QA/QC – monitoring and data analysis

Karin Sjöberg
IVL

The Refresher Training Programme for Malé Declaration Monitoring
25-28 March 2008
AIT, Bangkok, Thailand

QA/QC definitions

Quality Control

the routine use of procedures designed to achieve and maintain a specified level of quality for a measurement system

Quality Assurance

a set of coordinated actions as plans, specifications, and policies used to assure that a measurement program can be quantifiable and produce data of known quality

Quality Assurance

expressed by laboratory personnel at IVL

- is to use common sense in a systematic way
- makes it more likely to do things correct from the beginning
- creates confidence

Difference between QC and QA ?

Quality control is a system of activities to provide a quality product

Quality assurance is a system of activities to provide assurance that the quality system is performing adequately

⇒ QA is QC for QC

QA/QC - monitoring

- monitoring site
- monitoring methods
- sample collection and handling *(incl. storage)*
- analysis
- reporting
- intercomparisons

Monitoring methods for precipitation

- bulk collectors (wet and dry deposition)
- wet-only collectors (wet deposition)

QA/QC for sampling methods may include intercomparisons between

- collectors of same type (bulk or w/o)
- collectors of different types (bulk and w/o)
- bulk/wet-only collectors and standard meteorological gauges (for precipitation amount)

Swedish National Air Quality and Precipitation Monitoring Network

- w/o and bulk samplers in parallell at some sites
- duplicate bulk samplers for inorganic analyses
- triplicate bulk samplers for heavy metals

Rörvik June 2000 -June 2001

	Wet-only	Bulk	dry dep.
	mmol m^{-2} y^{-1}		%
mm	903	931	(3%)
H^+	2.39	2.28	-5%
$SO_4^{2-}{}_{ex}$	0.86	0.93	9%
Cl^-	4.66	5.18	11%
NO_3^-	2.98	3.01	1%
NH_4^+	2.41	2.68	11%
Ca^{2+}	0.24	0.25	4%
Mg^{2+}	0.49	0.54	11%
Na^+	4.26	4.85	14%
K^+	0.13	0.25	87%

bird dropping?

Precipitation monitoring studies in India

Kulshrestha Indian Institute of Chemical Technology, Hyderabad, India
Granat and Rodhe, MISU, Sweden
Engardt, SMHI, Sweden

Wet-only collectors

- less than 5-10% loss due to delay in lid removal,
  at sites with moderate wind speeds

Bulk collectors

- usability depends critically on the nature of the surrounding environment,
  large variations for duplicate samplers can be observed due to local emissions sources
- difference between bulk/wet-only in forested area
  30% for Ca^{2+} and 2% for SO_4^{2-}

Bulk and wet-only data in Japan

- no difference in precipitation amount observed

- concentrations of bulk samples higher than those of wet-only samples
  - around 40 % at the urban site
  - around 20 % at the rural site

Operational checks - precipitation

Conductivity of deionized water used for rinsing and cleaning

Wet only collector
- proper rainfall sensor response and operation of lid opening
- mechanical operation of the collector
- lid fits snugly on the collection bucket
- lid is not broken
- battery is charged
- cleanliness of collecting funnel and vessels

Bulk collector
- cleanliness of collecting funnel and vessels
- collection bottle and tubing are wrapped properly with aluminium foil
- no leak between funnel and tubing

Operational checks – air sampling

PM_{10}	- air flow
	- undamaged filter
	- leakage test
Gas wash bottle	- volume of solution

Sample handling

Precipitation

Preservation ?

Storage: cold and dark if possible

Volume measurement at site ?

Contamination of equipment (funnel, volume gauge)? Could be checked with de-ionized water

General

Sample has to be properly sealed and labelled

Any digression should be noted in the sampling protocol that has to be filled in, signed, and returned to the laboratory together with the sample

Sample "flow chart"

sampling equipment preparation (site/laboratory)

⇓

sampling equipment distribution (laboratory → site)

⇓

sampling (site)

⇓

sample return (site → laboratory)

⇓

sample registration

⇓

sample storage

⇓

sample preparation for analysis

⇓

analytical equipment preparation

⇓

analysis

⇓

evaluation/calculation of results

⇓

results report

An optimal quality system

- is easy to use
- directs all activities
- comprises complete, but short, descriptions

Important parts of the quality system

- Quality assurance manual (description of the system)
- Choice of method (for sampling, pre-treatment, analysis)
- Training
- Laboratory environment and equipment
- Quality control routines (for temperature, weight, volume, water)
- Routines for sample administration (registring, labelling system, storage)
- Calibration routines, certified standards, intercomparisons, traceability
- Quality control of calculations and results
- Documentation (what has occured)

QUALITY ASSURANCE MANUAL

1. Introduction
   scope, application, references, definitions

2. Quality control policy

3. Quality assurance system
   formation, documentation, administration, updating

4. Organisation
   hierarchy, structure, positions, responsibility for quality control

5. Training
   credentials, training program, introduction of new personnel, training in quality control, laboratory safety

