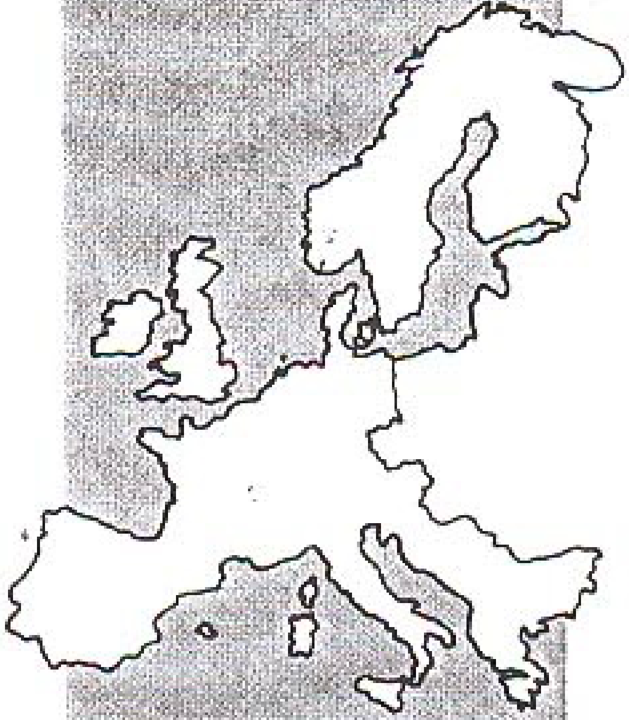

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NITRIC ACID AND NITRATES IN THE ATMOSPHERE OF ATHENS AND THEIR EFFECTS ON PENTELIC MARBLE

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Summary

The low sulphur fuels burned in Athens and the high photochemical activity (high $[NO_2]/[NO]$ ratios, but low O_3 concentrations because of a 20 hour per day traffic peak) could mean that the molar ratio of $[NO_3^-/[SO_4^=]$ in the atmosphere of Athens is often greater than one. This in turn, could mean that the adverse effects of HNO_3 and NO_3^- on marble monuments are relatively important. Nitric acid, nitrates, sulphates, chlorides etc. in the atmosphere of the Acropolis were sampled with a transition flow reactor and analysed by ion chromatography. Their effects on Pentelic marble are being investigated by drawing air through a bed of coarse and graded Pentelic marble powder, washing the marble with deionized water, analyzing the ions in the wash by ion chromatography and using thermodynamic data from the literature.

1. INTRODUCTION

Concentrations of atmospheric nitrates (nitric acid - HNO_3 and nitrate salts - NO_3^-) were determined by several methods, during all seasons and on days characterized by different meteorological conditions and levels of air pollution. The effect of those pollutants on Pentelic marble is being investigated with specially designed reactors.

2. HNO_3, NO_3^- AND $SO_4^=$ CONCENTRATIONS IN AMBIENT AIR

The literature abounds in references (1), (2), (3), (4), (5), (6), (7) stressing the weaknesses of the High Volume Sampler (HVS) methods for the determination of $[HNO_3]$ and $[NO_3^-]$ in air. In spite of this, 110 HVS filters from several different positions of the Athens basin were analyzed by ion chromatography. These gave indications of seasonal variation and the effect of meteorological conditions, position and other pollutant concentrations (Tables 1-4) (8). Most measurements were performed in central Athens ("Ministry"). Near this position routine measurements of other air pollutants are being made on a continuous basis.

TABLE 1 ($\mu g/m^3$) RAINY DAYS - POSITION "MINISTRY"

	AVG		STD		MAX		MIN		
PERIOD	NO_3^-	$SO_4^=$	NO_3^-	$SO_4^=$	NO_3^-	$SO_4^=$	NO_3^-	$SO_4^=$	N
SPRING	2.65	11.84	0.51	0.10	3.16	11.94	2.14	11.74	2
SUMMER	13.05	15.79	0.00	0.00	13.05	15.79	13.05	15.79	1
AUTUMN	3.77	15.03	0.75	2.35	4.44	16.77	2.72	11.71	3
WINTER	4.37	13.43	3.13	3.31	11.32	17.66	1.31	7.67	9
YEAR	4.60	13.70	3.39	2.97	13.05	17.66	1.31	7.67	15

