Pure & Appl. Chem., Vol. 62, No. 1, pp. 163–176, 1990.
Printed in Great Britain.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

APPLIED CHEMISTRY DIVISION
COMMISSION ON ATMOSPHERIC CHEMISTRY*

INVENTORY OF CURRENT TROPOSPHERIC SAMPLING PROGRAMS

Prepared for publication by
J. SLANINA
Netherlands Energy Research Foundation, ECN, P.O. Box 1,
1755 ZG Petten, Netherlands

Inventory of current tropospheric sampling programs

SYNOPSIS

The problems regarding network design and operation are such that harmonization and standardization of networks is called for.
The value of the results obtained by networks is dependent on the quality control measures. At present comparison of results obtained by different networks is hampered by a lack of consistent quality control measures.
The design of many networks is not optimized in line with their objectives.
Sampling procedures are the most important source of errors. The available analytical methods for measurement of SO_2, NO_x, O_3, CO, CO_2 in air and of so-called bulk elements in precipitation are generally adequate for monitoring purposes. For other components the situation is less satisfactory.

INTRODUCTION

The increasing concern regarding the possible obnoxious effects of air pollutants on human health, on vegetation, surface waters, groundwater and on buildings, especially monuments has led to the development of networks of sampling and measuring devices to characterize air quality or to measure the deposition of these pollutants.
The early networks for environmental control were installed to get a first inventory of the concentrations of air pollutants. They were generally situated in areas close to large emission sources and only a limited number of components were measured, primarily SO_2 and total dust or particulate matter.
As the need for more detailed knowledge on the behavior of pollutants became clear, networks expanded in both scope and size. Thus more pollutants were measured and networks were implemented outside the areas with high emissions. As gradually legislation was introduced to curb emissions and to control ambient concentrations, networks were needed to enforce these environmental rules.

The data from these networks are nowadays of vital importance with respect to the following objectives:
-Monitoring the concentrations of pollutants in air in order to provide data on air quality;
-Probing whether levels are reached which necessitate corrective measures such as emission control;
-Providing inventories of the deposition of air pollutants by way of either wet deposition (precipitation) or dry deposition (deposition of gases and aerosol particles);
-Elucidating the effects of pollution on vegetation, soils, water bodies and materials. Correlation of observed effects with measured concentrations of pollutants is very often investigated in order to get a first approximation of the impact of pollutants as a function of their concentration [1];
-To monitor trends in the concentrations of pollutants as a function of time [2,3,4];
-To investigate transport, chemical conversion and residence times in the atmosphere of pollutants [5].

For the first two points a guarantee of the trustworthiness of the results of networks is obviously a requirement. Often the results of networks are used to test whether air quality standards are met in a given area. The alarm function of a number of networks, i.e. to provide a warning at too high concentrations of pollutants, generally followed by emission control measures, necessitates a high degree of reliability.

The use of network data for atmospheric research requires a certain degree of accuracy. More and more the effectiveness of control measures for air pollution is deduced from the application of models, describing the emission, transport and deposition of pollutants over a large area [6]. The results obtained from networks are an indispensable tool for parameterizing and validating these models.
The detection and quantification of trends in the concentration or deposition of pollutants as a function of changing emissions provides necessary information on the effectiveness of emission control measures.

The application of network data to investigations which encompass large areas, such as investigations on long range transport and correlative effect studies, requires a minimum degree of harmonization in siting and operation. The aim of this study is to evaluate the existing networks for the monitoring of pollution on a worldwide scale and to initiate harmonization and/or standardization of these network operations.
To this purpose a questionnaire, added as appendix 1, has been sent (on a very large scale) to authorities responsible for the operation of networks. A response from 73 networks was received. The Commission realizes that a large effort was involved in responding to this questionnaire and is very grateful to the persons and organizations who collaborated in this investigation.

DESCRIPTION OF THE NETWORKS

GENERAL

The list of the networks which have responded to our questionnaire before the date of 1-5-87 is given in table 1. A response was received from 12 countries and from NILU (Norwegian Institute for Air Research), the principal institute involved in the ECE/EMEP network (United Nations Economic Commission for Europe/Cooperative program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe).
Based on the answers to the questionnaire a tabulated description of the networks has been made; see table 2,3 and 4 with corresponding legends.

As the modes of operation in measuring wet deposition, monitoring gas or aerosol concentrations are quite different, all activities are described separately, even when a networks encompasses them simultaneously.