6. Routines for receiving samples
   sample handling, labelling, storage, control of results, report generation

QUALITY ASSURANCE MANUAL *continued*

7. Laboratory equipment
   suitability of lab area, equipment, safety routines, admission to lab, rooms for employees, temperature control

8. Sampling methods

9. Analytical methods
   methods directory, choosing methods, introduction of new methods

10. Analytical apparatus and material
    Inventory list, "out of service" labelling, service, repairs, calibration, reference standards

11. Verifying results
    Internal quality control, intercomparisons, computer routines, judgement of results

12. Reporting

QUALITY ASSURANCE MANUAL *continued*

13. Archiving
    archiving time, location

14. Purchasing

15. External resources and co-operation
    external resources, subcontractors, co-operation woth customer and with accreditation institute

16. Diagnostic routines and error checking

17. Evaluation and revision of quality assurance program

18. Responsibility for damages

CHOICE OF ANALYTICAL METHODS

In choosing an analytical method, one must take into account:

- sample concentration
- existence of interfering substances
- requirements for accuracy and precision
- time aspect
- available analytical instrumentation
- available reference standards

Analytical methods can be chosen from (listed in order of preference)

1. Method specified in national or international control program, or by general directive from state agency

2. International or national standard method

3. Modified standard method (as long as the modification has been thoroughly tested and verified)

4. Method published in international scientific publication

5. Method developed by the laboratory itself

IMPORTANT QUALITY CONTROL ROUTINES

It is important when looking at the following list to use common sense - what is the accuracy and precision required by the laboratory; ± 5%, ± 15% ?

- calibration of:
  - analytical balances
  - thermometers and temp controllers
    incl.refrigerators, freezers, cold rooms, ovens
  - volumetric glassware, autopipettes, dispensers
- control of:
  - water purity
  - fume hoods
  - laboratory temperature

IMPORTANT QUALITY CONTROL ROUTINES *continued*

- Reference solutions, certified standards
- Logbooks
- Labelling - *every sample has a unique code*
- Dish washing routines
- Control of data calculations

CALIBRATION

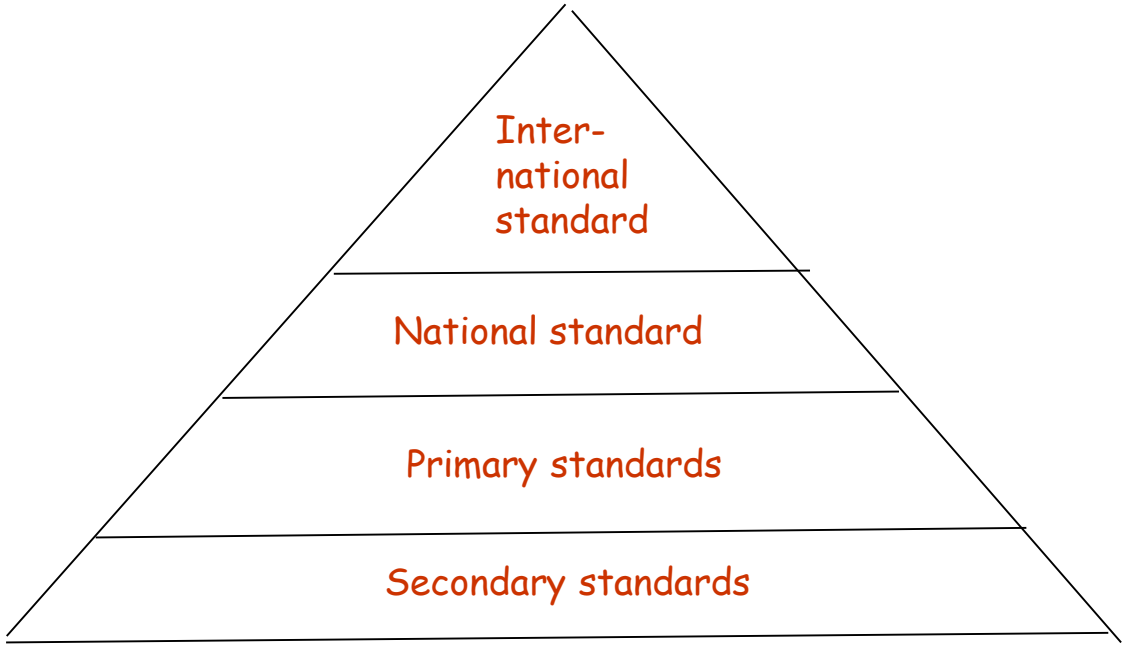
An operation that under specific conditions establishes the relation between;

1) the value given by an analytical instrument
2) the corresponding value of a certified standard

The result of a calibration is documented in a "certificate of calibration", which also includes the uncertainty in the measurements made using the instrument.

TRACEABILITY

Property of a measurement that means that it can be related to a suitable reference standard, normally national or international, by an unbroken chain of comparisons.



CERTIFIED STANDARD

A standard whose value (concentration) has been established by replicate analyses at a number of specially chosen laboratories specialized in the analysis of the standard in question.

