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LONG-RANGE TRANSBOUNDARY AIR POLLUTION**

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Item 4 (e) of the provisional agenda

**FLUXES AND TRENDS OF NITROGEN AND SULPHUR COMPOUNDS
AND BASE CATIONS**

Summary report by the Programme Centre of the International Cooperative Programme on
Integrated Monitoring of Air Pollution Effects on Ecosystems

I. BACKGROUND

1. In the past two decades, both national and international environmental regulations and agreements have led to widespread declines in the emissions of air pollutants in Europe and North America. In Europe the emissions of sulphur (S) and nitrogen (N) compounds have declined by 34% (SO₂), 14% (NO₂) and 18% (NH₃) respectively, between 1988 and 1995 (Olendrzynski 1997). The protocols to the Convention and legislation of the European Union have been the key international activities causing this positive development. The first signs of recovery in sensitive ecosystems have also been reported. The International Cooperative Programmes (ICPs) of the Working Group on Effects have been an important source of information in this respect (e.g. Stoddard *et al.* 1999, WGE 1999).

Documents prepared under the auspices or at the request of the Executive Body for the Convention on Long-range Transboundary Air Pollution for GENERAL circulation should be considered provisional unless APPROVED by the Executive Body.

2. The purpose of this study has been to evaluate the expected positive impact of the protocols on the state of the ecosystems, by analysing fluxes and trends of sulphur (S) and nitrogen (N) compounds, base cations and hydrogen ions at sites in the International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP IM) network across Europe. The ICP IM sites are well suited to the monitoring of the effects of these emission reductions, since the sites are located in natural/semi-natural areas with a minimum of local disturbance. In addition, a comprehensive monitoring programme, covering several ecosystem compartments, is carried out.

3. The evaluation of fluxes and trends of key chemical elements in ecosystems is relevant to the assessment of the effects of air pollution control policies by providing: (i) a description of different biogeochemical processes regulating buffering properties and retention of elements, determining the long-term impact of the emitted compounds; (ii) identification of empirical critical threshold values for deposition inputs; and (iii) documentation of the magnitude of ecosystem recovery or deterioration.

II. MATERIAL AND METHODS

4. As a result of the availability of internationally reported data in the ICP IM database (Kleemola and Forsius 1999), 22 sites were selected for the analysis (fig. I). The sites are mainly covered with coniferous forest. The trend assessment was performed mainly for the period 1988/89 - 1998. Time series with a minimum of five years of monthly data were accepted for the statistical analyses. Trends were evaluated for non-marine (* denotes non-marine fraction) SO_4^* and $(\text{Ca} + \text{Mg})^*$, H^+ , NO_3 and NH_4 (except runoff). Deposition (bulk and throughfall deposition) and output (runoff/soil water) fluxes were calculated from the quality and quantity of water using mean monthly values for water fluxes and chemical analyses (weighted means where available). The calculations have been made by the ICP IM Programme Centre in cooperation with the National Focal Points.

5. Fluxes for the budget calculations of the available data were calculated as the average of the past three years in order to reduce yearly variability. C/N-ratios (g/g) in the organic (Oh) soil layer were calculated for sites with available data. The methods for collecting, storing and analysing chemical samples are described in the programme manual (Manual for Integrated Monitoring 1998).

6. The trend analyses were done using well-recognized standard techniques. The analyses were carried out with the DETECT software package (Cluis *et al.* 1989), containing a suite of non-parametric methods for trend analyses. DETECT recommends the most appropriate method based on the presence or absence of statistical seasonality. The monotonic trend was used as a default trend type, and the following tests were used: (i) Hirsch and Slack test for series with seasonality and persistence; (ii) seasonal Kendall test for series with seasonality only; (iii) Kendall test for time series without seasonality and persistence; and (iv) Spearman/Lettenmaier test for series with persistence only.



Figure I

Location of ICP IM sites included in the calculations of fluxes and trends

The boundaries shown on this map do not imply official endorsement or acceptance by the United Nations.

7. The reduction in deposition of S and N compounds at the sites, foreseen in the new Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone, was estimated with the use of transfer matrices of EMEP/MSC-W, incorporated in the DAIQUIRI model (Syri *et al.* 1998), and officially reported emissions (EMEP/MSC-W 1998) for the reference year 1996 and the target year 2010. The change in deposition at the individual sites, resulting from the implementation of the Protocol, was estimated as the difference in deposition between these two years. Deposition was interpolated from the four nearest grid squares using inverse distance weighting.

