Technical Report:

EMEP observations at the Met Éireann Valentia Observatory, Co. Kerry, Ireland

Compiled by: Dr. Wasim Bashir and Dr Frank McGovern,
Environmental Protection Agency,
Centre of Excellence,
McCumiskey House ,
Richview, Clonskeagh Road
Dublin 14
Ireland

Margaret Ryan and Liam Burke
Met Eireann,HEADQUARTERS,
Glasnevin Hill,
Dublin 9,
Ireland

October 2004

Executive summary

Concerns in the United Nations Economic Commission for Europe (UNECE) area with respect to the environmental impacts of acidifying species have resulted in a series of international agreements to reduce emissions of acidifying species. Most recently, these have culminated in the targets established under the Gothenburg protocol. The Gothenburg targets have also been introduced into EU legislation through the National Emission Ceilings (NEC) Directive.

The European EMEP network, established in the 1970s under the UNECE, provides the structure for development of scientific understanding of emissions and their impacts. EMEP also acts as the co-ordinating body for measurements of ambient levels of key pollutants across Europe.

Since the 1980s, considerable progress has been reported in Europe and nationally on reductions of sulphur species. These emissions reductions have resulted in reduced ambient SO_2 and sulphate (SO_4) levels over Ireland. The greatest reductions are seen in SO_2–S levels for which an average decrease of 0.036 $\mu g\ m^{-3}$ per annum has been observed. This amounts to a decrease of about 60% in ambient SO_2 levels during the measurement period.

The reduction in ambient SO_4-S levels is less pronounced at 0.019 $\mu g\ m^{-3}$ per annum. Nevertheless, this also amounts to a decrease of approximately 40% over the measurement period. This analysis may be influenced by the presence of natural SO_4 associated with sea spray at the measurement location. The NO_2-N data series is not as extensive as that for the sulphur species. No trend is evident for the annual average data.

Wind sector analysis of the SO_2–S and SO_4–S data shows that the highest concentrations of these species are correlated with winds coming from an easterly direction. These levels also displayed the greatest rate of decrease over the measurement period. The SO_2-S levels observed in air from westerly directions are also decreasing. This observation requires further analysis but is considered to be largely associated with reduced local emissions of SO_2.

The overall reductions in ambient SO_2 and SO_4 levels are considered to show the success of international actions in addressing the challenges of acidification. These reductions have positive consequences both in term of impacts on ecosystems and human health, as well as for commercial crops and buildings.

As SO_4 is a significant component of ambient particulate matter (PM), the reduction of SO_4 levels will also contribute towards the achievement of air quality targets for PM10 and PM2.5. However, further significant reductions in acidifying species, particularly nitrogenous species, are required in order to meet current emissions targets by the 2010 deadline.

1 Introduction

This EPA National Environmental Research Centre of Excellence (COE) report, produced in co-operation with Met Eireann, is the first in a series on air pollution and acidification. This series of reports will provide background information, and national analyses of measures, in relation to the International Convention on Long Range Transboundary Air Pollution (CLRTAP) and inform national responses to the EU Clean Air For Europe (CAFÉ) initiative. Synergies with other areas such climate change will also be explored.

This report provides an analysis of changes in ambient levels of pollutant species, covered under international agreements on transboundary air pollution and, more recently, regulated under the EU National Emissions Ceiling Directive, that are measured as part of national monitoring programmes. The data were collected over a period of more than 20-years at the Met Eireann Observatory at Valentia. This site is also a meteorological observatory and houses a phenological garden.

The analysis of these data provides an opportunity to evaluate if and how reported reductions in emissions of species covered under international transboundary pollutant agreements have been observed in Ireland. The analysis presented here is confined to air pollutant data. Analyses of wet deposition/rainfall data will be published in subsequent reports.