TABLE I

1	USA	VIRGINIA ACID POLL.NETW.
2	USA	NATION. ATM.DEPOSITION PROGR./NAT.TR ENDS NETW
3	USA	ALASKA AMBIENT AIR MONITORING
4	USA	WYOMING AMBIENT AIR QUAL.
5	USA	SOUTH DAKOTA AMB. AIR MON.NETW.
6	USA	GREAT LAKES ATM.DEP.PROGRAM
7	USA	IOWA AMB. AIR QUALITY
8	USA	TENNESSEE AMB.AIR MON.NETW.
9	USA	NEVADA AIR QUAL. SAMPLING NETW.
10	USA	ILLINOIS AIR MON. NETW.
11	USA	WISCONSIN AMB.AIR MON.NETW.
12	USA	MASSACHUSETTS STAREWIDE MON.NETW.
13	USA	MARYLAND AIR MON.NETW.
14	USA	US GEOL.SURV.WATER RES.DIV.MISSISSIPPI
15	USA	WASHINGTON STATE AIR MON.NETW.
16	USA	OREGON SLAMS NETWORK
17	USA	ALABAMA AMB.MON.NETW.
18	USA	NOAA/ARC/ATDD DRY DEP. RESEARCH CORE PROGR.
19	USA	CALIFORNIA AMB.AIR QUAL.MON.NETW.
20	USA	NORTH CAROLINA SLAMS NETWORK
21	USA	ARIZONA AMB.AIR NETW.
22	USA	COOK COUNTY ENV.CONTR.
23	USA	FLORIDA AIR MON. NETW./ ACID RAIN NETW.
24	USA	CALIFORNIA AIR RESOURCES BOARD NETW.
25	USA	DELAWARE AMB.AIR NETW.
26	USA	PUERTO RICO AIR QUAL.MON.NETW.
27	USA	NEW JERSEY MON.NETWORK
28	USA	UTAH BUREAU OF AIR QUAL.NETW.
29	USA	MONTANA AIR QUAL.BUREAU AMB.AIR MON. NETW.

30	USA	HAWAII AIR MON. NETW.
31	IT	IT.MET.SERV. BAPMON NETW.
32	IT	C.N.R. IST.IT.IDROB. LAGO MAGGIORE N ETW.
33	IT	AMM.PR.VENETIA RETE CONTRONOINQUIN.A TM.MAGHERA
34	IT	ENEL-CRTN WET DEP.NETW.
35	IT	ENEL ATM.DEP.CHEM.NETW.
36	IT	TOSCANARAIN DEP.NETW.
37	IT	TORINO SRIA NETW.
38	IT	RETE ANTNQUINAMENTO MAGHERA
39	VEN	VENEZUELA REDPANAIRE/GEMS NETWORK
40	NETH	NETH.NAT.MEAS.NETW.AIR POLL.
41	BELG	BELGIUM AUTOMATIC NETW. AIR POLL.CONTROL
42	NORW	NORWAY ARTIC HAZE PROGRAM
43	NORW	NORWAY NATL.BACKGROUND NETW.
44	NORW	NORWAY OZONE NETWORK
45	AUST	AUSTRALIA OZONE NETW.
46	AUST	AUSTRALIA REGION. BAPMON NETW.
47	AUST	AUSTRALIA CSIRO TRACE GAS MON. NETW.
48	N.ZEAL	N.ZEALAND CHLORIDE NETW.
49	N.ZEAL	N.ZEALAND NECAL NETW.
50	N.ZEAL	N.ZEALAND MET.SERV. NETW.
51	N.ZEAL	N.ZEALAND ELECTR.DIV.MIN.ENERG.NETW.
52	N.ZEAL	N.ZEALAND NZAS NETW.
53	N.ZEAL	N.ZEALAND CO2 NETW.
54	SWITS.	SWISS NABEL NETW.
55	FRG	FRG UBA NETW.
56	FRG	FRG BADEN/WUERTEMBERG NETW.
57	FRG	FRG BAYERN NETW.
58	FRG	FRG SCHLESWIG-HOLSTEIN/HAMBURG NETW.
59	FRG	FRG HESSEN NETW.
60	FRG	FRG NIEDERSACHSEN NETW.
61	FRG	FRG NORDRHEINLAND/WESTFALEN NETW.
62	FRG	FRG RHEINLAND-PFALZ/SAAR NETW.
63	FRG	FRG BERLIN NETW.
64	SPAIN	SPAIN BAPMON/EMEP INST.NAC.MET.NETW.
65	SPAIN	SPAIN MED POL NETW.
66	CAN	CANADA CAPMON
67	CAN	CANADA EPS NETW.
68	CAN	CANADA NARMON NETW.
69	CAN	CANADA REPQ NETW.
70	CAN	CANADA APIOS NETW.
71	CAN	CANADA N.SASKATCHEWAN PREP. NETW.
72	CAN	CANADA ALBERTA ENVR NETW.
73	ECE	EMEP NETW.

NETWORKS FOR GAS (Table 2)

The first column of table 2 (networks for gas measurement) identifies the network according to the number allotted to each network in table 1.

The second column gives information on the siting criteria. In some cases these are given by central organizations, e.g. WMO (World Meteorological Organization), ECE/EMEP, or US EPA (United States Environmental Protection Agency). In others information regarding siting criteria is given in the answers on the questionnaire, but in about 20% of the answers no mention of siting criteria was made.

In the next column (3) the objectives of the networks are tabulated. Networks in the US and Canada are generally responsible for the air quality data, necessary to enforce air quality legislation. For the other networks general monitoring and detection of trends in air concentrations are given as objectives. In some countries emission abatement measures are taken during episodes of high pollution concentrations, based on the results of monitoring networks. A number of networks in "background areas" measure parameters important to assess climatological impacts of trace components in the atmosphere.

The fourth column gives an overview of the analytical methods employed for the measurement of SO_2. Pulsed fluorescence detection, ultraviolet spectrophotometry and wet chemical methods such as coulometry and colorimetry by way of the tetrachloromercury complex, are in general use.

In the fifth column the methods for NO_x (NO_2 and NO) are tabulated. Chemoluminescence detection using the NO/O_3 reaction and colorimetric methods employing sodium arsenite are most widely applied.