III. RESULTS AND DISCUSSION

A. Ion fluxes

8. The key results of the calculations are summarized in table 1. Regarding the ion fluxes, the results of the ICP IM sites generally follow well-known patterns: efficient retention of N compounds and hydrogen ions (due to nutrient uptake and buffering processes) and release of base cations (due to weathering and ion exchange reactions). For SO_4^* retention, apparent steady-state and release were observed. The results of the Swiss site (CH01) indicate a clear geological S

source with very high base cation and S output fluxes. High H^+ leaching was observed at the sites NO01, SE02 and SE04 (Norway and southern Sweden). At site DE01 (southeastern Germany) the results may have been influenced by an insect attack affecting tree health during recent years.

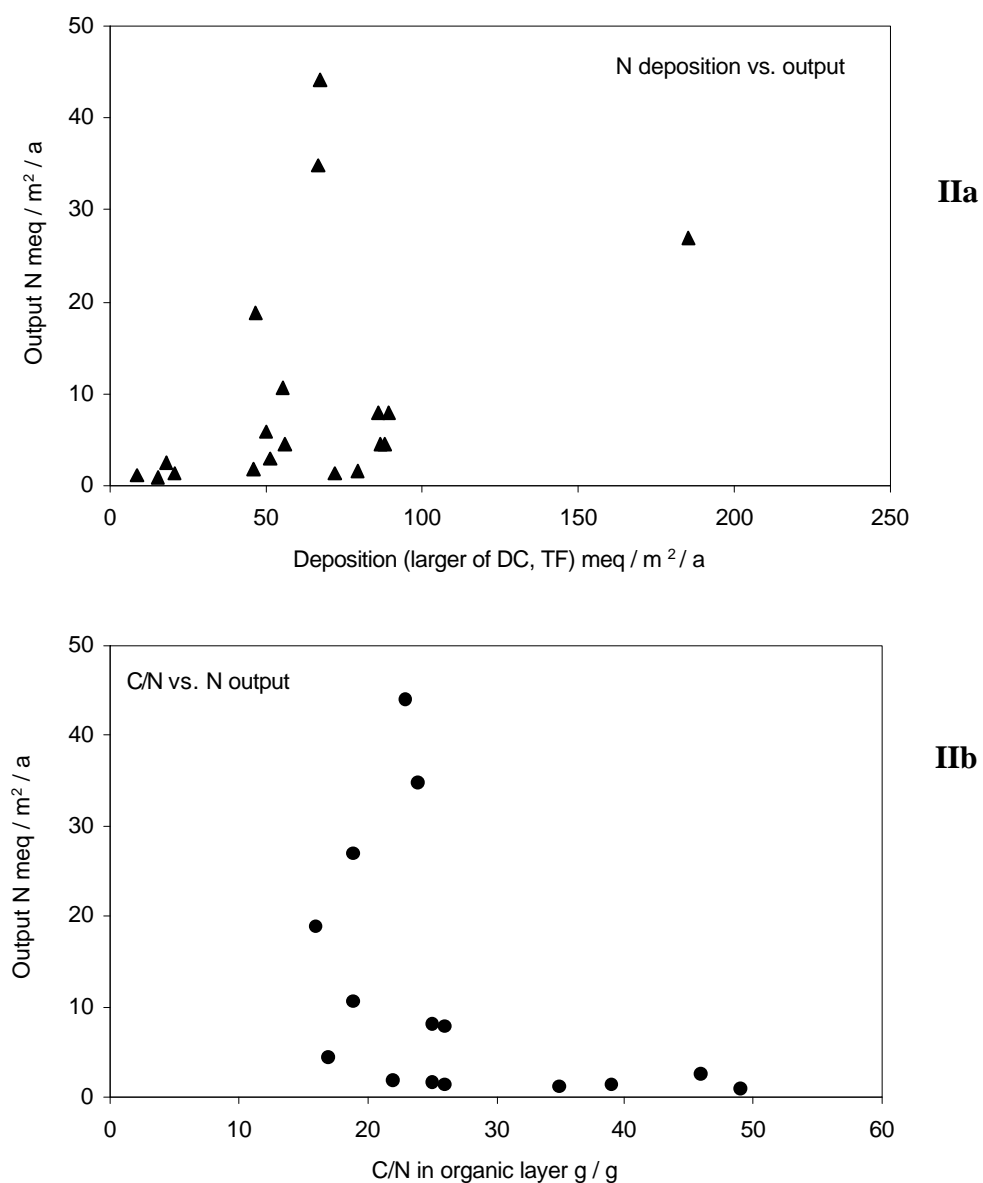


Figure II

The relationship between N deposition and N output flux (IIa), and C/N-ratio of the soil organic matter and N output flux (IIb) at the ICP IM sites (DC = bulk deposition; TF = throughfall deposition)

9. Accelerated N leaching in ecosystems may cause harmful effects in terms of both eutrophication and acidification. Assessment of empirical data from European forest ecosystems (Dise and Wright 1995, Dise *et al.* 1998, Gundersen *et al.* 1998) have indicated that three broad

criteria are necessary (but not themselves sufficient) for sites to leach NO_3^- : (i) high fluxes of dissolved inorganic N in deposition ($> \text{ca. } 65\text{--}70 \text{ meq m}^{-2} \text{ a}^{-1} = 9\text{--}10 \text{ kg N ha}^{-1} \text{ a}^{-1}$); (ii) low C/N-ratio (below about 25-30) in the organic layer of the soil; and (iii) low mineral soil pH (below about 4.3).

10. The relationship between N deposition and N output flux (fig. IIa), and C/N-ratio and N output flux (fig. IIb) at the ICP IM sites are generally consistent with these criteria. Sites with higher N deposition and lower C/N-ratios clearly show a higher risk of high N output fluxes. These results cannot be considered as an independent evaluation of the above criteria because data from some ICP IM sites have been used in their derivation. However, there is a great potential in using such relationships from intensively studied sites in conjunction with regional survey data for risk assessment and mapping of deposition effects on the large regional scale.