2 Background

Scientific and public concerns in relation to the impacts of acidifying species on ecosystems and human health, which emerged during the 1970s, have resulted in a series of international agreements to reduce or eliminate such emissions. EMEP was initiated in 1977 as a special programme under the United Nations Economic Commission for Europe (UNECE) under the convention on Long-range Transboundary Air Pollution (CLRTAP). EMEP provides scientific support for the Convention and acts to co-ordinate monitoring activities at an extensive range of sites throughout the UNECE area. Data from EMEP sites, which are operated by the member states, contribute to efforts to understand transport and impacts of the monitored pollutants.

Considerable reductions in European emissions of SO_2 and other acidifying species have been reported. These reductions have been brought about though a series of factors including, change of fuel use, the introduction of new clean technologies and economic restructuring. These achievements have been coupled with greater understanding of the complexities and inter-linkages of pollution emission, transport and transformation, as well as health and ecological impacts as well as other damages. This has resulted in a broadening of the scope of species described as transboundary pollutants and the concomitant evolution of monitoring requirements. The increased understanding of the role of transboundary pollutants such as sulphate and ozone in climate change is of particular note (IPCC, 2001).

Ireland's location on the western boundary of Europe, combined with the dominance of mid-latitude north Atlantic westerly winds, favours good air quality conditions. However, long-range pollution transport from North America and particularly short and medium range transport from Europe increases ambient levels of pollutant species.

3 National monitoring of trans-boundary pollutants

The Met Eireann 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 Electricity Supply Board (ESB) subsequently established additional sites at Turlough Hill (1991), The Burren (1997) and the Ridge of Capard (1997). The location of these sites is shown in Figure 1 and other details are given in Table 1. An extensive suite of atmospheric measurements is also carried out at the National University of Ireland (NUI) Galway atmospheric research station at Mace Head, some of which are reported to the EMEP database.

The three ESB sites were closed in 2003. However, three replacement sites have been established at Carnsore, Co Wexford, Oakpark, Co Carlow and Malin Head, Co Donegal in 2004. These have been established by the EPA in co-operation with Met Eireann, as part of an EPA COE project on trans-boundary air pollution and acidification. The locations of the new sites are also shown in Figure 1. The sites provide enhanced geographical coverage and operate under the new EMEP operational protocol, which has been developed to address current trans-boundary pollution issues, such as PM10 and PM2.5.

Organisation	Measurement site	Database code	Geographical co-ordinates	EMEP co-ordinates (50 km)	Altitude above sea-level (m)	In operation since
Met Éireann	Valentia	IE0001R	51,56 N 10,15 W	73.39, 44.83	9	1980
ESB	Turlough Hill	IE0002R	53,02 N 06,24 W	77.35, 49.33	420	1991
ESB	Burren	IE0003R	53,00 N 96 W	73.96, 47.74	90	1997
ESB	Ridge of Capard	IE0004R	5,37 N 07,27 W	75.94, 48.88	340	1997
NUIG	Mace Head	IE0031R	53,20 N 09,54 W	73.30, 47.86	340	1988

Table 1.0 Details on EMEP sites in Ireland. The Valentia and Mace Head sites are regional and Global Atmospheric Watch sites. The ESB sites were closed down in 2002. Three new sites are being established at Oakpar, Malin Head and Carnsore.

