and analysis, <http://www.nilu.no/projects/ccc/manual/>