B. Trends

11. Statistically significant downward trends of SO_4^{2-} and NO_3^- bulk deposition (fluxes or concentrations) were observed at 11 of the 22 ICP IM sites (table 1). Significant decreasing H^+ trends (fluxes or concentrations) were observed at 7 sites. Decreasing NO_3^- trends were more common than those of NH_4^+ . These results seem to be consistent with the reported decreases in European SO_2 , NO_2 and NH_3 emissions (Olendrzynski 1997).

12. A decreasing trend in concentrations and deposition of base cations, especially for calcium, has been observed in northern parts of Europe and the United States of America over the past two or three decades, although the rate of decrease appears to have been slower in the more recent years (Hedin et al. 1994). Such results have ecological significance because the ecosystem effects of the deposition depend on the relative contribution of acidifying and neutralizing compounds. Deposition of $(\text{Ca}+\text{Mg})^+$ shows decreasing trends at ICP IM sites in southern Fennoscandia, and sites NL01 and CZ01. Thus, the observed decrease in H^+ deposition is smaller than would be expected from the S and N trends alone.

13. Implementation of the Gothenburg Protocol will further decrease the deposition of S and N at the ICP IM sites in western and northwestern parts of Europe (Table 1). The decrease in SO_4^{2-} deposition (-36% on average at the studied sites) is expected to be larger than for NO_3^- (-24% on average). Changes in NH_4^+ deposition are expected to be rather small at all the ICP IM sites. At sites in more eastern and northeastern European regions (Baltic States, Finland, Belarus, Russian Federation) the expected decrease in both SO_4^{2-} and NO_3^- deposition will be smaller or non-existent. This is because the new Gothenburg Protocol allows some growth in emissions from the present (reference year 1996) level in many eastern European countries. For western Europe the Protocol implies a significant further decrease in sulphur and nitrogen oxides emissions.

14. The site-specific trend results regarding surface water fluxes are less clear than those of deposition (table 1). This is to be expected, because the deposited compounds are involved in numerous complex processes in the ecosystems (e.g. Likens *et al.* 1996), the end results of which are not always evident.