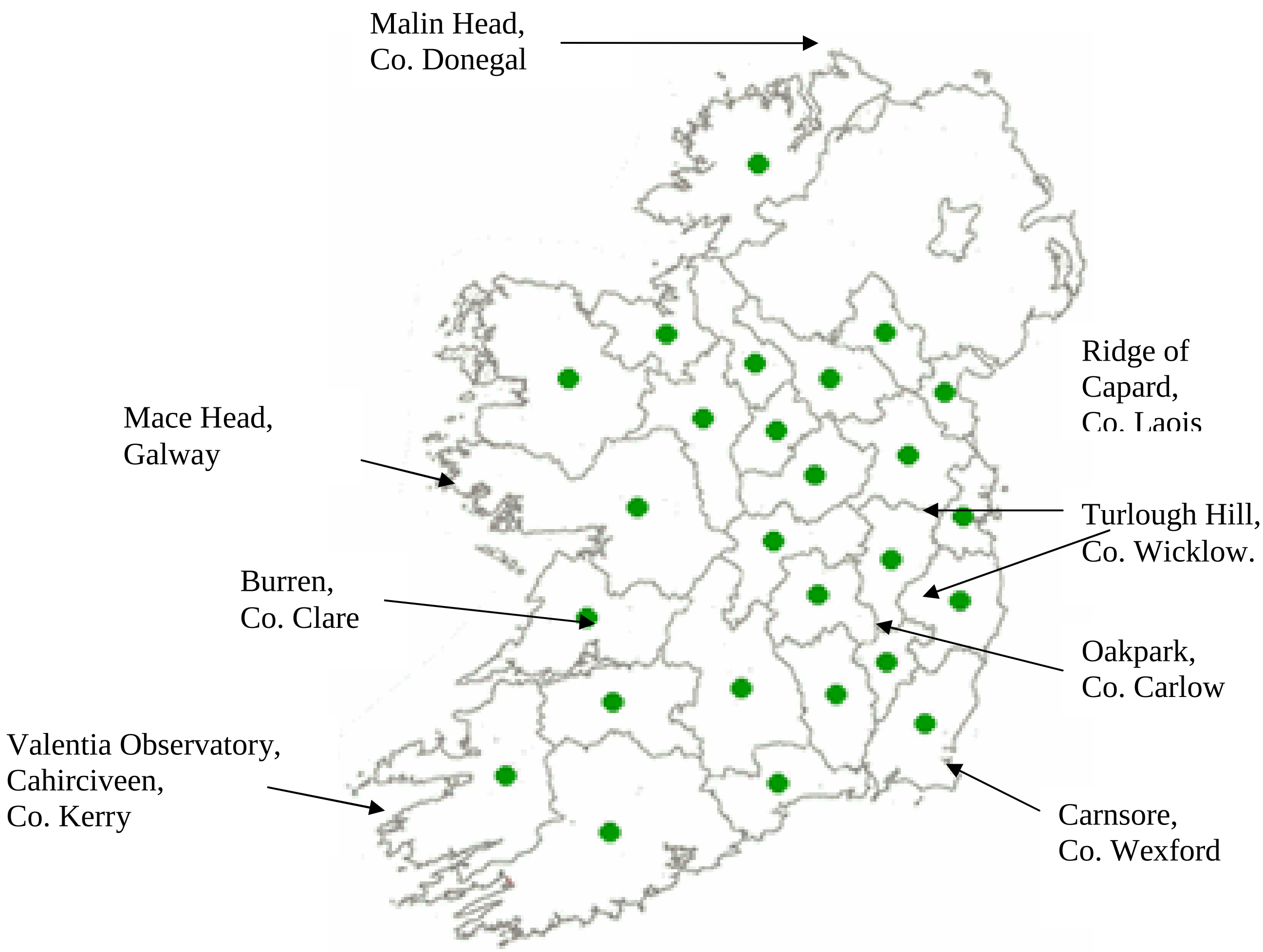


Figure 1. Map of Ireland showing the locations of Met Éireann, Valentia Observatory, Burren, The NUIG Atmospheric research station at Mace Head, Malin Head, Ridge of Capard, Turlough Hill, Oakpark, and Carnsore.