TABLE 2 (μg/m³) SUNNY DAYS - POSITION "MINISTRY"

PERIOD	AVG NO_3^-	AVG $SO_4^{=}$	STD NO_3^-	STD $SO_4^{=}$	MAX NO_3^-	MAX $SO_4^{=}$	MIN NO_3^-	MIN $SO_4^{=}$	N
SPRING	9.03	14.80	4.68	4.19	19.36	23.25	3.99	7.52	13
SUMMER	8.70	18.26	3.33	4.67	14.02	28.65	3.79	12.01	11
AUTUMN	3.21	14.13	0.69	2.59	3.90	16.72	2.52	11.54	2
WINTER	6.93	17.51	3.18	4.21	13.47	28.03	2.93	13.21	8
YEAR	8.09	16.52	4.07	4.59	19.36	28.65	2.52	7.52	34

TABLE 3 (μg/m³) RAINNY DAYS, ALL SEASONS, DIFFERENT POSITIONS IN ATHENS

STATIONS	AVG NO_3^-	AVG $SO_4^{=}$	STD NO_3^-	STD $SO_4^{=}$	MAX NO_3^-	MAX $SO_4^{=}$	MIN NO_3^-	MIN $SO_4^{=}$	N
ELEFSIS	3.50	11.13	0.00	0.00	3.50	11.13	3.50	11.13	1
ASPROPIRGOS	-	-	-	-	-	-	-	-	-
PATISSION	3.79	13.58	2.54	3.70	9.12	17.26	1.17	6.85	8
REDIS	4.17	15.74	1.43	4.87	6.79	25.43	2.61	10.50	6
DRAPETSONA	4.27	14.36	2.91	4.04	12.97	24.49	1.12	8.15	14

TABLE 4 (μg/m³) SUNNY DAYS, ALL SEASONS, DIFFERENT POSITIONS IN ATHENS

STATIONS	AVG NO_3^-	AVG $SO_4^{=}$	STD NO_3^-	STD $SO_4^{=}$	MAX NO_3^-	MAX $SO_4^{=}$	MIN NO_3^-	MIN $SO_4^{=}$	N
ELEFSIS	5.05	17.45	1.90	2.30	8.55	20.93	3.12	15.45	5
ASPROPIRGOS	4.72	15.46	2.30	6.71	8.96	29.49	2.54	8.52	6
PATISSION	5.73	15.85	1.53	3.01	7.11	19.20	3.15	10.96	4
REDIS	6.27	17.20	2.28	3.47	9.81	22.07	2.23	12.30	10
DRAPETSONA	5.44	18.77	1.99	5.73	8.85	30.59	2.82	12.18	8

Table 5 shows that for the position "Ministry" the molar ratio $[NO_3^-]_{total}/[SO_4^{=}]$ has exceeded unity on several occasions, thus confirming one of the authors' working hypotheses, namely that Athens is one of the cities that the above mentioned ratio can exceed unity. During February - March 1989 measurements (9) were made with methods based on the use of the Transition Flow Reactor (TFR) (10). The TFR method measures $[NO_3^-]_{total}$, but also $[HNO_3]$ and $[NO_3^-]$. This is regarded as important in view of the fact that HNO_3 and NO_3^- react differently with Pentelic marble.

TABLE 5 MOLAR RATIO $K=NO_3^-{}_{total}/SO_4^{=}$ HVS FILTERS

	AVG	STD	MAX	MIN	N	K>1
TOTAL	0.556	0.276	1.622	0.110	110	8
RAINY DAYS	0.453	0.231	1.280	0.110	44	2
SUNNY DAYS	0.624	0.282	1.622	0.231	66	6
"MINISTRY" R. D.	0.496	0.303	1.280	0.190	15	2
"MINISTRY" S. D.	0.746	0.323	1.622	0.305	33	6
"MINISTRY" SUNNY DAYS						
SPRING	0.892	0.348	1.622	0.475	12	3
SUMMER	0.767	0.299	1.254	0.323	11	3
AUTUMN	0.350	0.012	0.361	0.338	2	0
WINTER	0.596	0.176	0.790	0.305	8	0