15. Decreasing SO_4^* and base cation trends in output fluxes and/or concentrations were commonly observed at the ICP IM sites (table 1). The decreasing base cation trends are a logical consequence of decreasing trends in deposition of both base cations and strong acid anions (e.g. Likens *et al.* 1996). Statistically significant decreasing H^+ trends (increasing pH) are observed only at sites SE04, SE08, NO02, and LT01. Some sites (e.g. CH01, LT01) are well-buffered and large changes in H^+ fluxes are not to be expected. Decreasing NO_3 trends were observed at 5 sites in the Nordic countries. At several sites the time series are still too short (or sufficient data are lacking) for trend analysis.

16. Detailed studies at site SE04 (Gårdsjön) have indicated that surface water recovery can proceed rapidly before soils begin to recover (Moldan 1999). Likens *et al.* (1996) observed a large depletion of the base cation pool in the catchment soils at Hubbard Brook (United States), which was expected to retard the response of the ecosystem to the emission reductions. Stoddard *et al.* (1999) observed a lack of surface water recovery in several regions in North America which was attributed to strong regional declines in base cation concentrations exceeding the decreases in SO_4^* . Dynamic model calculations at ICP IM sites have indicated that recovery due to emission reductions will often be slow (Forsius *et al.* 1998). In addition, interaction between climate-induced changes and acidification processes has been observed (e.g. Wright 1998), which further complicates the evaluation of changes. Thus, although recovery can be observed over large regions in both Europe and North America, it should be recognized that the recovery at many sensitive sites can be slow and that the response at individual sites may vary greatly.

IV. CONCLUSIONS

17. Statistically significant downward trends of SO_4^* and NO_3 deposition (fluxes and/or concentrations) were observed at 11 of the 22 ICP IM sites. Significant decreasing H^+ trends were observed at 7 sites. The observed decrease in H^+ deposition is smaller than would be expected from the S and N trends alone due to simultaneous decreases in base cation deposition. Decreasing NO_3 trends were more common than those of NH_4 . These results seem to follow the reported decreases in European emissions. Implementation of the 1999 Gothenburg Protocol to the Convention will further decrease the deposition of S and N at the ICP IM sites in western and northwestern parts of Europe. At sites in more eastern regions the decreases are expected to be smaller or non-existent. Changes in NH_4 deposition are expected to be rather small at all the ICP IM sites.

18. The relationships between N deposition and N output flux, and C/N-ratio and N output flux at the ICP IM sites were consistent with previous observations from European forested ecosystems. Sites with higher deposition and lower C/N-ratios clearly showed a higher risk of high N output fluxes. Such empirical relationships are useful for regional-scale mapping exercises and risk assessment. Accelerated N leaching in ecosystems may cause harmful effects in terms of both eutrophication and acidification.

19. Decreasing SO_4^* and base cation trends in output fluxes and/or concentrations of surface/soil water were commonly observed at the ICP IM sites. At several sites in Nordic countries decreasing NO_3 and H^+ trends (increasing pH) were also observed. These results partly confirm the effective implementation of emission reduction policies in Europe. However, clear

responses were not observed at all sites, showing that recovery at many sensitive sites can be slow and that the response at individual sites may vary greatly. Continued national and international monitoring and research efforts are needed to obtain scientific evidence of the recovery process to support future emission reduction policies.

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Notes

The references, the figures and the table were reproduced as received.

In table 1 “*” denotes non-marine fraction; DC = bulk deposition; TF = throughfall deposition; RW = runoff water; SW = soil water. The trend analysis has been carried out for both fluxes and concentrations. Significance levels (*P<0.05, **P<0.01, ***P<0.001) and slopes for statistically significant trends are shown (n.s.t.= not statistically significant; n.d. = insufficient data). Trend directions (+ or -) and the rate of change are expressed in slope values as $\text{meq m}^{-2} \text{ a}^{-1}$ (fluxes) and $\mu\text{eq l}^{-1} \text{ a}^{-1}$ (concentrations). The statistical methods and tests used are explained in chapter II. The column “% diff 2010” shows the estimated change in deposition of SO_4 , NO_3 and NH_4 between years 1996 and 2010, expected by the implementation of the Protocol to Abate Acidification, Eutrophication and Ground-level Ozone. The change in deposition has been estimated with transfer matrices of the EMEP/MSC-W. The C/N ratio (g/g) of soil organic matter at the sites is also shown.

