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Towards development of a deposition monitoring network for air pollution in Europe; Description of a deposition monitoring system

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The TNO Institute of Environmental Sciences, Energy Research and Process Innovation is engaged in research into environmental pollution arising from human activities, and to advise Government and Industry on appropriate measures for environmental management with due regard to the limits of nature's resilience.

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3 Description of the deposition system

The LIFE monitoring system consists of the following units:

1) Dry deposition and micro meteorological unit
   This includes a specific unit to measure concentrations of gases and aerosols in air required to estimate deposition according to the inference method and a software package for data acquisition and data reduction.

2) Wet deposition unit.

3) Cloud and fog unit.

The individual items are described separately in more detail in the sequel. The equipment used and its specifications is described in table 1. The concentration and flux of ozone (O_3) is measured as well. Measuring the ozone concentration allows correction of NO and NO_2 fluxes for chemical reactions between the gases in the air between the inlet and ground (Duyzer et al., 1995).

Table 1 *Overview of methods used in the LIFE project.*

component	Process	Method	Described in
SO_2, NO, NO_2, NH_3, O_3	Dry deposition	Gradient	3.1.1
HNO_3, HNO_2, HCL	Dry deposition	Inference	3.1.2
Cl, NO_3, SO_4, NH_4	Dry deposition	Inference	3.1.3
Na, K, Mg, Ca	Dry deposition	Inference	3.1.3
Cd, Pb, Cu, Zn, Ni, Cr	Dry deposition	Inference	3.1.3
SO_4, NO_3, NH_4, Cl	Wet deposition	Wet only collectors	3.2
Na, Ca, Mg, K	Wet deposition	Wet only collectors	3.2
Zn, Pb, Cd, Cu, Ni, Cr	Wet deposition	Wet only collectors	3.2
SO_4, NO_3, NH_4, Cl	Fog deposition	Cloud water collectors	3.3
Na, Ca, Mg, K	Fog deposition	Cloud water collectors	3.3
Zn, Pb, Cd, Cu, Ni, Cr	Fog deposition	Cloud water collectors	3.3

3.1 Dry deposition and micro meteorological unit

The dry deposition flux unit consists of the five functional units:

1) A micro meteorological unit necessary to calculate the turbulent diffusion coefficient k_z and several other parameters.
2) A gradient-valve unit which allows the gradient in the concentration of nitrogen oxides, sulphur dioxide and ozone to be determined.

3) An ammonia gradient unit which allows the gradient in the concentration of ammonia to be determined.
4) A datalogging system.
5) A software package developed to derive monthly averaged concentrations, fluxes etc.

3.1.1 The micro meteorological unit

The equipment contained in the micro meteorological package is listed in table 2a. It contains sensors to measure the magnitudes necessary to calculate the turbulent exchange coefficient such as the friction velocity $u*$ and the sensible heat flux H. A three dimensional sonic anemometer is used for this purpose. The friction velocity is derived from the surface stress; the covariance of the vertical component of the windspeed w and the horizontal component u. The sensible heatflux H is derived from the covariance between w and the air temperature T observed by the sonic :

$$u_* = \sqrt{(-\overline{uw})};\ H = \rho c_p \overline{wT}$$

Where ρ is air density an c_p is the specific heat. In addition to that there is a complete set of instruments to measure radiation : Photosynthetic Active Radiation (*PAR*), global radiation (Q_{glob}) and net radiation (Q_{net}). These magnitudes play an important role in the interpretation and generalization process. In addition to that the Bowen Ratio system provides additional information on water vapour fluxes. Air temperature and water vapour concentration are measured at two levels above the surface. In addition soil heat fluxes are measured. Combined with net radiation these quantities allow determination of the sensible heatflux and the latent heatflux (evaporation rate). From this information the stomatal resistance can be calculated.

3.1.2 The gradient unit

The gradient valve system

The gradient system consists of a set of electronic valves connecting one out of four sample lines to a central manifold. The sample line inlets are all mounted on different heights above the surface. When the measurement cycle is started one of the lines is connected to the manifold and thereby to one or more of the gas-monitors. After a period of time, sufficient to allow the monitor to adapt to new conditions, the signal of the monitor is logged. After a short period of logging the valves switch to another level an the procedure is started again. The time scale of this switching depends on the possibilities of the monitor. An optimum needs to be chosen for each monitor.

Summary

In January 1994 a joint project between four Dutch institutes KEMA, ECN, TNO, RIVM, a German institute; IfT (Leipzig) and a British institute; ITE (Edinburgh) was started under contract with the Commission of the European Communities (DG XI). In the project a system was developed, tested and applied to monitor deposition fluxes of acidifying gases and aerosols.