4.0. Results and analysis of data from the Valentia site

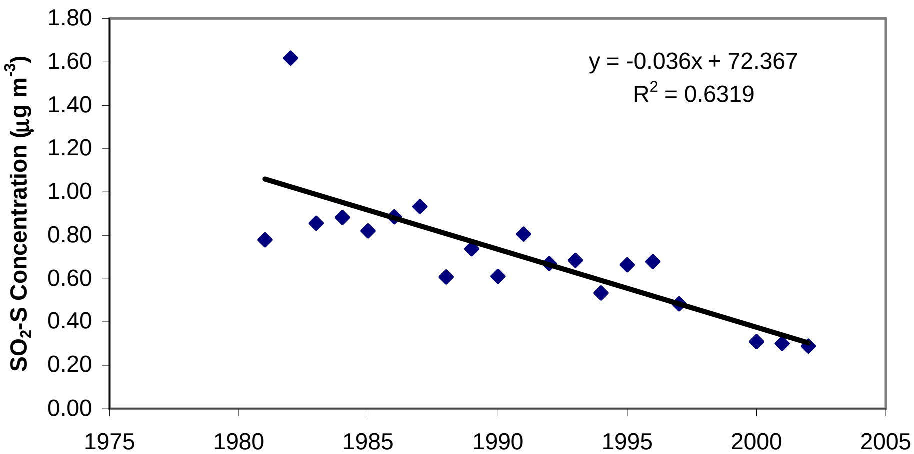
This report concentrates on results for the Valentia Observatory. This site has the most extensive data record for SO_2-S, SO_4–S and NO_2-N available for Ireland. Measurements of SO_2 and SO_4 commenced in 1980. The measurements of NO_2 commenced in 1988. The data record was interrupted during 1998/99 due to instrumentation problems and site re-organisation.

4.1. Sulphur dioxide (SO_2)

The time series of annual average SO_2-S concentration data along with standard deviation values are shown in Figure 2. A clear downward trend towards lower concentration levels is evident from these data. The linear regression[1] trend line shown in Figure 3 indicates an average concentration reduction rate of 0.036 $\mu g\ m^{-3}$ per annum over the measurement period. This analysis suggests that annual average levels have decreased from approximately 1.0 $\mu g\ m^{-3}$ in 1981 to less than 0.4 $\mu g\ m^{-3}$ in 2002. This represents a 60% reduction in annual average levels. Further analysis of the data shows that this was primarily due to a reduction in peak levels, which is supported by the observation that the standard deviation values also decrease over this period. This is considered to reflect a reduction in the magnitude variation in peak concentration levels experienced at the site.

4.2. Sulphate (SO_4)

Annual average SO_4–S data and standard deviation values are shown in Figure 3. As was the case for SO_2–S, a clear trend towards lower levels is evident for the annual average data. The linear regression trend-line indicates a concentration reduction rate of 0.012 $\mu g\ m^{-3}$ per annum. This rate of decrease is not as large as that observed for SO_2–S. A number of factors including the contribution of sea-salt sulphate[2] at this site may have contributed to the observed levels. However, SO_4, which is largely formed in the atmosphere through oxidation of SO_2, may be transported over long distances. This means that a range of sources anthropogenic sources, including North American sources, may have contributed to these observations.



---

[1] Linear regression analysis is not fully applicable to these data but is used as a first approximation.

[2] Salt arising from sea spray is a source for sulphate. Sea-salt ions such as sodium (Na^+) and chlorine (Cl^-) were not determined. Therefore it was not possible to determine the sea-salt contribution i.e. to determine non-sea-salt/anthropogenic sulphate levels. Current sample analysis allows for this.

Figure 2. Annual average SO_2–S levels (µg m^{-3}) for the period 1981 to 2002. The linear regression-based trend line shows a significant reduction in ambient levels over the measurement period.