Table 1Fluxes and trends of SO_4^* , $(\text{Ca}+\text{Mg})^*$, H^+ , NO_3 and NH_4 at the ICP IM sites

		DC flux	TF flux		RW/SW flux	DC flux	DC flux	DC conc.	DC conc.	RW/SW	RW/SW	RW/SW	RW/SW	C/N g/g
Site	Variable	meq/m2/a	meq/m2/a	%diff 2010	meq/m2/a	test	slope	test	slope	flux test	conc. slope	conc. test	conc. slope	org. layer
DK01	SO4*	37.5		-48.1	27.9	4	(n.s.t.)	4	(n.s.t.)	1	(n.s.t.)	4	(n.s.t.)	26
	(Ca+Mg)*	4.7			0.1	3	(n.s.t.)	3	(n.s.t.)		(n.d.)		(n.d.)	
	H+	9.5			34.7	3	(n.s.t.)	3	(n.s.t.)	2	(n.s.t.)	3	(n.s.t.)	
	NO3	29.8		-31.5	0.7	3	(n.s.t.)	4	(n.s.t.)		(n.d.)		(n.d.)	
	NH4	42.2		-22.2	0.7	4	(n.s.t.)	3	(n.s.t.)					
FI01	SO4*	15.4	35.3	-13.9	33.4	4	-2.78	1	-3.06**	1	(n.s.t.)	1	-1.30*	39
	(Ca+Mg)*	3.6	26.7		39.0	1	-0.52**	2	-0.35***	1	(n.s.t.)	1	-1.20**	
	H+	14.8	11.4		10.4	4	-1.42	1	-1.41**	1	(n.s.t.)	1	1.85**	
	NO3	12.0	6.0	-19.3	0.5	4	-0.86	1	-0.72*	1	-0.11*	1	-0.13*	
	NH4	8.7	4.2	-3.2	0.8	1	-1.36	1	-1.69*					
FI03	SO4*	13.9	16.8	-10.9	11.9	1	-2.00**	2	-1.98***	1	-1.10*	1	-1.87***	49
	(Ca+Mg)*	3.1	10.1		32.5	1	-0.23**	2	-0.16*	1	(n.s.t.)	1	(n.s.t.)	
	H+	15.2	14.5		0.3	4	-0.92	2	-1.29***	2	(n.s.t.)	1	(n.s.t.)	
	NO3	9.7	8.1	-11.9	0.5	4	-0.53	1	-0.69**	1	(n.s.t.)	1	-0.08**	
	NH4	5.7	4.6	-11.5	0.4	3	-0.90***	2	-0.95***					
NO01	SO4*	46.1	61.0	-43.1	82.0	3	-4.13***	1	-3.01**	1	(n.s.t.)	4	-1.75	25
	(Ca+Mg)*	5.3	27.6		35.8	3	-0.53***	2	-0.67***	1	-2.99*	4	-1.83	