In addition to the monitoring set up a software package was developed which allows calculation of dry deposition fluxes from raw data and reduction of the data to monthly or annual averages.

Field tests of the various parts of the system were carried out by KEMA, TNO and ECN before complete monitoring sets were installed on three sites.

A complete year of monitoring was carried out on three sites by RIVM, ITE and IfT. One site was located on grassland in a polluted region near Leipzig, one over forest in a moderately polluted site in the Netherlands, a third site was operated over moorland in Scotland. The results of these measurements are reported elsewhere. Good quality results could be obtained with the complete system.

The investment in equipment to assemble a complete monitoring system would cost Dfl. 375 000 (or 170 000 ECU) approximately at the 1994 prize level. Operating costs (chemical analyses) would be from the order of Dfl. 125 000 (or 60 000 ECU) per year. Running the system would require six months of a person per year.

In this report the complete system is described. The description of the hardware is sufficient to allow other scientists to assemble; implement and run a similar system.

Contents

1 Introduction

In the framework of the LIFE initiative of the Commission of the European Communities (DGXI) a project was started by Dutch institutes RIVM[1], ECN[2], TNO and KEMA[3] together with two partners from other member states ITE[4] (Edinburgh) and IfT[5] (Leipzig) also participated in the project. Within the project which was called: **Towards development of a deposition monitoring network for air pollution in Europe** a system was developed and tested to monitor deposition fluxes of acidifying gases and aerosols. In this report the system is described. For more detail on the performance of the system and tests the reader is referred to individual papers and reports :

Duyzer, J.H., J.H. Weststrate, R. van Oss (1996).
Towards development of a deposition monitoring network for air pollution of Europe. (Contribution by TNO), *TNO report.*

Wyers, G.P., Otjes, R.P. and Slanina, J. (1993a).
A continuous-flow denuder for the measurement of ambient concentrations and surface exchange fluxes of ammonia. *Atmospheric Environment* 27A, 2085-2090.

F.G. Römer and A.A. Veldkamp.
Test results of a selected aerosol sampler to be applied in the CEC LIFE project.
KEMA-report 63944-KES/MLU 94-3231.

This report is part of a series of reports describing the results of the project i.e. three reports describing the results obtained at the three monitoring sites:

Towards development of a deposition monitoring network for air pollution of Europe. The Melpitz site in Germany results of measuring in 1995 (Results from IfT site).
Spindler, G. and A. Grüner (1996).

Dry deposition monitoring over the Speulder forest; I Project description and final results.
Erisman, J.W., G.P.J. Draaijers, M.G. Mennen, J.E.M. Hogenkamp, E. van Putten, W. Uiterwijk, E. Kemkers, H. Wiese, J.H. Duyzer, G.P. Wyers.

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[1] RIVM: National Institute of Public Health and the Environment, Bilthoven, the Netherlands

[2] ECN: Netherlands Energy Research Foundation, Petten, the Netherlands

[3] KEMA: Environmental Services, Arnhem, the Netherlands

[4] ITE: Institute of Terrestrial Ecology, Penicuik, United Kingdom

[5] IfT: Institut für Troposphären-forschung, Leipzig, Germany

RIVM report R 722080012, Bilthoven, The Netherlands

Measurements of pollutant concentration and deposition fluxes to moorland at Auchencourt Moss in Southern Scotland, 1995 Europe. (Results from ITE site).
Fowler, D, C. Flechard, E. Nemitz, C. Milford, K.J. Hargreaves, R. Storeton-West, M.A. Sutton.

A synthesis of all results is described in:
Towards development of a deposition monitoring network for air pollution of Europe.
Erisman, J.W., D. Fowler, G. Spindler, J.H. Duyzer, W. Ruigrok. RIVM report R 722108012, Bilthoven, The Netherlands

In this report the system is described in general terms only. However all relevant items required to build the system are listed in this report. Together with the global description this listing should be sufficient to enable scientists to assemble and run a monitoring station.

2 Theory

2.1 Introduction

The LIFE deposition monitoring system is meant to monitor the deposition flux of acidic species to ecosystems. Three mechanisms are known to contribute to deposition:

Wet deposition: The transport of species from the atmosphere to the earth in precipitation such as rain and snow.

Dry deposition: The transport of species from the atmosphere to the earth without any interference from precipitation.

Cloud and fog deposition: This mechanism is the deposition associated with cloud and fog.