In the sixth column the methods for ozone are described. Chemoluminescence detection based on the O_3/ethylene reaction and UV spectrophotometry are the most important.

For CO (column 7) non-dispersive infrared absorbance measurement is the most important method.

The same applies to CO_2 (column 8).

Column 9 describes the methods used to determine the concentrations of hydrocarbons. Generally the sum of volatile hydrocarbons is measured by means of flame-ionization detectors. If compounds are measured specifically (e.g. CH_4 or Poly-Aromatic Hydrocarbons), this is mentioned together with the analytical method (generally GC, gas chromatography or HPLC, high performance liquid chromatography).

Column 10 gives an overview of other gaseous compounds measured and the employed analytical method. Fluoride and HNO_3 are mentioned most frequently.

In column 11 the measurement frequency is given. Many monitors are operated on a more or less continuous basis, measurements of specific organic compounds, nitric acid, fluorides etc. are performed discontinuously and the frequency is indicated.

The next column (12) provides information on the quality assurance procedures of the networks. The situation is as described for siting criteria. In some cases regulations for quality assurance are provided by central organizations, e.g. WMO, ECE/EMEP, or US EPA . In others information regarding quality control procedures is given in the answers on the questionnaire, but again, in about 20% of the answers no information is forwarded.

TABLE 2

COL. 1	2	3	4	5	6	7	8	9	10	11	12
	SITING	OBJECT.	SO2	NOx	O3	CO	CO2	ORG.COUMP.	OTHER	FREQ.G.	QUAL.CONTR.
1	FEDR	AIRST	PF	CLO	UV	NDIR				CON	EPA
4	EPA	AIRST	PF,PR	CLO,SA	CLE					CON,D6	EPA
5	FEDR	AIRST	PR	SA						D6	EPA
7	EPA	AIRST	PF,FPD,UV	SA	CLE,UV	NDIR				CON,D6	EPA
8	FEDR	AIRST	UV		CLE					CON	FEDR
9	DC	AIRST		CLO	CLE	NDIR				CON	FEDR
10	EPA	AIRST	PF	CLO	UV	NDIR				CON	FEDR
11	EPA	AIRST	FL	CLO	CLE,UV	NDIR		POL,CHO		CON,H2	EPA
12	EPA	AIRST	PF	CLO	CLE,UV	NDIR				CON	EPA
13	DC	AIRST	PF	CLO	CLE,UV	NDIR				CON	QA
15	EPA	AIRST	PF	CLO	UV	NDIR				CON	FEDR
16	DC	AIRST	NG	NG	NG	NG				CON	EPA
17	DC	AIRST	PF		UV					CON	EPA
18	DC	DRYD	PF,FILTP		UV				FILTP,HNO3	CON,D7	QA
19	EPA	AIRST	PF	CLO	UV			GC,O(Cl)		CON,D12	EPA
20	EPA	AIRST	PF		UV	NDIR				CON	EPA
21	FEDR	AIRST	PF,FPD	CLO	CLE,UV	NDIR				CON	FEDR
22	FEDR	AIRST	PF	CLO	UV	NDIR				CON	FEDR
23	EPA	AIRST	PF,UV	CLO	CLE	NDIR				CON	FEDR

TABLE 2 CONTINUED

COL. 1	2	3	4	5	6	7	8	9	10	11	12
24	FEDR	AIRST	PF	CLO	UV	NDIR		GC,FID		CON	FEDR
25	FEDR	AIRST	NG	NG	NG	NG		FID,PID		CON	FEDR
26	FEDR	AIRST	PF		UV	NDIR				CON	FEDR
27	EPA	AIRST	PF	CLO	CLE	NDIR				CON	EPA
28	NG	AIRST	PF	CLO	CLE	NDIR				CON	NG
29	FEDR	AIRST	PF			NDIR				CON	QA
30	FEDR	AIRST	PR	SA	CLE	NDIR				CON,D6	EPA
31	NG	CLIM			UV		NDIR			CON,H4	WMO
33	DC	AIRST	C	C, CLO	CLE			FID		CON,H2	QA
37	DC	AIRST,TR	C	CLO	UV	NDIR				CON	QA
38	DC	ALARM	C							CON	QA
39	DC	AIRST	ACT							D1	WMO
40	DC	AIRST,TR	C, UV	CLO	CLE	C				CON	QA
41	DC	AIRST	FPD	CLO	CLE	NDIR				CON	QA
42	NG	SRCE	FILTP	TGS				GC,FID		NG	NG
43	EMEP	MON	FILTP	TGS						D1	NG
44	NG	MON			CLE,UV					CON	
45	NG	STRAT			UV,C					D1	QA
47	NG	CLIM				NDIR,GC	NDIR	GC,FID,EC CH4,FREON		CON	QA
48	NG	DRYD								NG	NG
49	DC	MON	WC							D1	QA
50	DC	CLIM STRAT			UV	GC	GC	GC		D1	QA
51	DC	MON							FL,H2S	CON	QA
52	DC	MON							EL,F	CON/D1/D7	QA
53	DC	CLIM				NDIR		CH4,C(I)		CON/M	QA
54	DC	MON	UV,WC	CLO,SA	UV,CLE		NDIR	FID		CON/D1	QA
55	NG	MON,AIRST	TCM,FPD,C UV	CLO, SA	UV			FID		CON	NG
56	NG	MON,AIRST	UV	CLO,SA	UV			FID		CON	NG
57	NG	MON,AIRST	UV,CORR	CLO,SA	UV			GC,NMETH		CON	NG
58	NG	MON,AIRST	COND,UV FID	CLO,SA	UV,CLE			FID		CON	NG
59	NG	MON,AIRST	COND,FID	CLO,SA	UV,CLE			FID		CON	NG
60	NG	MON,AIRST	UV	CLO	UV			FID		CON	NG
61	NG	MON,AIRST	COND	CLO,SA	UV			FID		CON	NG
62	NG	MON,AIRST	TCM,FID	CLO,SA	KI,UV			FID		CON	NG
63	NG	MON,AIRST	COND	CLO,SA	UV			HPLC,PAH		CON	NG
64	EMEP	MON	WC	SA						D1	EMEP
65	WMO	MON									
66	DC	MON,TR	FILTP						FILTP,HNO3	D1	QA
67	DC	MON			CLE,UV					CON	QA
69	DC	MON	UV,C	CLO	CLE	NDIR			COL,H2S,F	CON/H12	QA
70	DC	MON,SRCE	FILTP						FILTP,HNO3	D1	QA
72	DC	MON,TR	PF,C,FPD	CLO	CLE,UV	NDIR,CORR		FID	UV,NH3	CON	QA