	H+	46.1	42.9		22.6	1	-4.68*	4	-2.38	1	(n.s.t.)	1	(n.s.t.)	
	NO3	47.0	36.0	-30.0	8.0	1	(n.s.t.)	2	-1.45*	1	-0.94**	1	-0.75**	
	NH4	42.6	29.0	-9.6		3	-2.98*	3	-2.19**					
NO02	SO4*	7.3	8.3	-30.3	13.9	1	(n.s.t.)	1	(n.s.t.)	1	-0.71**	1	-0.29*	46
	(Ca+Mg)*	4.1	1.9		38.4	3	(n.s.t.)	4	(n.s.t.)	1	-0.97*	1	(n.s.t.)	
	H+	9.5	9.4		1.4	2	-0.30*	2	-0.24*	1	-0.05*	1	-0.02*	
	NO3	6.6	5.5	-21.1	2.5	2	(n.s.t.)	2	(n.s.t.)	1	(n.s.t.)	1	0.07***	
	NH4	11.7	6.2	-5.1		2	(n.s.t.)	2	-0.14**					
SE02	SO4*	47.5	117.2	-69.0	79.8	4	-4.32	4	-1.50	1	(n.s.t.)	4	(n.s.t.)	26
	(Ca+Mg)*	6.1	61.5		56.7	1	(n.s.t.)	1	(n.s.t.)	1	-3.07*	4	(n.s.t.)	
	H+	40.0	12.3		22.7	2	-3.10*	3	-1.10**	1	(n.s.t.)	1	(n.s.t.)	
	NO3	42.7	31.5	-33.9	7.1	2	(n.s.t.)	4	(n.s.t.)	1	(n.s.t.)	1	0.48**	
	NH4	43.0	15.0	-5.1	0.8	1	-3.19*	1	(n.s.t.)					
SE04	SO4*	38.0	65.7	-44.0	118.8	4	-4.85	1	-4.23**	1	(n.s.t.)	4	(n.s.t.)	25
	(Ca+Mg)*	6.6	39.6		40.8	3	-0.49*	3	(n.s.t.)	1	-2.98*	4	-4.48	
	H+	29.4	35.7		37.2	4	-7.13	4	-5.17	1	-1.96*	1	-1.12*	
	NO3	34.9	47.0	-31.2	0.6	1	-2.30*	2	-1.63*	1	-0.02**	3	-0.07**	
	NH4	32.1	26.4	-10.1	1.0	3	-1.66*	2	(n.s.t.)					
SE08	SO4*	8.8		-27.2	16.9	1	-1.00*	1	(n.s.t.)	2	-1.40**	4	-0.75	35
	(Ca+Mg)*	2.3			132.3	2	(n.s.t.)	1	(n.s.t.)	2	-15.4***	3	(n.s.t.)	
	H+	11.1			0.3	3	-0.60*	3	-0.80**	3	-0.11*	3	(n.s.t.)	
	NO3	5.8		-20.9	0.7	3	(n.s.t.)	3	(n.s.t.)	2	-0.11***	2	-0.17**	
	NH4	2.9		-4.4	0.4	4	-0.53	2	-0.58**					