The methods used in the LIFE project to determine fluxes by all three mechanisms will be discussed below.

2.2 Wet deposition

Gases and aerosols can be taken up in precipitation (Fowler *et al.,* 1991). Determining the wet input to a site is relatively straightforward. Precipitation is collected using specially designed collectors. These consists of bottles connected to a funnel. In order to avoid bias by dry deposition to the funnels the collectors are opened only during precipitation events. The amount of precipitation is determined. The concentration of ions in the volume is determined afterwards in the laboratory. The amount of precipitation and the concentration of ions allows calculation of the wet deposition flux.

2.3 Dry deposition

Several methods are available to measure dry deposition fluxes. For an overview the reader is referred to Hicks *et al.* (1980). In the LIFE project the flux of most compounds is determined by the micro meteorological gradient method.

The gradient method is one of the most important micro meteorological techniques used (Fowler and Duyzer, 1989). The flux is estimated from the vertical gradient of the pollutant concentration and a turbulent exchange coefficient k_z. The vertical concentration gradient $\partial c/\partial\delta z$ at height z and the vertical flux F_z of a compound are related according to the flux profile assumption:

$$F_z = -k_z \left(\frac{\partial c}{\partial z}\right)_z \quad \dots\dots \quad (1)$$

If the flux is constant with height F_z is equal to the surface flux F_0.

In practice the surface flux F_0 (at the roughness length z_o) of an inert compound can easily be derived from the integrated form of equation (7):

$$C_{z_2} - C_{z_1} = \frac{F_0}{ku}\left(\ln\left(\frac{z_2}{z_1}\right)\right) - \Psi_c\left(\frac{z_2}{L}\right) + \Psi_c\left(\frac{z_1}{L}\right) \quad \dots\dots \quad (2)$$

with $\Psi_C\ (z/L)$ the integrated flux-profile function Φ_C Φ_C is required to correct for the effect of atmospheric stability k is von Karman's constant (0.4), u_* the so called friction velocity and L is the Monin Obukhov length scale.
To generalize results from measurements a resistance model is often used. In it's simplest form the canopy resistance R_c is calculated from the flux as

$$R_c = \frac{1}{v_d} - R_a - R_b \quad \dots\dots \quad (3)$$

where R_a and R_b are the aerodynamic resistance and the boundary layer resistance calculated from the measurements. All parameters have their conventional meaning as described in Duyzer and Fowler (1994).
The deposition velocity v_d is calculated as : $-F/C_{ref}$. With C_{ref} the concentration of the gas at the reference height.

In order to derive the flux, the concentration gradient needs to be determined with high accuracy. The flux is then derived from measurements of the friction velocity u^* and a measurement of the sensible heat flux to correct for the effects of atmospheric stability. In this project the heat flux and the friction velocity are measured using a sonic anemometer.
The concentration gradient in the lowest meters of the boundary layer is very small. High accuracy monitors are therefore needed to determine the gradient. These are not available for all compounds. In this project the gradient method is only used for sulphur dioxide, ammonia and nitrogen oxides. These compounds however are representative for different gases.

For other gases, monitors to determine the gradient in a routine monitoring system are not available. For nitrous acid, nitric acid and hydrochloric acid and aerosol constituents therefore only the concentration in air is determined. The flux is then calculated from an estimate of the deposition velocity v_d (based upon measurements of the friction velocity etc.). For a more detailed description of the inference method as it is used in this project the reader is referred to Erisman *et al.,* (1996)

2.4 Cloud and fog deposition

To determine the input by occult deposition is rather complex (Fowler *et al.,* 1991). Firstly the occurrence of fog conditions needs to be detected. When fog is detected sampling of liquid cloud water is started. In this project fog water is collected by impaction on teflon strings. A certain water volume is collected. In the laboratory the concentration of several ions in this volume is determined. The amount of fog water and the concentration of the ions allows the input by fog to be determined.

In Figure 1 the system is displayed schematically. This system is applied for NO_x, O_3 and SO_2. NH_3 is measured differently using a system described below. It is important to note that in the proposed system the intake lines are flushed continuously. When the concentration of the gases at a given level is measured the lines are flushed at a faster rate.
This set up has the advantage that flushing of the lines before the actual measurements can take place can be limited since the air in the tubes is continuously in equilibrium with the ambient air at the level.