LEGENDS OVERVIEW GAS NETWORKS (Table 2)

Column 1: Networks identified by number, see table 1 and 1A.

Column 2: Siting criteria,
DC = description of criteria is given in more or less elaborate form,
EMEP = according to EMEP regulations,
EPA = according US EPA regulations,
FEDR = according US federal regulations,
WMO = according to WMO regulations,
NG = not given in the questionnaire.

Column 3: Objectives of the network,
AIRST= related to air quality standards,

ALARM= warning for episodes of high pollutant concentration,
CLIM = measurements related to climatology,
DRYD = dry deposition measurement,
MON = general monitoring purposes,
STRAT= Stratospheric research,
TR = detection of trends.

Column 4:Analytical methods for SO_2,
ACT = acidimetric titration,
C = coulometry,
COND = by means of conductivity measurement,
CORR = correlation spectrometry,
FILTP= filterpack method,
FL = continuous fluorescence,
FPD = flame photometric detection,
PF = pulsed fluorescence,
PR = pararosaniline colorimetric method,
TCM = colorimetric method of tetrachloromercury complex,
UV = UV spectrophotometry,
WC = assorted wet chemical methods,
NG = not given.

Column 5: Analytical methods for NO_x,
C = coulometry,
CLO = chemoluminescence with ozone addition,
SA = sodium arsenite colorimetric method,
TGS = TGS-AINSI method,
UV = UV spectrophotometry,
NG = not given.

Column 6: Analytical methods for ozone,

CLE = chemoluminescence with ethylene addition,
KI = potassium iodide spectrophotometric method,
UV = UV spectrometry,
NG = not given.

Column 7: Analytical methods for carbon monoxide,
C = coulometry,
CORR = correlation spectrometry,
GC = gas chromatography
NDIR = non-dispersive infra-red spectrophotometry,
NG = not given.

Column 8: Analytical method for carbon dioxide,
GC = gas chromatography
NDIR = non-dispersive infra-red spectrophotometry.

Column 9: Analytical methods for organic compounds.
If no compounds are mentioned, volatile hydrocarbons are measured. In other cases the method is mentioned first, followed by the measured compounds.
EC = electron capture detector
GC = gas chromatography,
FID = flame ionization detector,
FL = fluorescence measurement
HPLC = high performance liquid chromatography,
PID = photo-ionization detector,
POL = polarography
CH4 = methane,
CHO = aldehydes,
C(I) = carbon isotopes,
FREON= freons,
NMETH= hydrocarbons, not methane.
O(Cl)= chlorocompounds,
PAH = Poly Aromatic Hydrocarbons,

Column 10: Other compounds, specified.
COL = colorimetric methods,
EL = ion selective electrode,
FITP = filterpack,
POL = polarography,
NG = not given.

Column 11: Frequency of gas measurements,
CON = continuously,
D(followed by number) = 1 measurement per x days,
H(followed by number) = 1 measurement per x hours.

Column 12: Quality control of gas measurements,
QA = questionnaire describes more or less elaborate QA
EMEP = according to EMEP,
EPA = quality control according to US EPA regulations,
FEDR = quality control according to US Federal Regulations, procedures,
WMO = quality control according to WMO regulations,
NG = not given.

NETWORK FOR AEROSOL MEASUREMENT (Table 3)

The first three columns give the same information as in the case of the gas measurement networks, identification of the network, siting criteria and objective respectively.

Column 4 describes the sampling methods for aerosols. High-volume sampling techniques are still by far dominant, the use of sample inlet systems which limit the sampling to aerosol particles with a diameter of 10 micron or less is limited to the US. Total suspended material is determined in many cases. Individual compounds measured are given.

The measurement of the visibility (column 5) is given in this part of the table in view of the close relation to particle concentration.

Column 6 describes the measurement frequency for aerosols.

Quality assurance procedures for the sampling and measurement of aerosols are given in the last column (7). The situation here resembles closely the conditions described for the measurements of gaseous compounds (column 12, table 2).