(continued)

Table 1

Fluxes and trends of SO_4^* , $(\text{Ca}+\text{Mg})^*$, H^+ , NO_3 and NH_4 at the ICP IM sites
(Continued)

		DC flux	TF flux		RW/SW flux	DC flux	DC flux	DC conc.	DC conc.	RW/SW	RW/SW	RW/SW	RW/SW	C/N g/g
Site	Variable	meq/m ² /a	meq/m ² /a	%diff 2010	meq/m ² /a	test	slope	test	slope	flux test	conc. slope	conc. test	conc. slope	org. layer
BY02	SO_4^*	36.1		5.4		4	-2.92	2	-3.92***		(n.d.)		(n.d.)	
	$(\text{Ca}+\text{Mg})^*$	25.6				3	(n.s.t.)	3	(n.s.t.)		(n.d.)		(n.d.)	
	H^+	10.7				1	(n.s.t.)	1	(n.s.t.)		(n.d.)		(n.d.)	
	NO_3	21.3		-2.9		4	-1.14	4	-2.13		(n.d.)		(n.d.)	
	NH_4	24.2		-13.1		4	-5.20	4	-8.75					
LT01	SO_4^*	21.9	42.5	-13.6	422.0	4	-5.03	4	-9.04		(n.d.)		(n.d.)	
	$(\text{Ca}+\text{Mg})^*$				1190.9		(n.d.)		(n.d.)		(n.d.)		(n.d.)	
	H^+	3.9	6.8		0.0	4	-6.46	1	-10.3*	4	(n.s.t.)	3	-0.01*	
	NO_3	15.1	19.7	-8.3	5.3	1	(n.s.t.)	1	(n.s.t.)		(n.d.)		(n.d.)	
	NH_4	23.2	30.3	21.4	0.5		(n.d.)		(n.d.)					
LT02	SO_4^*	33.8	53.6	-28.3	165.0	3	(n.s.t.)	3	-7.34***		(n.d.)		(n.d.)	
	$(\text{Ca}+\text{Mg})^*$				536.1		(n.d.)		(n.d.)		(n.d.)		(n.d.)	
	H^+	3.8	3.8		0.0	4	-5.30	4	-12.0	3	-0.00***	3	-0.00*	
	NO_3	17.8	15.7	-14.0	2.4	3	(n.s.t.)	3	(n.s.t.)		(n.d.)		(n.d.)	
	NH_4	33.5	28.3	13.9	0.6	3	(n.s.t.)	3	-6.53**					
LV01	SO_4^*	45.8	67.4	-29.9	107.5	3	(n.s.t.)	4	(n.s.t.)		(n.d.)	3	-16.9**	
	$(\text{Ca}+\text{Mg})^*$	17.1	34.7		580.1		(n.d.)		(n.d.)		(n.d.)	1	(n.s.t.)	
	H^+	16.3	18.9		0.0	1	(n.s.t.)	1	(n.s.t.)		(n.d.)	4	-0.02	
	NO_3	34.8	31.7	-22.1	1.8	3	(n.s.t.)	3	(n.s.t.)		(n.d.)	4	(n.s.t.)	
	NH_4	53.0	33.3	36.3	2.8	3	(n.s.t.)	4	(n.s.t.)					
LV02	SO_4^*	34.3	37.5	-5.9	97.5	3	-6.34*	1	(n.s.t.)	4	(n.s.t.)	3	(n.s.t.)	
	$(\text{Ca}+\text{Mg})^*$	18.0	26.2		587.8		(n.d.)		(n.d.)	4	(n.s.t.)	2	(n.s.t.)	
	H^+	14.9	14.5		0.0	2	(n.s.t.)	3	(n.s.t.)	3	(n.s.t.)	3	(n.s.t.)	
	NO_3	20.5	19.7	-9.9	1.8	3	(n.s.t.)	4	(n.s.t.)	4	(n.s.t.)	3	(n.s.t.)	
	NH_4	35.6	20.7	34.5	2.8	3	-4.18**	4	(n.s.t.)					
RU15	SO_4^*	50.5		-8.9	45.7	4	-13.4	4	-14.6	3	-18.3*	4	(n.s.t.)	16
	$(\text{Ca}+\text{Mg})^*$	170.6	185.9		269.3	4	(n.s.t.)	4	(n.s.t.)	1	(n.s.t.)	1	-30.6*	
	H^+	51.5	28.0		0.1	1	(n.s.t.)	1	(n.s.t.)	3	(n.s.t.)	3	0.01*	
	NO_3	10.4	9.0	0.4	8.5	4	-3.22	3	-2.51***	2	(n.s.t.)	3	(n.s.t.)	
	NH_4	31.1	36.1	3.5	10.3	4	(n.s.t.)	1	(n.s.t.)					

(continued)

Table 1

Fluxes and trends of SO_4^* , $(\text{Ca}+\text{Mg})^*$, H^+ , NO_3 and NH_4 at the ICP IM sites
(Continued)