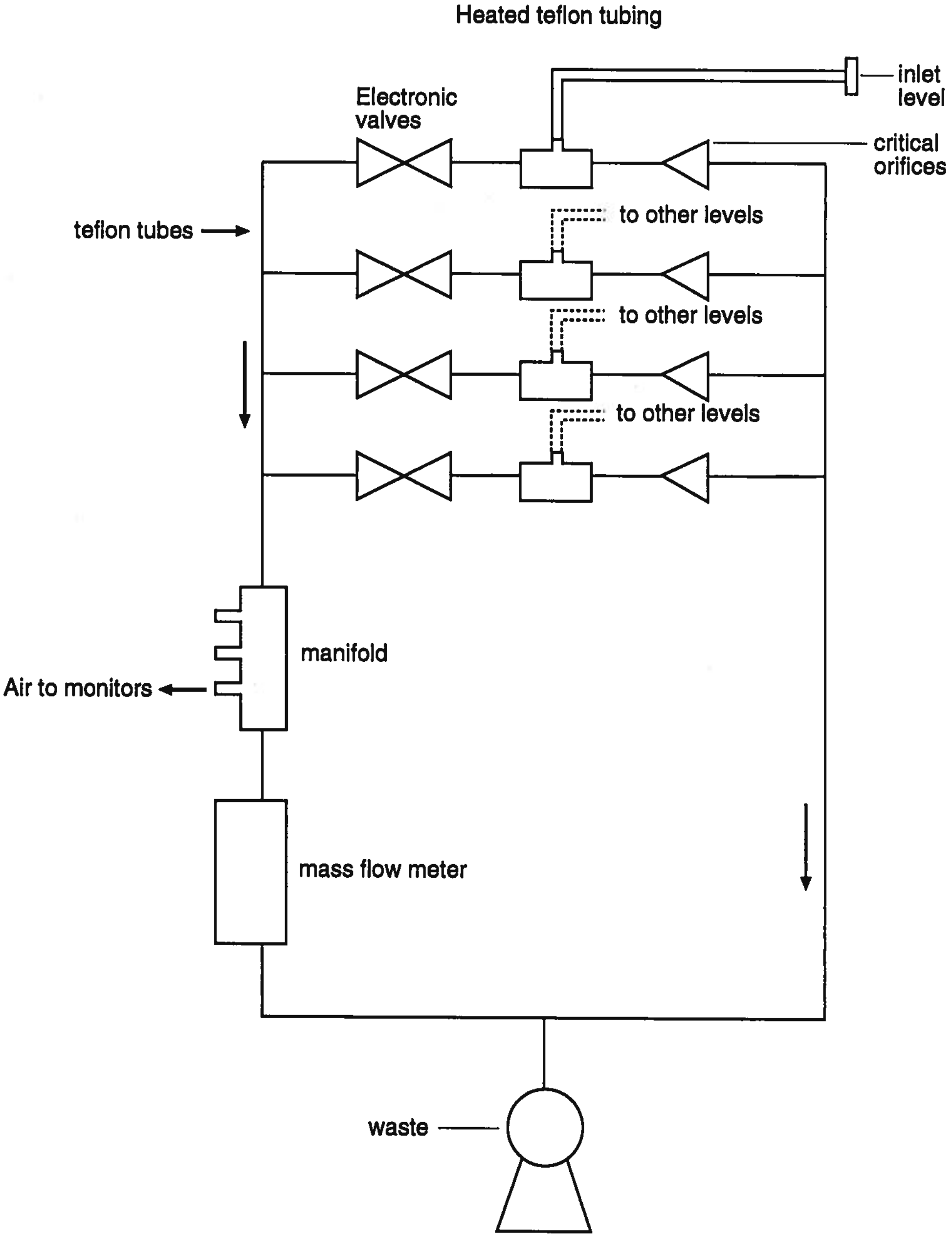


Figure 1 Schematic overview of the gradient system.

The inlets of the sample lines are located in the tower at for example 4, 2, 1, 0.5 m above ground. Usually heights are chosen at logarithmic equal distances. Sample lines should be of equal length and should be kept as short as possible. A residence time less than 5 seconds can usually be achieved. Monitors can draw air directly from the manifold. In this case only a NO_x monitor and an O_3 monitor was used. For SO_2 a separate system was used.
The teflon tubes are protected from contamination using PTFE inlet filters. The pressure in the tubing system is monitored continuously. This allows control of proper operation of the system and can be used to correct gradients if required.