The use of the TFR as a Filter Pack (FP) yielded comparable total nitrate concentrations but the ratio of $[HNO_3/[NO_3^-]$ differed appreciably. This fact plus some anomalous results with the TFR (negative values of $[NO_3^-])$ lead to two modifications of the TFR theory, namely TFRA and TFRB

(11). Tables 6-7 show HNO_3, NO_3^-, $SO_4^=$, total nitrate concentrations and the ratios $[NO_3^-{}_{total}/SO_4^=]$ and $[HNO_3]/[NO_3^-]$ based on the TFRA theory. The filters for the same period are being analyzed for cations. Ammonium ion (NH_4^+) concentrations will throw further light on the $[HNO_3]/[NO_3^-]$ ratios.

TABLE 6 TFRA MODIFICATION 22 HOURS (10:30AM-8:30AM) AIR SAMPLING μg/m³

	AVG	STD	MAX	MIN	N
HNO_3	1.190	0.626	2.224	0.289	7
NO_3^-	4.864	1.600	6.974	2.592	7
$SO_4^=$	18.242	11.663	36.397	6.003	7
$NO_3^-{}_{total}$	6.036	2.158	8.641	2.876	7
$NO_3^-{}_{total}/SO_4^=$	0.658	0.244	1.006	0.327	7
HNO_3/NO_3^-	0.230	0.076	0.345	0.111	7

TABLE 7 TFRA MODIFICATION 6 HOURS (9AM-3PM) AIR SAMPLING μg/m³

	AVG	STD	MAX	MIN	N
HNO_3	2.212	1.267	4.580	0.259	12
NO_3^-	8.531	7.166	24.629	1.358	12
$SO_4^=$	14.201	9.548	40.255	2.823	12
$NO_3^-{}_{total}$	10.708	7.871	26.599	2.318	12
$NO_3^-{}_{total}/SO_4^=$	1.212	0.551	2.299	0.354	12
HNO_3/NO_3^-	0.381	0.224	0.796	0.062	12

3. EFFECTS OF HNO_3 AND NO_3^- ON PENTELIC MARBLE

Preliminary experiments on the action of dilute HNO_3 and NH_4NO_3 solutions on marble were performed. As expected it was found that HNO_3 solutions dissolved marble at a higher rate than equomolar NH_4NO_3 solutions.

Three seasonal experiments were performed during spring, summer and autumn 1988. In all cases the ambient air on the Acropolis hill was drawn through a bed of coarse and graded Pentelic marble powder placed in a specially designed reactor. At the end of each period the marble was washed with deionized water and the ions in the wash were analyzed by ion chromatography.

Table 8 shows the total nitrate concentrations from these experiments ($[NO_3^-]_{reactor}$) and the corresponding total nitrate concentrations in ambient air ($[NO_3^-]_{HVS}$), in μgr/m³.

TABLE 8

SEASON	$NO_3^-{}_{reactor}$	$NO_3^-{}_{HVS}$
SPRING	0.023	5.61
SUMMER	8	7.97
AUTUMN	0.0229	4.16

Table 9 shows the seasonal variations of anion concentrations from these experiments. For each anion the figures in the table represent the concentrations for each season relative to that for summer. It can be seen that for all three anions the summer concentrations are much higher than the concentrations during the other seasons.

TABLE 9

SEASON	NO_3^-	$SO_4^=$	Cl^-
SPRING	0.03	0.11	0.04
SUMMER	1	1	1
AUTUMN	0.03	0.13	0.08

Table 10 shows cation concentrations (figures multiplied by 10^{-7} show concentrations in μmoles/m^3) measured recently in the solution from the autumn experiment.

TABLE 10

SEASON	K^+	Na^+	NH_4^+	NO_3^-	$SO_4^{=}$	Cl^-
AUTUMN	3.0	9.2	16.7	3.69	34.3	22.4

It is intended to modify the reactor with the aim of achieving a complete ionic balance. It is believed that this ionic balance and thermodynamic data from the literature will make possible the determination of the amount of Ca^{++} mobilized by HNO_3 and NO_3^-.

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