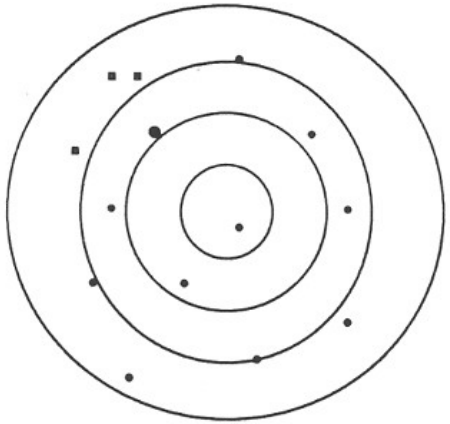
Only certified bodies (for example The National Institute of Standards, NIST, in the US or the Community Bureau of Reference, BCR, in Europe) are authorized to supervise the preparation, analysis, and distribution of certified standards.

INTERNAL QUALITY CONTROL

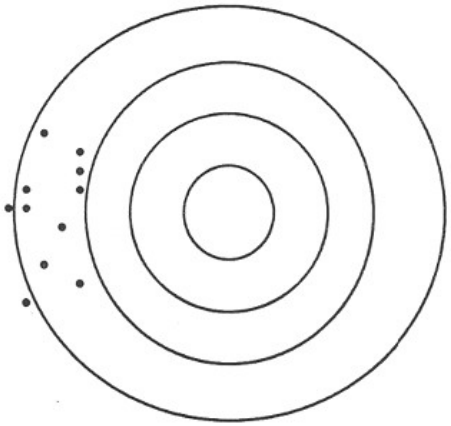
All chemical analyses are subject to errors that lead to results, deviating more or less from a "true value"

<u>random errors</u>
affect analytical precision

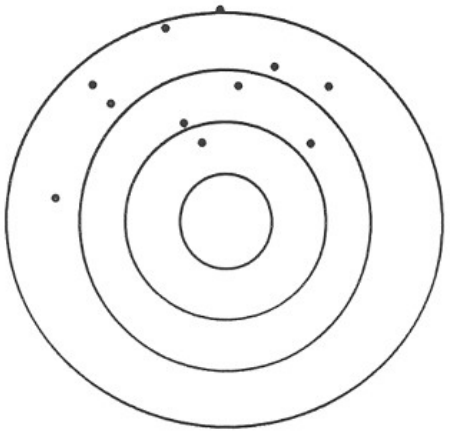
<u>systematic errors</u>
affect analytical accuracy



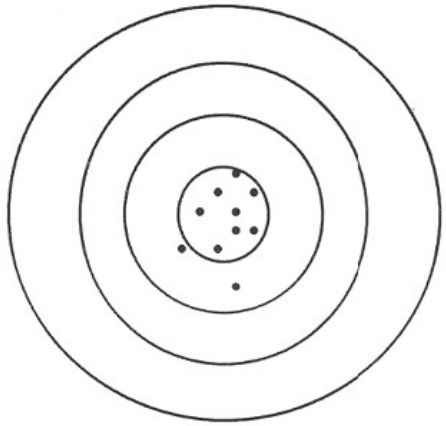
poor precision



poor accuracy



poor precision
and accuracy



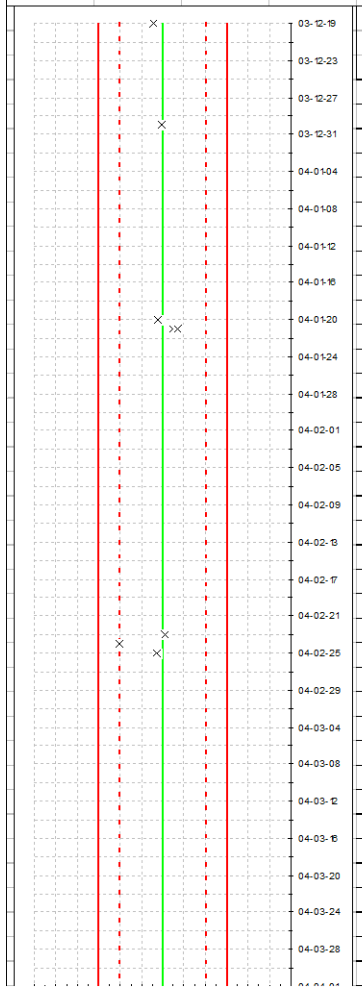
good precision
and accuracy

ANALYSIS OF PRECIPITATION SAMPLE

- start with pH, NH_4^+, conductivity (before dilution)
- check the conductivity of the de-ionized or distillled water
- use analysis quality of chemicals
- note dates when chemicals were received and first opened
- use ampoules (when possible) to prepare standard solutions
- use mass instead of volume for making dilutions
- check the analytical balance
- make duplicate analysis whenever possible
- always analyse a reference solution
- let the calculations be double checked by another person
- note all verifications in a diary