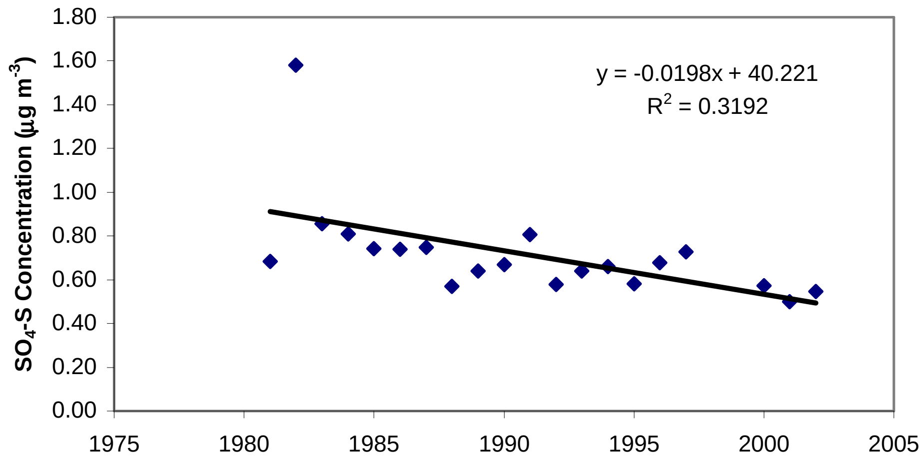


Figure 3. Annual average SO_4–S levels (µg m^{-3}) for the period 1981 to 2002. The linear regression trend line indicates a significant reduction in ambient levels over the measurement period.

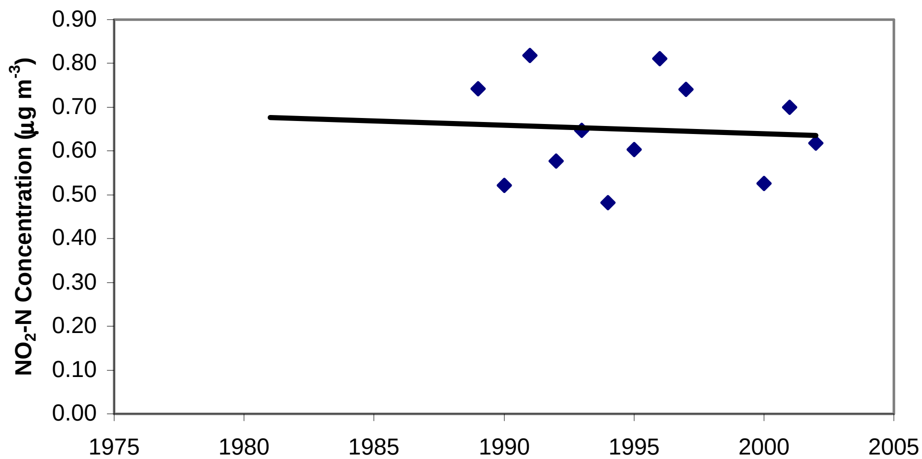


Figure 4. Annual average NO_2–N levels (µg m^{-3}) for the period 1989 to 2002. The linear regression based trend line shows that ambient levels remained relatively stable over the measurement period with no distinct trend

4.3 Nitrogen dioxide (NO_2)

The time series of annual average NO_2–N data for Valentia is shown in Figure 4. The levels have remained relatively stable throughout the measurement period, which commenced in 1989. The data set is therefore less extensive than that for SO_2–S and SO_4–S. An annual wintertime peak is apparent in the daily data. Further analysis of this feature is required.

5 Wind direction based analysis

The daily concentration data were sectored according to the daily average wind direction. Average concentrations of SO_2–S[3], SO_4–S[4] and NO_2–N[5] data for six wind local sectors are shown in Figures 5, 6 and 7 respectively. The data and figures clearly show that the highest pollutant concentrations were recorded for East and North Easterly directions. The lowest concentrations were found for westerly directions.

The difference in concentrations between east and westerly data is clearest for the SO_2–S and NO_2–N data. The difference in concentration is not as large for SO_4–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 also notable that the SO_2–S and NO_2–N values are non-zero for westerly directions.