TABLE 3

COLUMN 1	2	3	4	5	6	7
	SITING	OBJECT.	AEROSOL	VISIB.	FREQ.AER.	QUAL.CONTR
1	FEDR	AIRST	HVOL, Pb		D6	EPA
4	EPA	AIRST	HVOL, PM10		D6	EPA
5	FEDR	AIRST				
7	EPA	AIRST	HVOL, PM10		D6	EPA
8	FEDR	AIRST	HVOL		D6	FEDR
9	DC	AIRST				
10	EPA	AIRST	HVOL, As,Sb,Be,Cd Fe,Mn,Ni,Se,Pb,S,N		D6	
11	EPA	AIRST	HVOL, PM10, Pb		D6,D2	EPA
12	EPA	AIRST				
13	DC	AIRST				
15	EPA	AIRST	HVOL, NEPEL, PM 10	IN	D6,D3,D	FEDR
16	DC	AIRST	HVOL, MVOL TR(-), TR(+)	IN	D6,CON	EPA
17	DC	AIRST	HVOL		D6	EPA
18	DC	DRYD				
19	EPA	AIRST	HVOL, PM10		D6	EPA
20	EPA	AIRST	HVOL		D6	EPA
21	FEDR	AIRST	HVOL, Pb		D6	FEDR
22	FEDR	AIRST				
23	EPA	AIRST	HVOL		D6	FEDR
24	FEDR	AIRST	HVOL, PM10	REFL.	D6,H2,CON	QA
25	FEDR	AIRST				
26	FEDR	AIRST	HVOL, PM10		D6	FEDR
27	EPA	AIRST	HVOL, PM10, TR(+)		D6	EPA
28	NG	AIRST	HVOL, PM10		D6,D1	NG
29	FEDR	AIRST	HVOL, PM10, DS Pb,As,Cd,Cr,Zn,Cu		D6,D3	QA
30	FEDR	AIRST				
31	NG	CLIM	HVOL		D6	NG
33	DC	AIRST	HVOL, F		CON,D7	QA
37	DC	AIRST,TR	HVOL, TSP		D1,H2	QA
38	DC	ALARM				
39	DC	AIRST	HVOL, RFBSM		D1	WMO
40	DC	AIRST,TR	HVOL, LVOL, SO4 NO3, BSM	IN	D1,CON	QA
41	DC	AIRST	LVOL,Pb,Cd,As,Sb,Tl Cr,Cu,Mn,Ni,Se,Ti,V,Zn		D1	QA
42	NG	SRCE	HVOL, Pb,Ni		NG	NG
43	EMEP	MON	HVOL, SO4		D1	NG
44	NG	MON				NG
45	NG	STRAT				
47	NG	CLIM	HVOL, TR(+)		M	QA
48	NG	DRYD	HVOL, Cl,Na,Ca,Mg,Br		M	
49	DC	MON	HVOL, DS, TSP, Pb		D7	QA
50	DC	CLIM STRAT	HVOL, TR(+)	IN	M	
51	DC	MON				
52	DC	MON	FILTP, F		D1/D7	QA
53	DC	CLIM				
54	DC	MON	HVOL, TSM, BSM, SO4 Be		D1/M	QA

TABLE 3 CONTINUED

COLUMN 1	2	3	4	5	6	7
55	NG	MON,AIRST	HVOL, TSM		D1	NG
56	NG	MON,AIRST	HVOL, TSM		D1	NG
57	NG	MON,AIRST	HVOL, TSM		D1	NG
58	NG	MON,AIRST	HVOL, TSM		D1	NG
59	NG	MON,AIRST	HVOL, TSM		D1	NG
60	NG	MON,AIRST	HVOL, TSM		D1	NG
61	NG	MON,AIRST	HVOL, TSM		D1	NG
62	NG	MON,AIRST	HVOL, TSM		D1	NG
63	NG	MON,AIRST	HVOL, TSM		D1	NG
64	EMEP	MON	HVOL, TSM, H,NH4,SO4	IN	D1/H8	EMEP
65	WMO	MON	HVOL, NO2,NO3,NH4,SO4,SiO2 H		D1	WMO
66	DC	MON,TR	LVOL, SO4,NO3,NH$,Cl,Na		D1	QA
67	DC	MON	HVOL, SO4		D1	QA
69	DC	MON	HVOL, TSM, SO4,NO3,Pb		D6	QA
70	DC	MON,SRCE	HVOL, SO4,NO3,NH4		D1	QA
72	DC	MON,TR	HVOL, DS, TSM, PYR,SO4,N Pb		D6	QA

LEGENDS AEROSOL MEASUREMENT NETWORKS (Table 3)

Column 1-3, see description of column 1-3 of gas measurement networks.

Column 4: Sampling method for aerosol, followed by measured compounds,
HVOL = high volume sampling,
MVOL = medium volume sampling method,
LVOL = low volume sampling technique,
PM10 = sampling with a 10 micron limited inlet,
DS = dichotomous sampler,
BSM = Black smoke measurement,
NEFEL= nefelometry,
RFBSM= black smoke measurement by reflectance,
TR(+)= analysis trace cations,
TR(-)= analysis trace anions,
TSM = Total suspended material.
TSP = total suspended material by beta activity measurement,

Column 5: Measurements related to visibility,
IN = integrating nefelometer,
RF = reflectance measurement.