X-card nitrate medium

Reference standard:	F23		number of values	8
Method	A1		average (x):	2.9874
Parameter, conc.	NO3-N	3.000 mg/L	variance (s*2):	0.002452
			std. dev. (s):	0.04952
Alarm level (x±2s):	2.888	3.086	%CV:	1.66%
Action level (x±3s):	2.839	3.136	difference from ref.	0.421%



conc.	date	notes	sign.	
2.975	03-12-19	(1)		SH
2.998	03-12-30	(1)		SH
2.987	04-01-20	(1)		nn
3.031	04-01-21	(1)		nn
3.041	04-01-21	b		nn
3.006	04-02-23	(1)		nn
2.879	04-02-24	(1)		nn
2.982	04-02-25	(1)		nn
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		
		(1)		

Internal quality control routines X-CHART

Accuracy and precision in analysis of certified standard

single results plotted
about 20 points → mean value, std deviation
*2 * std deviation → alarm level*
*3 * std deviation → action level*

mean value < 5% of cert. standard
< 7 points in a row on same side of mean value
< 3 points in a row outside alarm level
no points outside action level

Internal quality control routines
R-CHART

precision in analysis of natural samples

duplicate analyses

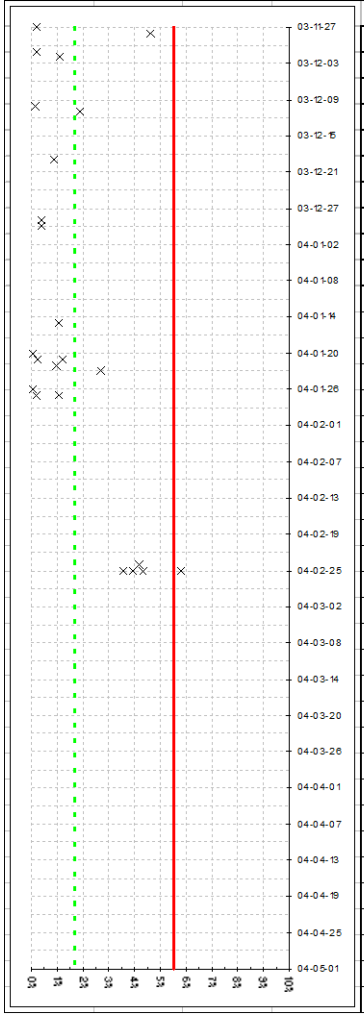
absolute % difference plotted

about 20 points → mean value (<5%)

*3.267 * mean value → action level*

R-card Method A1

Method:	A1	Detection limit mg/L	0.029
Parameter:	nitrate	Alarm level (R%):	1.69%
Number of values:	23	Action limit (3.267*R%):	5.53%



1:a	2:a	R%	date	notes	sign.	
3.509	3.503	0.17%	03-11-27			SH
2.458	2.574	4.61%	03-11-28			SH
1.897	1.901	0.21%	03-12-01			SH
0.806	0.815	1.11%	03-12-02			SH
4.890	4.896	0.12%	03-12-10			SH
0.218	0.214	1.85%	03-12-11			SH
0.808	0.815	0.86%	03-12-19	Below det. lim.		SH
0.811	0.808	0.37%	03-12-29			SH
2.484	2.493	0.36%	03-12-30			SH
0.962	0.972	1.03%	04-01-15			NN
3.696	3.695	0.03%	04-01-20			NN
1.770	1.766	0.23%	04-01-21			NN
3.777	3.823	1.21%	04-01-21	b		NN
0.418	0.414	0.96%	04-01-22			NN
0.770	0.791	2.69%	04-01-23			NN
3.259	3.260	0.03%	04-01-26			NN
2.413	2.408	0.21%	04-01-27			NN
0.386	0.382	1.04%	04-01-27	b		NN
3.352	3.495	4.18%	04-02-24	three new analysis		NN
2.418	2.515	3.93%	04-02-25			NN
2.451	2.540	3.57%	04-02-25			NN
3.325	3.472	4.33%	04-02-25			NN
0.183	0.194	5.84%	04-02-25	three new analysis		NN
1	1	1	DATE			
1	1	1	DATE			
1	1	1	DATE			
1	1	1	DATE			
1	1	1	DATE			
1	1	1	DATE			
1	1	1	DATE			
1	1	1	DATE			
1	1	1	DATE			
1	1	1	DATE			
1	1	1	DATE			
1	1	1	DATE			
1	1	1	DATE			
1	1	1	04-05-01			

CHECKING OF RESULTS

Precipitation

- calculate ion balance
- compare measured with calculated conductivity
- contamination ?

  high NH_4^+ and pH can indicate bird dropping contamination

Air samples

- Is PM_{10} reasonable?
- Are gas phase concentrations reasonable?

Bulk or wet-only?