5.1 Trends for sectoral SO_2–S and SO_4–S data

It has been shown above that the annual average SO_2–S and SO_4–S data display significant decrease in concentration levels since measurements commenced in 1980. It is apparent that reductions in ambient levels occur for all wind directions. Linear regression analysis shows that the greatest rate of decrease, i.e., 0.06 $\mu g\ m^{-3}$ per annum, was observed in SO_2–S levels measured during easterly winds. This is considered to largely reflect largely local emissions reductions, i.e., in Ireland and Britain. These analyses are given in Appendix 1

The data for NE are less well defined and may be influenced by industrial emissions in the Shannon basin region. More surprisingly, the concentrations measured in samples from westerly air display a small but significant reduction over the measurement period, i.e. 0.012 $\mu g\ m^{-3}$ per annum for the south-westerly sector. Long-range transport of SO_2 from North America is not considered to a significant influence on the measurements. Natural oceanic sources such as seasonal emissions from phytoplanton are also not expected to display such a decline. Therefore, this observation is considered to reflect decreased SO_2 levels in re-circulated air from largely local sources. However, further examination of this feature is required.

Trends in the NO_2-N data were less defined.

---

[3] To convert SO_2–S ($\mu g\ m^{-3}$) to SO_2 ($\mu g\ m^{-3}$), multiply SO_2–S ($\mu g\ m^{-3}$) by 2.
[4] To convert SO_4–S ($\mu g\ m^{-3}$) to SO_4^{2-} ($\mu g\ m^{-3}$), multiply SO_4–S ($\mu g\ m^{-3}$) by 3.
[5] To convert NO_2–N ($\mu g\ m^{-3}$) to NO_2 ($\mu g\ m^{-3}$), divide NO_2–N ($\mu g\ m^{-3}$) by 0.3.

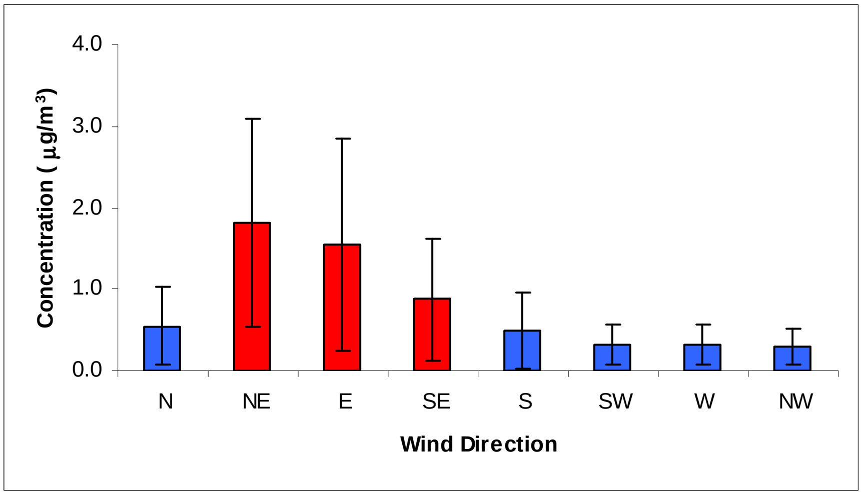


Figure 5. Average SO_2–S levels (µg m^{-3}) over the period 1981 to 2002 for different wind sectors at the Valentia Observatory. Standard deviation values are also shown.

