ESI Table 1. The methods used for the analysis of precipitation samples from Valentia Observatory, Co, Kerry, Ireland for 1980 – 2004.

	Flame Photometry	Thorin Method	Nesslers Method (After Reduction)	Nesslers Method	AAS	Ion Chromatography
Sodium	1981 –	----	----	----	1986 -	1992 – present
Potassium	1985	----	----	----	1992	1992 - present
Ammonium	----	----	----	1986 -	1986 -	1992 - present
Magnesium	----	----	----	1992	1992	1992 - present
Calcium	----	----	----	----	----	1992 - present
Nitrate	----	----	1986 -	----	1987 -	1992 - present
Sulphate	----	1980 –	1992	----	1992	1992 – present
	----	1991	----	----	1986 -	
					1992	

ESI Table 2. The trend significance (*** ($\alpha = 0.001$) and blank cell ($\alpha > 0.1$)) and Sen's slope estimate with its 99 % confidence interval (Qmax and Qmin) for sulphur dioxide (SO_2-S), sulphate (SO_4-S) and nitrogen dioxide (NO_2-N) concentrations ($\mu g\ m^{-3}$) based on air samples from Valentia Observatory, Co, Kerry, Ireland for 1981 – 2004.

	Mann Kendall trend			Sen's slope estimate		
	Test Z	Significance		Q	Qmax 99%	Qmin 99%
SO_2-S	-4.46	***		-0.03	-0.04	-0.02
SO_4-S	-3.44	***		-0.01	-0.02	-0.003
NO_2-N	-0.33			-0.002	-0.02	0.03

ESI Table 3. The trend significance (*** ($\alpha = 0.001$), ** ($\alpha = 0.01$), * ($\alpha = 0.05$), + ($\alpha = 0.1$) and blank cell ($\alpha > 0.1$)) and Sen's slope estimate with its 99% confidence interval (Qmax and Qmin) for seasonal (1) sulphur dioxide (SO_2-S), (2) sulphate (SO_4-S) and (3) nitrogen dioxide (NO_2-N) concentrations ($\mu g/m^3$) based on air samples from Valentia Observatory, Co, Kerry, Ireland for 1981 – 2004.
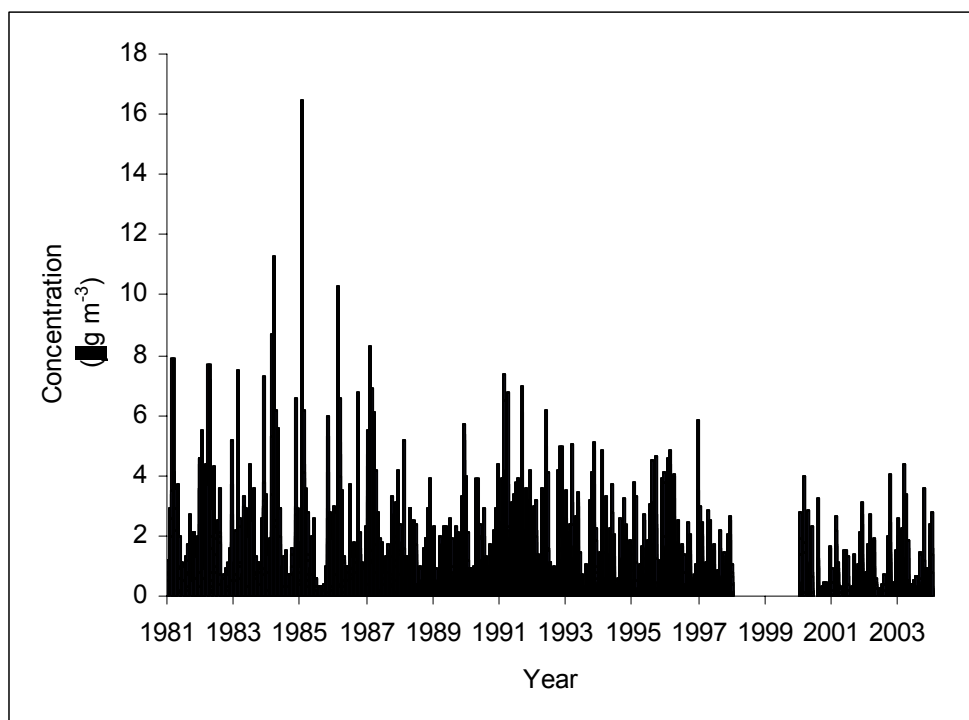
	Mann Kendall trend			Sen's slope estimate		
	Test Z	Significance		Q	Qmax 99%	Qmin 99%
Spring[1]	-4.23	***		-0.04	-0.07	-0.02
Summer[1]	-2.88	**		-0.02	-0.03	0.0
Autumn[1]	-1.80	+		-0.01	-0.03	0.01
Winter[1]	-3.17	**		-0.03	-0.06	-0.01
Spring[2]	-2.37	*		-0.02	-0.04	0.0
Summer[2]	-2.71	**		-0.02	-0.04	0.0
Autumn[2]	-1.13			-0.01	-0.02	0.01
Winter[2]	-0.57			0.0	-0.01	0.01
Spring[3]	0.66			0.01	-0.05	0.04
Summer[3]	-1.42			0.0	-0.01	0.01
Autumn[3]	0.99			0.02	-0.02	0.06
Winter[3]	-1.16			-0.03	-0.11	0.04