Column 6: Frequency aerosol measurements,
CON = continuously,
D(followed by number) = 1 measurement per x days,
H(followed by number) = 1 measurement per x hours.

Column 7: Quality assurance procedures for aerosol measurements,
QA = questionnaire describes more or less elaborate QA
EMEP = according to EMEP,
EPA = quality control according to US EPA regulations,
FEDR = quality control according to US Federal Regulations, procedures,
WMO = quality control according to WMO regulations,
NG = not given.

NETWORKS FOR WET DEPOSITION (Table 4)

The information on networks for the measurement of wet deposition is given in table 4.

The first column identifies the network in the same way as done in tables 2 and 3.

The siting criteria are tabulated in column 2. The remarks made for siting criteria in the case of gas/aerosol networks also apply in this case (see remarks regarding column 2, gas/aerosol networks).

The objectives of the networks (column 3) are generally to determine the wet deposition of compounds or to detect trends in the composition of precipitation or wet deposition.

The fourth column provides information on the samplers employed in the network. Whereas in the US and Canada wet-only samplers (samplers opened during precipitation events only in order to prevent dry deposition) are generally in use, bulk samplers are still widely applied in the rest of the world. The sampler type is indicated, if this information was supplied.

In column 5 the sampling frequency is given. Sampling periods of one week and one month are most frequent.
Column 6 provides information on the analytical techniques applied to the measurements of so-called bulk compounds (sulfate, nitrate, chloride, hydronium ions, sodium, potassium, calcium, magnesium and ammonium). Ion-chromatography, atomic absorption spectrometry, ion-selective electrodes and colorimetric methods (especially for ammonium) are widely used.

In column 7 the methods used for the determination of trace compounds are described. Individual elements or compounds are mentioned if this information was available. Ion-chromatography, atomic absorption spectrometry and induction-coupled plasma emission spectrometry are important methods.

The description of the quality control procedures is given in column 8. Again the same observations can be made as mentioned for the gas/aerosol networks (see remarks on column 12, table 2).

TABLE 4

COLUMN 1	2	3	4	5	6	7	8
	SITING	OBJ	SAMPLER	PERIOD	BULK METHOD	TRACE METHOD	QUAl.CONT.
1	DC	DEP	AER	W	IC,AA,COL,EL	AA,Zn,Al,Fe,Mn,Ni, Pb,V,As,IC,NO2,Br	QA
2	DC	TR,DEP	AER	W	IC,AA,COL,pH	F	NADP
5	DC	DEP	AER	W	NG		EPA
6	DC	TR,DEP	AER	W	COL,AA,EL,TITR	ICP,AA.TR(+)	EPA
8	EPA	DEP	W/D,NG	CON	pH		EPA
9	DC	DEP	W/D,NG	W	NG	PO4,NG	USGS
11	NADP	DEP	AER	W/CUMM		GC,PCB,AA,Hg	NADP
13	NADP	TR,DEP	AER	W	NG	NG,Br,PO4,NO2,NG	QA
14	NADP	DEP	AER	W	USGS,	USGS,F,Br	NADP/USGS
15	NADP	DEP,SRCE	AER/BU	W	NG	NG,PO4,NO2,Pb	QA
16		NUIS	BU	NG		PART.	QA
17	EPA	DEP	MIC	W	NG	NG,F,NO2,Br,PO4	EPA
19	DC	AIRST	FOG/GLOB	D	NG,pH,SO4,NO3		QA
24	DC	DEP	AER	W	IC,AA,EL,COL		NADP
25	NADP/EPA	DEP,AIRST	AER/BU	W/E	IC,EL	IC,Br,NO2,PO4	QA
27	NADP	DEP	AER	W/E	IC,EL		USGS/EPA
31	WMO	DEP,TR	ELI	M/W	NG		WMO
32	DC	DEP	WO/BU	W	IC,AA,EL,HCO3	IC,Br	QA
34	DC	DEP	BU	W	ICP,IC,EL,COL,TITR HCO3		QA
35	DC	DEP(W/D)	W/D,NG	W	IC,AA,TR		QA
36	DC	DEP	BU	D/2W	EL,AA,	POL,NOT SP.	NG
38	DC	DEP,AIRST	BU	W	TUR,COL,EL,AA		QA
40			BU/ECN	W	IC,COL,EL,AA	AA,POL,ICP,Cu,Cd,Ni,I	
	DC	DEP,TR				Pb,V,Fe,Mn,As,Cr,Co,Se	QA
41		DEP,AIRST	NIL	D	IC,AA,EL	AA,Pb,Cu	QA
43	EM	DEP	NIL	D/W	IC,AA,COL,EL	NG,Pb,Zn,Cd,Fe	NG
46	DC	DEP	ERNI	W	IC,COL,AA,EL,TITR		WMO
48	NG	DEP OF CL	BU	M	CL,EL		NG
50	DC	DEP	W,SAN	M	COL,TUR,AA		WMO
52	DC	DEP OF F,	BU	M	EL,COL,F,Cl		NG
54			BU?				
55	NG	DEP	ERNI	W/M	NG		NG
56	NG	DEP	BU	W/D	NG		NG
57	NG	DEP	BU	NG	NG		NG