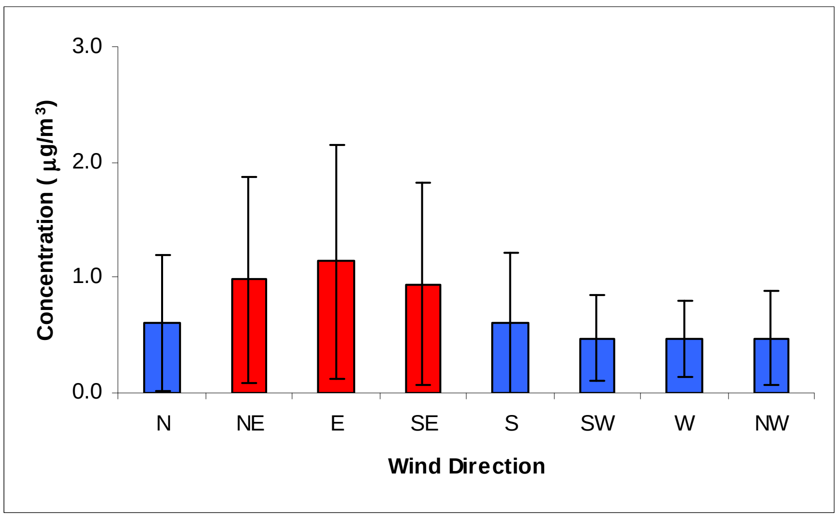


Figure 6. Average SO_4–S levels (µg m^{-3}) over the period 1981 to 2002 for different wind sectors at the Valentia Observatory. Standard deviation values are also shown.

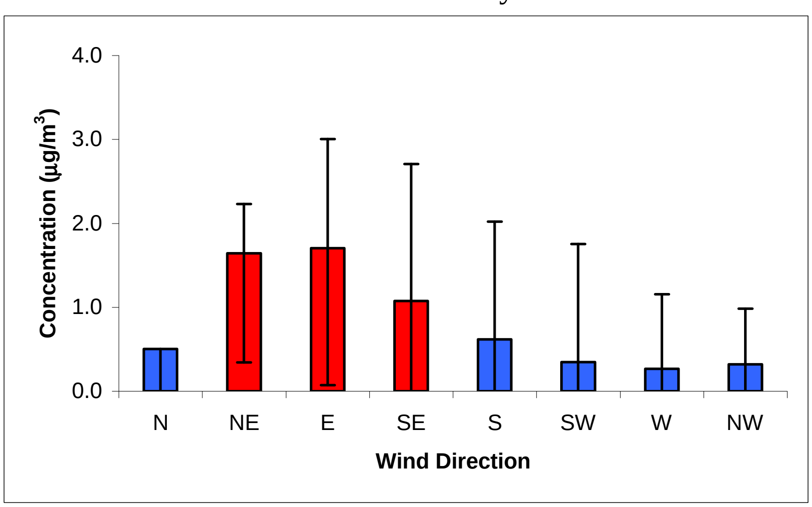


Figure 7. Average NO_2-N levels (µg m^{-3}) over the period 1989 to 2002 for different wind sectors at the Valentia Observatory. Standard deviation values are also shown.

6 Discussion

The Valentia data provide a relatively long-term perspective on variation of ambient SO_2, SO_4 and NO_2 levels at the western boundary of Europe. The data show the success of international emissions reduction actions in relation to ambient levels of sulphur species. The decrease in observed SO_2–S levels is most pronounced for easterly air masses but is also, and somewhat surprisingly, evident in westerly air masses. Similar reductions are observed in ambient SO_4 levels, although these are less pronounced. The NO_2–N data remain relatively stable and probably reflect the difficulties that exist in addressing emissions of oxides of nitrogen from combustion sources.

The SO_2 levels would be expected to decrease as local emissions are reduced. This observation therefore confirms the success of local emissions reductions actions. Sulphate is produced by oxidation of SO_2 in the atmosphere and is typically associated with NH_4. It is well known that SO_4 is an important and sometimes dominant component of ambient particulate matter (PM) levels. As particulate sulphate is typically found in size range less than 1μm it contributes to both PM10 and PM2.5 levels. McGovern and McGettigan (2003), show that the concurrence of peaks in ambient SO_4 levels at Valentia and peaks in urban PM10 levels e.g. Dublin and Cork city. The reduction in the observed SO_4 peak is therefore also welcome, as an indication that background PM levels have also been reduced.

The analysis of the SO_4–S data is somewhat hampered by the absence of analysis of the contribution from sea-salt to these levels. Sea-salt ions, such as Na^+ and Cl^- are now part of the regular EMEP chemical analysis. The newer data may provide a mechanism to estimate the contribution of sea-salt for historical concentration levels. Also, integrated analysis of these data with similar data for Mace Head, which have been corrected for sea-salt, may also help to estimate this contribution.