ESI Table 4. The trend significance (***, (α = 0.001), (+, (α = 0.1) and blank cell (α > 0.1)), Sen's slope estimate with its 99 % confidence interval (Qmax and Qmin) for the composition of precipitation samples from Valentia Observatory, Co, Kerry, Ireland for 1980 – 2004.

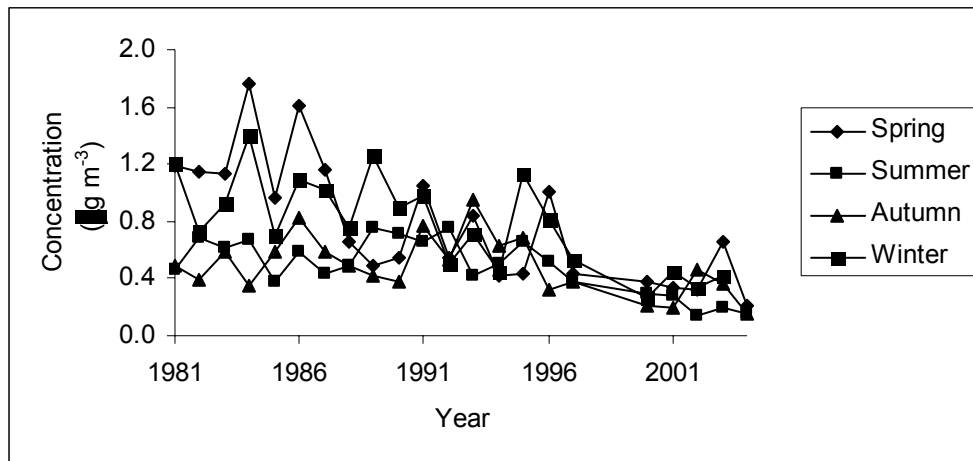|	Mann Kendall trend		Sen's slope estimate		
	Test Z	Significance	Q	Qmin 99%	Qmax 99%
Sodium	0.63		0.08	-0.39	0.51
Potassium	0.32		0.01	-0.03	0.03
Ammonium	1.03		0.00	-0.01	0.01
Magnesium	-0.86		-0.01	-0.09	0.06
Calcium	-1.19		-0.02	-0.06	0.03
Nitrate	-0.29		0.00	-0.004	0.004
Sulphate	-0.85		-0.01	-0.05	0.02
Non-sea salt sulphate	-3.93	***	-0.01	-0.01	0.0
pH	0.58		0.00	-0.02	0.03
Precipitation amount	1.80	+	0.05	-0.02	0.10
Chloride	-0.54		-0.26	-3.37	3.50

ESI Table 5. The ionic correlation between the weighted mean annual ionic concentrations of the precipitation samples from Valentia Observatory, Co, Kerry, Ireland for 1980 – 2004.