TABLE 4 CONTINUED

COLUMN 1	2	3	4	5	6	7	8
59	NG	DEP	W/D	NG	NG		NG
60	NG	DEP	BU	NG	NG		NG
61	NG	DEP	BU	NG	NG		NG
62	NG	DEP	NG	NG	NG		NG
64	WMO	DEP	ERNI	M	NG		WMO/EMEP
66	DC	DEP,TR	MIC	D	IC,AA,EL,COL	Fe	DC
67	DC	DEP	SAN	E/2W	ASTM		DC
68	DC	DEP	SAN	W	IC,AA,EL		DC
69	DC	DEP	AER	W2	IC,AA,COL,EL		DC
70	DC	DEP	MIC	M	IC,AA,COL,EL,ICP	ICP,AA,Zn,Fe,Ni,Cu,Pb,Al Cd,V,Mn	DC
71	DC	DEP	W	E	IC,AA,TITR,EL	ICP	DC
72	DC	DEP	W	M	IC,AA,EL		DC
73	DC	DEP	W/BU	D/M	MISC		DC

LEGENDS OVERVIEW NETWORKS PRECIPITATION

Column 1: Networks identified by number (table 1 and 1A)

Column 2: Siting criteria,
DC = description of the criteria is given in more or less elaborate form,
EMEP = according to EMEP,
EPA = criteria according USEPA,
NAPD = criteria according USNAPD,
WMO = criteria according WMO,
NG = not given.

Column 3: Objectives of the network,
AIRST= compliance to air quality standards.
DEP = measurement of wet or total deposition,
NUIS = detection of nuisance,
SRCE = detection of sources of compounds in precipitation,
TR = detection of trends,

Column 4: Samplers,
BU = bulk(open) sampler,
W = Wet-only sampler,
W/D = wet/dry sampler,
AER = Aerochem wet/dry sampler,
ECN = ECN wet-only sampler.
ELI = Elinap sampler,
ERNI = ERNI wet-only sampler,
FOG = fog sampler Global Cheochemistry,
MIC = Mic collector, Climatronics,
NIL = NILU sampler,
SAN = Sangamo sampler.

Column 5: Sampling period,
CON = continuously,
E = event,
D = day sampling,
W = weekly,
2W = sampling period of 2 weeks,
M = monthly sampling period,
CUMM = cumulative sampling.

Column 6: Analytical methods for bulk elements, if no elements are specified, all bulk elements are measured. In all other cases methods are given first, followed by measured compounds.
AA = atomic absorption spectrometry,
ASTM = methods according ASTM,
COL = colorimetric method,
EL = potentiometry using electrodes,
IC = ion chromatography,
ICP = induction coupled emission plasma spectrometry,
MISC = miscellaneous,
TITR = titration,
TUR = turbidimetric sulfate measurement,
USGS = methods according US Geological Service,
HCO_3 = bicarbonate is measured by titrimetry,
NG = not given.

Column 7: Analytical methods for trace elements, see column 6 plus:
GC = gas chromatography,
PART = particulate matter is measured by filtration,
PCB = polychlorobiphenyls,
POL = polarography,
TR(+)= trace cations,
NG = not given.

Column 8: quality assurance procedures,

QA = procedure is given in any form,
EMEP = according to EMEP,
EPA = according USEPA,
NAPD = according USNAPD,
USGS = according US Geological Service,
WMO = according WMO,
NG = not given.

TENTATIVE CONCLUSIONS

GENERAL

Even though the response on the questionnaire was relatively good, the available information on 73 networks is not necessarily representative in all aspects. A considerable number of networks has not responded yet and not all pertinent information was given in the answers we have received. Even so, a number of tentative conclusions can be drawn, based on the present material. There is only limited evidence that the mode of operation of networks is in a clear and direct way derived from the objectives of the networks. In the siting criteria of networks, rules are given to avoid an undue influence of local sources (this of course does not apply to networks dedicated to the detection of sources) and the problems regarding representative sampling are discussed. Sampling frequency, network density and overall accuracy and precision are generally not a function of network objectives.

Exceptions are found in The Netherlands and Canada.
The layout of the present Netherlands network has been defined in order to attain a preset level in accuracy regarding measurement of concentrations in air, depositions and trend detection. The results of former networks in The Netherlands have been used to derive an optimized configuration of stations, sampling frequency and the requirements on the sampling and analytical methods [7].
In the Canadian CAPMON network, network density is dependent on the average emission strengths in a given region, leading to more stations in more polluted regions. In this way the density of data is higher in regions where one expects strong gradients [8].
The rather inadequate situation in most other countries is reflected in the literature on this particular subject. Only a limited number of papers have been published examining this problem [7,9,10,11].

Quality control is also a problem. In both the US and Canada, central agencies have issued regulations for quality control and all responding networks in these countries apply these rules.
International organizations (WMO for the BAPMON, Background Pollution Monitoring international network and ECE for the EMEP international network) have also quality control measures in operation but these seem to be less stringent compared to e.g. the regulations issued by US EPA.
Still, as already stated in the introduction, it is of utmost importance that the results of networks can be compared on a worldwide scale, both to investigate emission-effects relations for pollutants and to expand our knowledge on atmospheric processes.
In view of the large diversity of sampling and analytical methods, employed in the different networks, the introduction of generally accepted quality control measures has a very high priority.