Form (Wet B) No.3 — **Results of wet deposition analysis (EC, pH, R1,R2, Precipitations)**

Site Name: Horipur, Nurnagar Station, Shamnagar, Satkhira. — **Funnel diameter: 203mm (20.3cm)**

Name of Laboratory : — **Name of reporter: Mizan, Chemist, Malé Monitoring Station.**

Method code 1:Rain Gause 2:Calculation by sample amount 3: Other

Sample No	Sampling Period				EC mS/m	fig1	fig2	fig3	pH	fig1	fig2	fig3	R1	fig1	fig2	fig3	R2	fig1	fig2	fig3	Amount of Sample(g)	fig1	fig2	fig3	Amount of precipitation (mm)	fig1	fig2	fig3	Method code	fig1	fig2	fig3	Date of Analysis	Note
	Start		End																														
	Date	Time	Date	Time																													
1	30.9.5	9:00	1.10.5	9:00	-				-												-				-				1				-	No rain
2	1.10.5	9:00	2.10.5	9:00	-				-												-				-				1				-	No rain
3	2.10.5	9:00	3.10.5	9:00	0.0				6.297												100ml				2460ml				1				3.10.05	Rain water
4	3.10.5	9:00	4.10.5	9:00	0.0				5.449												100ml				550ml				1				4.10.05	Rain water
5	4.10.5	9:00	5.10.5	9:00	0.0				6.729												100ml				730ml				1				5.10.05	Rain water
6	5.10.5	9:00	6.10.5	9:00	-				-												-				-				1				-	No rain
7	6.10.5	9:00	7.10.5	9:00	-				-												-				-				1				-	No rain
8	7.10.5	9:00	8.10.5	9:00	-				-												-				-				1				-	No rain
9	8.10.5	9:00	9.10.5	9:00	-				-												-				-				1				-	No rain
10	9.10.5	9:00	10.10.5	9:00	-				-												-				-				1				-	No rain
11	10.10.5	9:00	11.10.5	9:00	-				-												-				-				1				-	No rain
12	11.10.5	9:00	12.10.5	9:00	-				-												-				-				1				-	No rain
13	12.10.5	9:00	13.10.5	9:00	-				-												-				-				1				-	No rain
14	13.10.5	9:00	14.10.5	9:00	-				-												-				-				1				-	No rain
15	14.10.5	9:00	15.10.5	9:00	-				-												-				-				1				-	No rain
16	15.10.5	9:00	16.10.5	9:00	-				-												-				-				1				-	No rain
17	16.10.5	9:00	17.10.5	9:00	-				-												-				-				1				-	No rain
18	17.10.5	9:00	18.10.5	9:00	0.0				5.273												100ml				520ml				1				18.10.05	Rain water
19	18.10.5	9:00	19.10.5	9:00	0.0				5.927												100ml				1200ml				1				19.10.05	Rain water
20	19.10.5	9:00	20.10.5	9:00	0.0				5.369												100ml				1530ml				1				20.10.05	Rain water
21	20.10.5	9:00	21.10.5	9:00	0.0				6.301												100ml				2160ml				1				21.10.05	Rain water
22	21.10.5	9:00	22.10.5	9:00	-				-												-				-				1				-	No rain
23	22.10.5	9:00	23.10.5	9:00	0.0				7.227												100ml				750ml				1				23.10.05	Rain water
24	23.10.5	9:00	24.10.5	9:00	0.0				5.976												100ml				730ml				1				24.10.05	Rain water
25	24.10.5	9:00	25.10.5	9:00	0.0				5.568												100ml				1210ml				1				25.10.05	Rain water
26	25.10.5	9:00	26.10.5	9:00	-				-												-				-				1				-	No rain
27	26.10.5	9:00	27.10.5	9:00	-				-												-				-				1				-	No rain
28	27.10.5	9:00	28.10.5	9:00	-				-												-				-				1				-	No rain
29	28.10.5	9:00	29.10.5	9:00	-				-												-				-				1				-	No rain
30	29.10.5	9:00	30.10.5	9:00	-				-												-				-				1				-	No rain
31	30.10.5	9:00	31.10.5	9:00	-				-												-				-				1				-	No rain

EC is not measured, sometimes -, sometimes 0!

Amount should be expressed in mm! Automatic formulas could be there in the template.

DATA REPORTING FOR BULK COLLECTOR

Form Wet B No.3 Results of wet deposition analysis(EC, pH, R1 ,R2, Precipitation)

Site name : Bhur, Gelephu Bhutan, Bhutan

Name of Laboratory :

Sample No.	Sampling period				EC	flg1	flg2	flg3	pH	flg1	flg2	flg3	R1	flg1	flg2	flg3	R2	flg1
	Start		End															
	Date	Time	Date	Time	mS/m													
	05-jul-03	11:30	06-jul-03	11:30	0.43				6.78									
	06-jul-03	10:30	07-jul-03	11:30	0.61				5.85									
	07-jul-03	10:30	08-jul-03	10:00	0.56				6.22									
	08-jul-03	10:30	09-jul-03	10:00	0.35				6.06									
	09-jul-03	10:30	10-jul-03	10:00	0.69				6.16									
	10-jul-03	10:30	11-jul-03	10:00	0.68				6.92									
	11-jul-03	10:30	12-jul-03	10:00	0.18				6.38									
	12-jul-03	10:30	13-jul-03	10:00	0.41				7.47									

pH in bulk collector lower than in wet-only

DATA REPORTING FOR WET ONLY COLLECTOR

Form Wet W No.3 Results of wet deposition analysis(EC, pH, R1 ,R2, Precipitation)