		DC flux	TF flux		RW/SW flux	DC flux	DC flux	DC conc.	DC conc.	RW/SW	RW/SW	RW/SW	RW/SW	C/N g/g
Site	Variable	meq/m ² /a	meq/m ² /a	%diff 2010	meq/m ² /a	test	slope	test	slope	flux test	conc. slope	conc. test	conc. slope	org. layer
AT01	SO ₄	50.6	66.5	-50.1		2	(n.s.t.)	4	(n.s.t.)					
	(Ca+Mg)*													
	H ⁺													
	NO ₃	48.4	76.2	-32.8		3	(n.s.t.)	2	(n.s.t.)					
	NH ₄	61.2	67.0	-15.9		4	(n.s.t.)	4	(n.s.t.)					
CH01	SO ₄ *	55.3	69.9	-48.1	331.9	1	(n.s.t.)	1	-1.44*	2	8.41*	1	(n.s.t.)	19
	(Ca+Mg)*	26.2	48.9		4281.8	1	(n.s.t.)	1	(n.s.t.)	1	(n.s.t.)	1	-23.6*	
	H ⁺	29.7	32.3			3	(n.s.t.)	1	(n.s.t.)		(n.d.)		(n.d.)	
	NO ₃	39.8	95.0	-37.8	23.3	1	(n.s.t.)	1	-2.10*	1	(n.s.t.)	1	(n.s.t.)	
	NH ₄	74.0	90.6	-6.9	3.7	1	(n.s.t.)	1	(n.s.t.)					
CZ01	SO ₄ *	42.6	114.8	-63.0	51.2	1	(n.s.t.)	3	-4.39*	4	(n.s.t.)	4	(n.s.t.)	17
	(Ca+Mg)*	13.5	46.4		55.4	1	-1.07**	3	-4.84**	4	2.75	4	(n.s.t.)	
	H ⁺	18.2	30.0		0.0	2	-1.16**	3	-4.06**	3	(n.s.t.)	3	(n.s.t.)	
	NO ₃	30.8	41.0	-30.8	4.5	2	-0.70*	2	(n.s.t.)	4	(n.s.t.)	4	-4.65	
	NH ₄	38.6	45.5	3.2	0.1	1	(n.s.t.)	2	(n.s.t.)					
DE01	SO ₄ *	33.3	53.6	-56.9	68.2	2	(n.s.t.)	1	-4.23**	1	(n.s.t.)	1	(n.s.t.)	23
	(Ca+Mg)*	19.9	39.3		151.9	4	(n.s.t.)	2	(n.s.t.)	1	(n.s.t.)	1	(n.s.t.)	
	H ⁺	24.4	28.2		0.6	3	(n.s.t.)	4	-1.25	4	(n.s.t.)	4	(n.s.t.)	
	NO ₃	34.4	23.9	-33.7	39.9	2	(n.s.t.)	1	-2.93*	1	(n.s.t.)	1	(n.s.t.)	
	NH ₄	33.1	12.1	-13.5	4.2	2	-2.94*	1	-5.15*					
GB02	SO ₄ *	42.1		-59.4	84.4	3	(n.s.t.)	2	(n.s.t.)	1	(n.s.t.)	3	(n.s.t.)	24
	(Ca+Mg)*	14.2			75.3	1	0.78*	1	0.94**	1	(n.s.t.)	4	(n.s.t.)	
	H ⁺	20.8			15.2	4	(n.s.t.)	3	(n.s.t.)	1	(n.s.t.)	1	(n.s.t.)	
	NO ₃	28.5		-30.7	34.7	3	-0.77*	2	(n.s.t.)	1	(n.s.t.)	1	(n.s.t.)	
	NH ₄	38.1		-6.4		1	-1.20**	1	(n.s.t.)					
NL01	SO ₄ *	36.8	74.9	-45.4		3	(n.s.t.)	3	(n.s.t.)					12
	(Ca+Mg)*	8.7	17.5			3	-2.50**	3	-3.02**					
	H ⁺	18.0	9.6			4	-10.2	4	-15.7					
	NO ₃	34.8	58.5	-33.8		3	(n.s.t.)	3	-6.79*					
	NH ₄	60.3	139.3	-16.0		2	(n.s.t.)	4	(n.s.t.)					
IT01	SO ₄ *	25.6	30.1	-50.2	30.3	1	(n.s.t.)	4	(n.s.t.)	2	(n.s.t.)	3	(n.s.t.)	19
	(Ca+Mg)*	19.0	67.0		52.6	1	(n.s.t.)	1	(n.s.t.)	3	(n.s.t.)	3	(n.s.t.)	
	H ⁺	6.1	5.9		2.0	3	(n.s.t.)	3	(n.s.t.)	3	(n.s.t.)	3	(n.s.t.)	
	NO ₃	24.0	23.4	-39.7	9.9	1	(n.s.t.)	2	-2.62*		(n.d.)		(n.d.)	
	NH ₄	31.6	13.7	-2.1	0.7	1	(n.s.t.)	1	(n.s.t.)					
IT02	SO ₄ *	20.8	25.2	-50.9	6.0	1	(n.s.t.)	3	(n.s.t.)	3	(n.s.t.)	3	-8.90***	22
	(Ca+Mg)*	22.8	63.4		26.4	3	(n.s.t.)	2	(n.s.t.)	3	(n.s.t.)	4	(n.s.t.)	
	H ⁺	5.3	2.0		0.4	3	(n.s.t.)	3	(n.s.t.)	3	(n.s.t.)	3	(n.s.t.)	
	NO ₃	21.3	18.2	-40.4	1.6	1	(n.s.t.)	2	(n.s.t.)		(n.d.)		(n.d.)	
	NH ₄	24.6	23.2	0.3	0.3	1	(n.s.t.)	1	(n.s.t.)					