NETWORKS FOR GAS AND AEROSOLS

For SO_2 modern instrumental methods are generally in use. In view of the SO_2 concentrations generally encountered and the performance of these methods, no important problems are to be expected except in background area where very low SO_2 concentrations are encountered.
The situation is less favorable in case of NO_x. Commercial monitors have not only problems in measuring NO_x concentrations in background areas, but also regarding selectivity in view of the interference by HNO_3 and other components. Also a number of wet-analytical methods are in use for these compounds which are somewhat inferior regarding accuracy and precision.
The instrumental methods for the determination of ozone are thought to be sufficient for the present needs.
The nondispersive methods, generally used for CO and CO_2, do not present appreciable problems.
Methods for the measurement of individual hydrocarbons, nitric acid, hydrofluoric acid etc. are more in the stage of laboratory development with the exception of the application of FID for total volatile organics. In the latter method calibration presents a serious problem.

Less satisfactory is the situation regarding the measurement of aerosols. Many networks determine total suspended material, a not very useful parameter as it lacks selectivity.
Many high-volume methods can introduce artifacts in the measurement of trace

metals, due to contamination. This problem is well known for elements like Fe, Zn, Cd, Cu.
The usefulness of simple filter sampling techniques for the determination of ammonium is questionable in view of the lack of stability of ammonium nitrate. The same goes for nitrate in aerosols.
In general, the operators of networks seem to be more or less satisfied with the available methodology, with the exception of techniques for the measurement of organic compounds, strong acids and volatile inorganic compounds such as ammonium nitrate.

WET DEPOSITION NETWORKS

The use of bulk collectors, samplers which remain open if no precipitation occurs, hinders the interpretation of the results of networks, as a mixture of wet and dry deposition is sampled by these devices. This problem is less serious in some background areas where very low gas and aerosol concentrations are encountered, resulting in very low dry deposition rates. Funnel-type samplers, generally in use, are not suitable for sampling snow as the sampling efficiency is very dependent on wind speed.
The stability of precipitation samples is questionable if they are kept for more than a week under field conditions. Sampling periods of a month, if the samples are not cooled, can result in changes in ammonium, hydrogen ion and nitrate concentrations depending on local meteorological parameters.
The analytical methodology for bulk elements is sufficiently developed to guarantee acceptable results.
The situation is less favorable in the case of trace elements as contamination occurring both in the field and in the analytical laboratory, can cause severe problems.
Siting can be a source of errors for wet deposition networks. The influence of high objects in the vicinity of sampling sites is often underestimated. Their presence can lead to errors in the amount of precipitation sampled and to artifacts due to contamination.

Acknowledgement

This inventory was only possible by the support of all those who have responded to our questionnaire. We are very grateful for the time and effort which was devoted to answering all questions.
The members of the IUPAC subcommission on evaluation and harmonization of current tropospheric sampling networks (Dr. L.Horvath, Institute for Atmospheric Physics, Hungary, Dr.H.Martin, Environment Canada, Dr. D.Onderdelinden, RIVM, The Netherlands and Dr.R.T.McMillen, Atmospheric Turbulence and Diffusion Division of ARL, USA) have made very useful comments.
The contributions of Dr. H.J. Grosse, Dr. S. Penkett and Dr. R.A. Brown, all members of commission VI.4 have been very helpful.

LITERATURE

[1] H.Stratmann
Wirkungen von Luftveruntreinigungen auf die Vegetation
LIS-Berichte 49, 1984, LIS, Essen, BRD.

[2] L.Granat
On the Variability of Rain Water Composition and Errors in Estimates of Areal Wet Deposition.
Report AC-30, 1975, Department of Meteorology, University of Stockholm.

[3] L.A.Barrie
Interpretation of Network Data: Spatial and Temporal Variations
Proceedings Symp. on Monitoring and Assessment of Airborne Pollutants, Ottowa, 1982, Nat. Research Council Canada

[4] T.A.Buishand, G.T.Kempen, A.J.Frantzen, H.F.R.Reijnders and A.J.Eshof
Trend and Seasonal Variation of Precipitation Chemistry Data in The Netherlands
Atmospheric Environment, Vol. 22, 1988, pp 339-348

[5] W.H.Asman and A.J.Janssen
A Long-Range Transport Model for Ammonia and Ammonium for Europe
Atmospheric Environment, Vol 21, 1987, pp 2099-2119

[6] J.W.S.Young and W.R.Shaw
A Proposed Strategy for Reducing Sulphate Deposition in North America
1. Methodology for Minimizing Sulphur Removal
Atmospheric Environment, Vol. 20, 1986, 189-199

[7] N.D. van Egmond, H.Kesseboom en D.Onderdelinden
Statistische Optimalisatie van het Landelijk Meetnet voor de Regenwaterkwaliteit
RIVM-Report 218203001, 1985.

[8] R.J.Vet and M.E.Still
The Canadian Air and Precipitation Monitoring Network (CAPMoN): A Description
Report, 1986, Air Quality Monitoring and Assessment Division, Atmospheric Environment Canada

[9] L.Horvath
Effect of the Sampling Period and Method on the Measured Rate of Wet Deposition if Inorganic Compounds.
Idojaras, Vol. 84, 1980, pp 130-134.

[10] L.Haszpra
On the Planning of Precipitation Chemistry Network
1. Sulfate Data; Case of Uniformly Distributed Stations
Idojares, Vol. 84, 1980, pp 121-129

[11] J.Slanina
The Influence of Outliers on Results of Wet Deposition Measurements as a Function of Measurement Strategy
Atmospheric Environment, In Press.