Site name : Bhur, Gelephu, Bhutan

Name of Laboratory :

Sample No.	Sampling period				EC	flg1	flg2	flg3	pH	flg1	flg2	flg3	R1	flg1	flg2	flg3	R2	flg1
	Start		End															
	Date	Time	Date	Time	mS/m													
	06-jul-03	10:30	07-jul-03	11:30	0.87				6.16									
	07-jul-03	10:30	08-jul-03	10:00	0.58				6.54									
	08-jul-03	10:30	09-jul-03	10:00	0.33				7.56									
	09-jul-03	10:30	10-jul-03	10:00	0.43				6.23									
	10-jul-03	10:30	11-jul-03	10:00	0.77				6.85									
	11-jul-03	10:30	12-jul-03	10:00	0.23				6.66									
	12-jul-03	10:30	13-jul-03	10:00	0.39				7.35									
	13-jul-03	10:30	14-jul-03	10:00	0				0									
	22-jul-03	10:30	23-jul-03	10:00	0.68				6.13									
	19-aug-03	10:30	20-aug-03	11:30	0.53				5.98									

Examples of long range transport

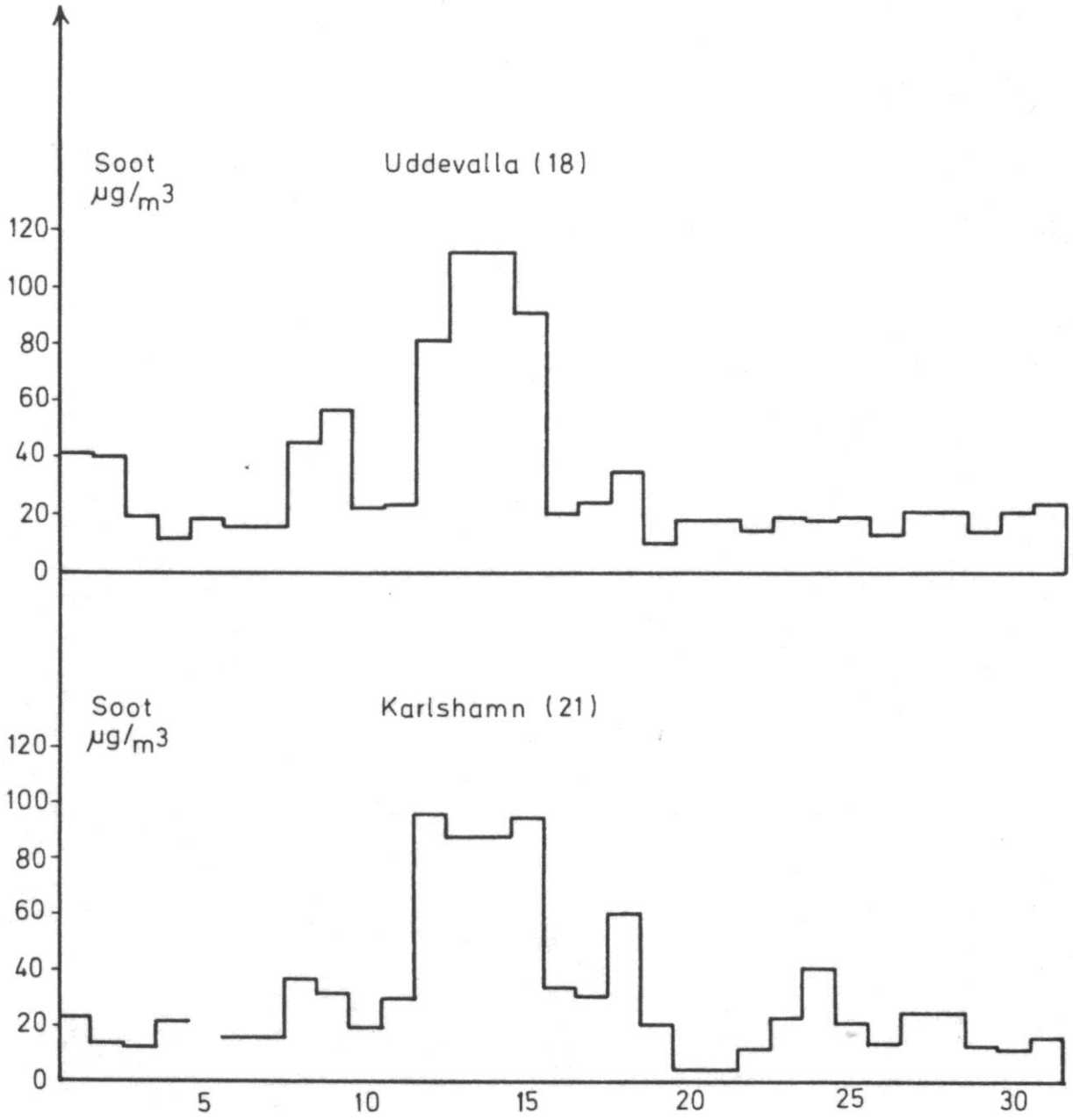


Fig. 2. Mean daily soot values in $\mu g/m^3$ for March 1965 from Uddevalla [18] (7 stations) and Karlshamn [21] (6 stations).