	Sodium	Sulphate	Non-sea salt sulphate	Calcium	Nitrate	Ammonium	Magnesium	Potassium	Chloride
Sodium	1.00								
Sulphate	0.82	1.00							
Non-sea salt sulphate	0.004	0.06	1.00						
Calcium	0.85	**0.92**	0.23	1.00					
Nitrate	0.004	0.05	0.23	0.02	1.00				
Ammonium	0.02	0.01	0.01	0.003	0.01	1.00			
Magnesium	0.76	**0.92**	0.001	**0.97**	0.06	0.002	1.00		
Potassium	0.49	0.63	0.02	0.52	0.08	0.02	0.76	1.00	
Chloride	**0.97**	0.98	0.002	**0.98**	0.2	0.003	**0.98**	0.79	1.00

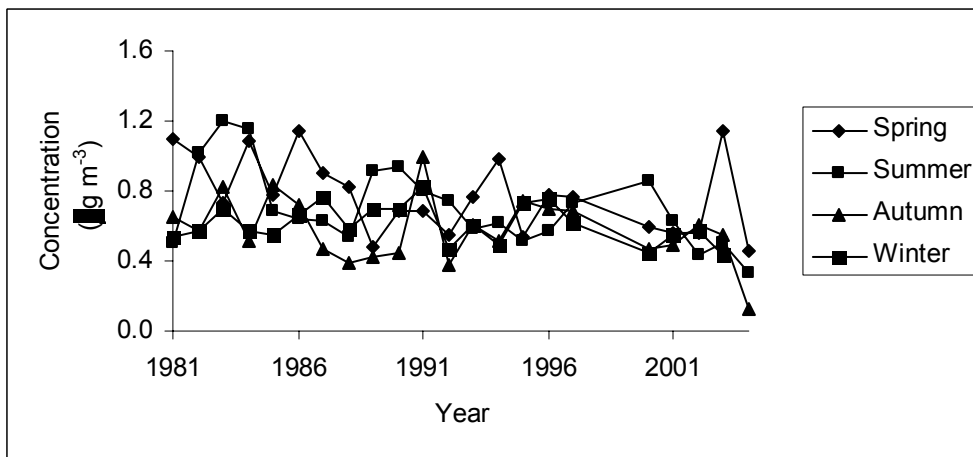**ESI Fig. S1** The trend for sulphur dioxide concentrations (μg m^{-3}) based on air samples from Valentia Observatory, Co, Kerry, Ireland from 1981-2004.
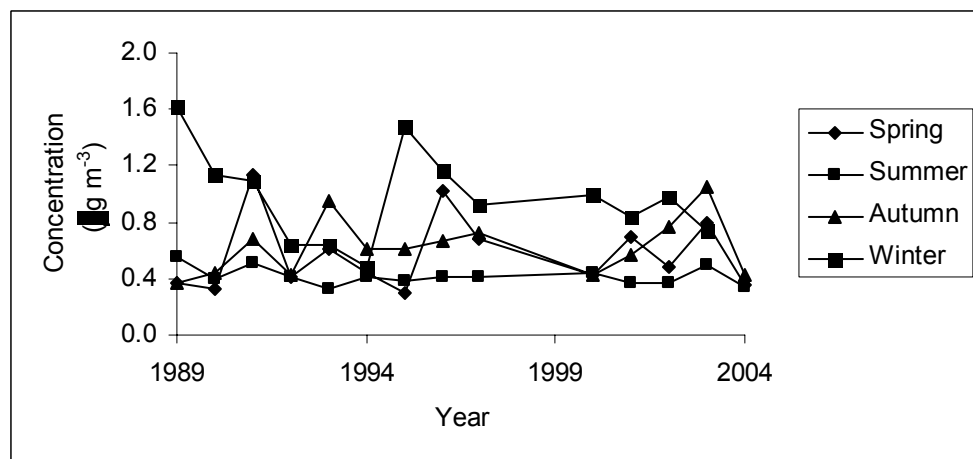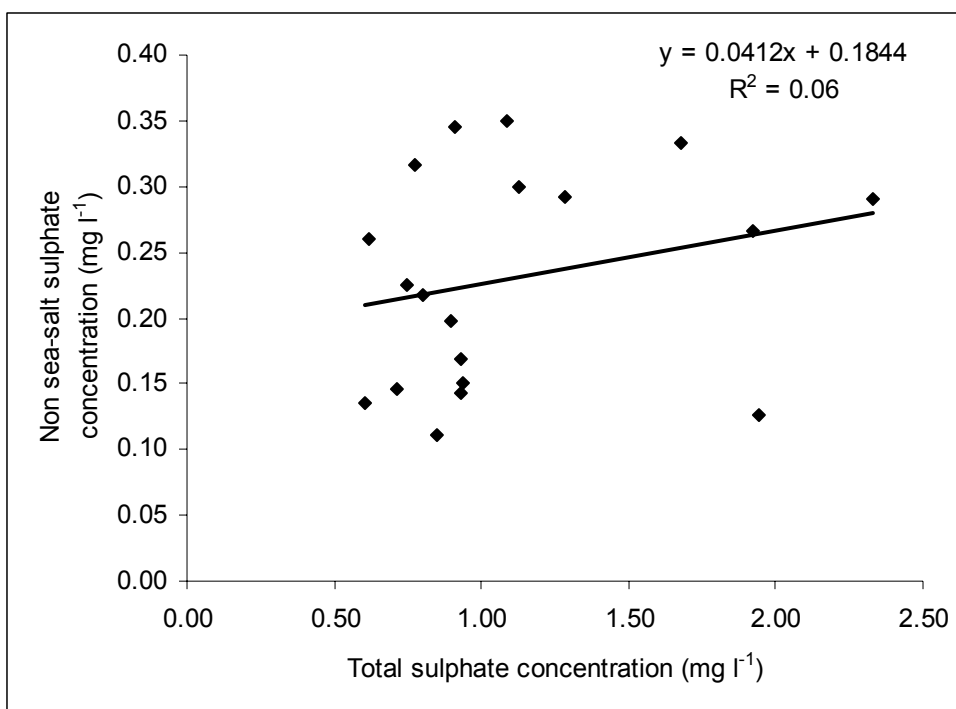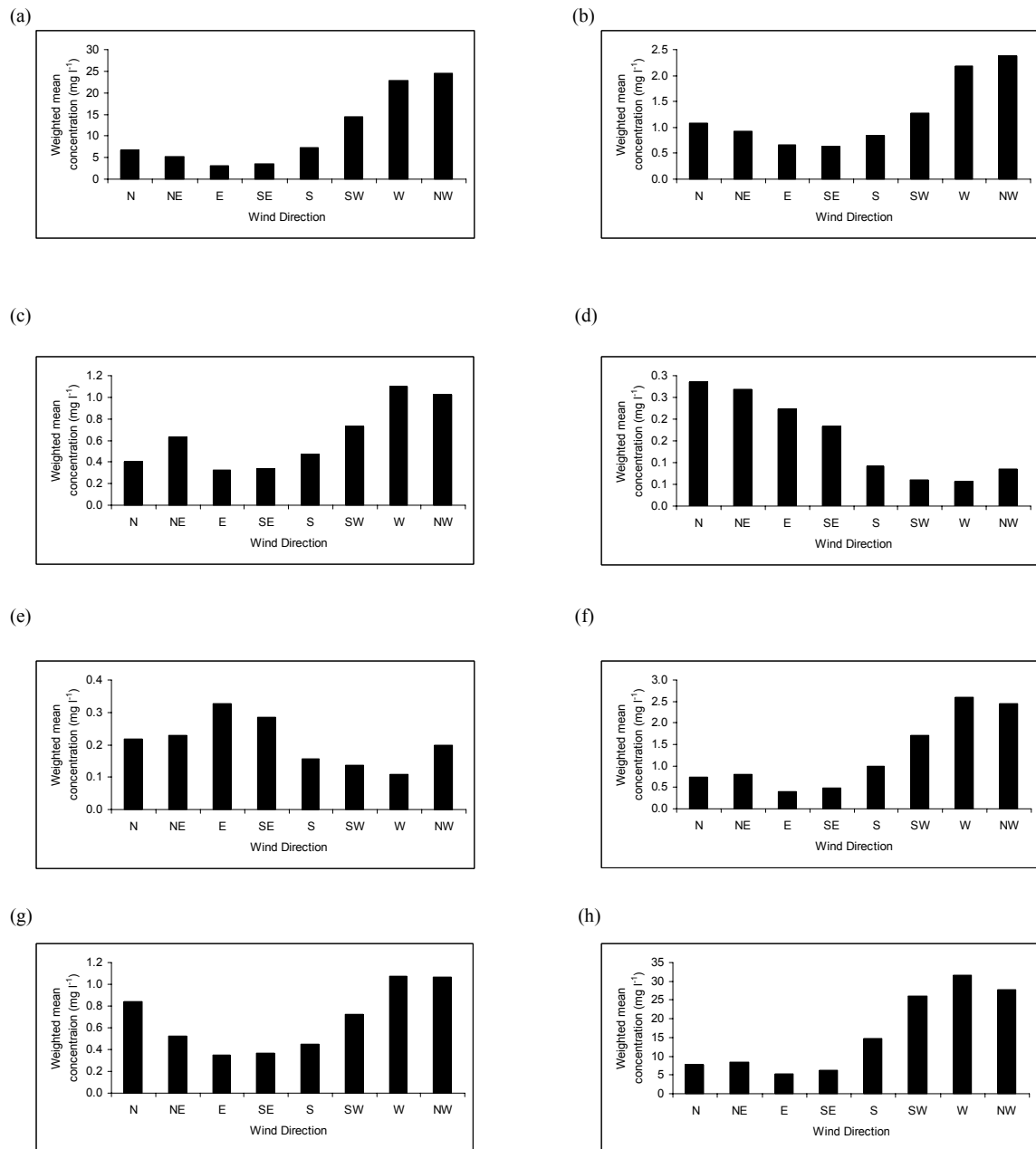
(a)

(b)

(c)

ESI Fig S2. The seasonal average concentrations ($\mu g\ m^{-3}$) for (a) sulphur dioxide (SO_2-S), (b) sulphate (SO_4-S) and (c) nitrogen dioxide (NO_2-N) based on air samples from Valentia Observatory, Co, Kerry, Ireland for 1981 – 2004.

ESI Fig. S3 The relationship between total sulphate and non-sea salt sulphate concentrations (mg l^{-1}) based on precipitation samples from Valentia Observatory, Co, Kerry, Ireland from 1980-2004.

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

ESI Fig. S4 The effect of wind direction on weighted mean concentrations (mg l^{-1}) of (a) sodium (Na^+), (b) sulphate (SO_4-S), (c) calcium (Ca^{2+}), (d) nitrate (NO_3-N), (e) ammonium (NH_4-N) and (f) magnesium (Mg^{2+}), (g) potassium (K^+) and (h) chloride (Cl^-) based on precipitation samples from Valentia Observatory, Co, Kerry, Ireland.