There is no clear trend apparent in the NO_2–N data although the daily data suggest that an annual winter peak exists. Further work on these data is required, including analysis of levels of linked species, such as ozone. This work will be enhanced through the current work being developed in the COE trans-boundary air pollution project. Also, the new EMEP analysis protocol requires a wider range of particulate ./aerosol ion species analysis.

7 Conclusions

The Valentia data constitute a valuable record of atmospheric change since 1981. 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 and SO_4 levels observed in Ireland. These reductions have positive consequences in term of impacts on ecosystems and human health, as well as for commercial crops and buildings. The main findings from the observational records are;

- SO_2–S levels have decreased at a rate of approximately 0.036 μg m^{-3} per year since 1981. The rate of decrease is greater for air masses originating from an easterly direction. Levels in westerly air have also decreased.

- SO_4–S levels have decreased at a rate 0.02 μg m^{-3} per year, however, the real rate of decrease may be masked by local influences

- The results for NO_2–N are not yet as clear. No trend has been observed in the ambient levels, which have remained relatively stable since measurements commenced.

Further and more detailed analysis of these data is required. This includes integration with new data for the Valentia site and inter-comparison with similar data for other national and international sites. This will contribute to the development of a broader understanding of these results.

It is envisaged that further reduction of emissions of acidifying species will occur in the coming years. This will lead to further reductions in ambient levels of these species and contribute to improvement of our environment. The ongoing monitoring and analysis of the data from the Valentia site, and other sites in Ireland, will provide evidence of the success of these reductions. The full data set can be obtained from http//coe.epa.ie

Appendix 1. Linear regression analysis for sectored data

The SO_2–S, SO_4–S and NO_2–N concentration data were segregated according to wind sectors based on wind direction data for the Valentia site. Table A3.1 shows linear regression analysis for annual average values these data. The values in bold are considered being statistically most relevant with respect to this type of analysis. It is notable that all the slope values are negative for the SO_2–S and SO_4–S data with the highest gradient/rate of decrease being observed for samples obtained from easterly air masses. There is no clear trend in the NO_2-N data.

SO_2-S	Slope	error	Constant	Err	R^2
W	-0.018	0.0020	36.3	4.02	0.82
NW	-0.015	0.0023	29.2	4.65	0.68
SW	-0.012	0.0019	24.8	3.97	0.68
E	-0.065	0.0113	130.0	22.7	0.64
SE	-0.035	0.0062	69.6	12.5	0.63
S	-0.017	0.0034	34.4	6.86	0.58
NE	-0.045	0.0266	91.0	53.1	0.14
N	-0.016	0.0183	32.4	36.	0.04

SO_4-S	Slope	error	Constant	Err	R^2
SE	-0.022	0.005	44.8	10.0	0.52
W	-0.006	0.002	12.0	4.2	0.3
S	-0.005	0.002	10.5	4.0	0.25
E	-0.023	0.0097	47.4	19.4	0.24
NW	-0.0073	0.004	15.0	8.0	0.15
N	-0.022	0.0132	45.3	26.2	0.14
SW	-0.0029	0.0018	6.3	3.6	0.12
NE	-0.017	0.0144	34.7	28.6	0.07

NO_2 N	Slope	error	Constant	Err	R^2
N	0.0334	0.0124	-66.3	24.73	0.42
NE	0.0981	0.0387	-194.0	77.16	0.39
E	0.0629	0.0249	-125.1	49.59	0.39
SE	0.0348	0.0149	-69.0	29.79	0.35
S	0.0270	0.0205	-53.3	40.81	0.15
SW	0.0152	0.0217	-29.2	43.24	0.05
W	0.0138	0.0335	-26.9	66.78	0.02
NW	-0.0058	0.0298	13.3	59.47	0.00