Examples of long range transport

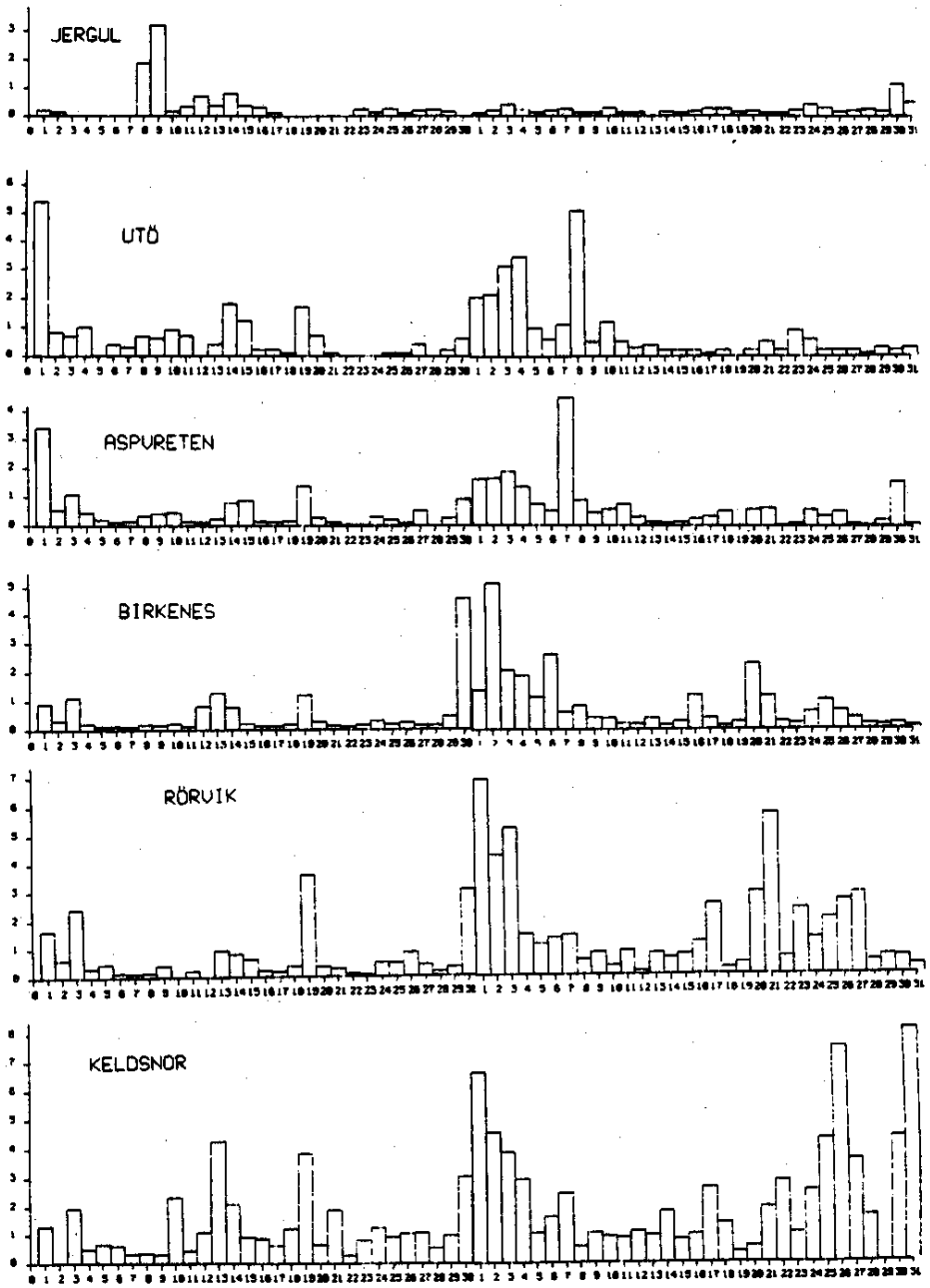


Figure 3. PARTICULATE SO_4 µg S/m^3 SEPTEMBER-OCTOBER 1985

Results of air concentration analysis (High Volume Sampler)

ıe:Institue of Agriculture and Animal Science (IAAS), Rampur, Chitwan.

f Laboratory:IAAS, Soil Laboratory

µg/m3

Sampling period														
Start		End		Manometer reading(m3/min)		Time totalizer reading(hrs)		Wt. of filter paper(gm)		Wt. of Dust Cup(gm)		Concentration (mg/m3)		
Date	Time	Date	Time	Initial	Final	Initial	Final	Initial	Final	Initial	Final	PM10	NRSPM	TSPM
2007-01-11	11:10	2007-01-12	11:10	1.24	1.19	5859.00	5882.28	2.7319	2.8296	17.2496	17.2764	58	16	74
2007-01-12	11:20	2007-01-13	11:20	1.24	1.18	5882.28	5903.43	2.7251	2.8408	17.3727	17.4029	75	20	95
2007-01-13	11:30	2007-01-14	11:30	1.23	1.18	5903.43	5923.74	2.7399	2.8744	17.3018	17.3313	92	20	112
2007-01-14	11:40	2007-01-15	11:40	1.22	1.16	5923.74	5947.14	2.7532	2.9875	17.3648	17.4090	140	26	166
2007-01-16	11:20	2007-01-17	11:20	1.24	1.17	5947.14	5970.07	2.7456	2.9660	17.4258	17.4953	133	42	175
2007-01-17	11:30	2007-01-18	11:30	1.23	1.16	5970.07	5990.70	2.7400	2.9128	17.3764	17.4035	117	18	135
2007-01-18	11:40	2007-01-19	11:40	1.23	1.16	5990.70	6013.11	2.7467	2.9483	17.2514	17.2831	125	20	145
2007-01-22	11:10	2007-01-23	11:10	1.24	1.19	6013.11	6063.16	2.7367	2.9375	17.4489	17.4683	119	12	131
2007-01-24	11:20	2007-01-25	11:20	1.24	1.17	6063.16	6057.31	2.7356	2.8862	17.3258	17.3405	98	10	108
2007-01-25	11:30	2007-01-26	11:30	1.22	1.15	6057.31	6080.27	2.7539	2.9156	17.4553	17.4725	99	11	110
2007-02-01														
2007-02-01														
2007-02-01														
2007-02-01														
2007-02-01														
2007-02-01														
2007-02-01														
2007-02-01														
2007-02-01														
2007-02-01														

Very high concentrations of PM10 for being a background site!
Is there any explanation for this?
The unit mg/m^3 should be µg/m^3 ?Still the particle concentrations are high.

QA/QC FOR DIFFUSIVE SAMPLERS

- Comparisons between diffusive samplers and active monitoring techniques
- Intercomparisons between different diffusive samplers

DATA CHECKING – Diffusive samplers

Station	Start time	Stop time	Temp C	SO_2 µg/m^3 STP *		NO_2 µg/m^3 STP *	O_3 µg/m^3 STP	*	Remarks
Nepal, Stn 1	2003-03-25 12:00	2003-06-07 12:00	20.0	0.6		6.4			
Nepal, Stn 1	2003-03-25 12:00	2003-06-07 12:00	20.0	0.9		6.7			
Nepal, Stn 1	2003-06-07 12:00	2003-07-31 12:00	20.0	0.3		2.8			
Nepal, Stn 1	2003-07-31 12:00	2003-09-15 12:00	20.0	0.2		1.5			
Nepal, Stn 1	2003-09-10 12:00	2003-10-12 12:00	20.0	<0.2	b	2.9			
Nepal, Stn 1	2003-10-12 12:00	2003-11-09 12:00	20.0	<0.2	b	9.8			
Nepal, Stn 1	2003-11-09 12:00	2003-12-09 12:00	20.0	<0.2	b	0.2			NO2 very low, unexposed??
Nepal, Stn 1	2003-12-09 12:00	2004-01-11 12:00	20.0	1.2		16.2			2 months exposure? Nov-Jan?
Nepal, Stn 1	2004-03-01 09:00	2004-04-01 08:45	20.0	2.5		9.1			
Nepal, Stn 1	2004-04-01 08:45	2004-05-01 08:45	20.0	1.1		7.5			

DATA CHECKING – Diffusive samplers

Station	Start time	Stop time	Temp C	SO_2 µg/m^3 STP *		NO_2 µg/m^3 STP *	O_3 µg/m^3 STP *	Remarks
Maldiv., Stn 4	2007-04-30 10:00	2007-05-31 10:00	31.0	<0.2	b	0.4	36	
Maldiv., Stn 4	2007-05-31 10:00	2007-06-30 10:00	31.0	0.3		0.3	33	
Maldiv., Stn 4	2007-06-30 10:00	2007-07-31 10:00	30.0	<0.2	b	0.4	36	
Maldiv., Stn 4	2007-07-31 10:00	2007-08-31 10:00	28.0	<0.2	b	0.5	27	
Maldiv., Stn 4	2007-08-31 10:00	2007-09-30 10:00	30.0	<0.2	b	0.3	61	O3:Sampler old (from 05-03). Results very uncertain.
Maldiv., Stn 4	2007-09-30 10:00	2007-10-31 10:00	30.0	<0.2	b	0.3	63	O3:Sampler old (from 2005-02). Results very uncertain. NO2:Holder broken, filter on land 1/10.
Maldiv., Stn 4	2007-10-31 10:00	2007-11-30 10:00	31.0	0.4		1.0	48	
Maldiv., Stn 4	2007-12-31 10:00	2008-01-31 10:00	29.0	0.8		1.1	50	

DATA CHECKING – Diffusive samplers