The selection of filters for the inlet of the tubes depends of the local contamination level. In some areas the proposed filters may need to be replaced by filters with a larger pore size. Especially for SO_2 it is recommended to heat the intake lines in order to prevent condensation of water in the tubes. It is also advantageous to prevent the penetration of light through the tubes. This prevents unknown shifts in equilibria between for example NO, NO_2 and O_3. Corrections for these shifts can be made if it can be assumed that no light penetrates. If the light intensity in the tubes is not zero corrections are very uncertain.

NO_x and O_3

The NO_x concentration is measured using a monitor based on the chemiluminescent reaction between nitric oxide (NO) and ozone (O_3). In a reaction chamber ozone is added to the sample and chemiluminescence is registered by a photomultiplier. The concentration of NO is directly proportional to the light intensity. In a measuring cycle nitrogen dioxide in the sample is converted to NO using a Molybden converter. In the conversion process some other gases such as peroxyacetylnitrate (PAN) or methylnitrate may be converted as well (Grosjean and Harrison, 1985). The contribution of this effect is assumed to be small however. NO_2 is calculated as the difference between the concentration of NO_x and the concentration of NO. More specific convertors (based on photolysis of NO_2) are available at the moment. These instruments, however, are very expensive and less suited for monitoring purposes. In Duyzer et al. (1996) more detail is given on the performance of the NO_x monitor. This includes information on bias by artifacts. The monitor is sensitive to other gases such as nitric and nitrous acid and ammonia (0.025 ppb per ppb NH_3). The sensitivity for nitric and nitrous acid is more than 100%. This should usually not affect gradient measurements. Only in cases where the NH_3 concentration is high compared to the NO_x concentrations this could be a problem.
The detection limit of the monitor is approximately 0.04 ppb.
Ozone can be measured with any suitable device. The detection limit and accuracy of currently available monitors is good. Usually the response time of monitors based on the chemiluminescent reaction between O_3 and ethylene is quite low so the O_3 monitor will not slow down the measurement cycle of the NO_x monitor.

The disadvantage of such monitors is the use of ethylene. High concentrations of ethylene may interfere with ozone and may even have a negative effect on the plants at the site. A suitable solution for the exhaust ethylene therefore needs to be found.
A more extensive description of the NO_x system is given in Weststrate and Duyzer (1994) and Duyzer and Weststrate (1995).

SO_2

For sulphur dioxide (SO_2) a similar system was used. The SO_2 concentration is measured using the pulsed fluorescence technique. The sample air is exposed to a pulsed UV light source. SO_2 molecules are exited which leads to fluorescence. The pulsed fluorescence is registered using a photomultiplier. The light intensity is proportional to the SO_2 concentration in the sample. The detection limit of the monitor is 0.2 ppb.
In view of the slow response of the monitor in this project a second separate gradient system for SO_2 was used. This changes only some of the run parameters given in table 2. At the RIVM site a slightly different set up was used. A second SO_2 monitor drew air continuously from the highest intake level. This monitor serves as a reference monitor for the second monitor scanning the other levels. By this procedure the influence of changes of the SO_2 concentration in air during a scan of all heights can be minimised. In those periods that both monitors are drawing air from the highest level a 'internal' calibration can be performed.
Prior to each gradient determination the monitor is zeroed. After switching to one level the tubing system is flushed for two minutes after that period the signal of the monitor is registered for one minute. In this way a complete gradient can be scanned every 15 minutes. A more extensive description is given in Mennen *et al.*, 1996.

The NH_3 gradient unit

Ammonia concentrations are measured at three heights (34, 28 and 24 m) using three continuous flow denuders (Wyers *et al.*,; 1993a). For a more detailed description see appendix 1. NH_3 is collected in a $NaHSO_4$ solution, present on the walls of rotating annular denuders. Downstream the denuder, addition of NaOH solution causes the conversion of ammonium into gaseous ammonia which is separated from the solution by diffusion through a semi-permeable membrane. At the other side of the membrane, ammonia is dissolved in demineralised water and the ammonium concentration is detected conductrimetrically (Wyers *et al.*, 1993a). For the profile measurements the three denuders were connected to a single detector. The ammonium-containing solutions from the three denuders are analysed successively for two minutes each. The ten 6 minute measurement cycles are averaged to hourly values, to match the SO_2 and NO_2 deposition measurements. The system was tested in the laboratory by sampling air with the three denuders using a common air inlet. The detection limit of the instrument, defined as three times the standar deviation of zero air measurements (30 min averages), was found to be 10 ng NH_3 m^{-3}. The precision of the instrument is smaller than

2% with no systematic differences (Wyers *et al.*, 1993; Mennen *et al.*, 1993). Figure 2 gives a schematic overview of the NH_3 gradient system.

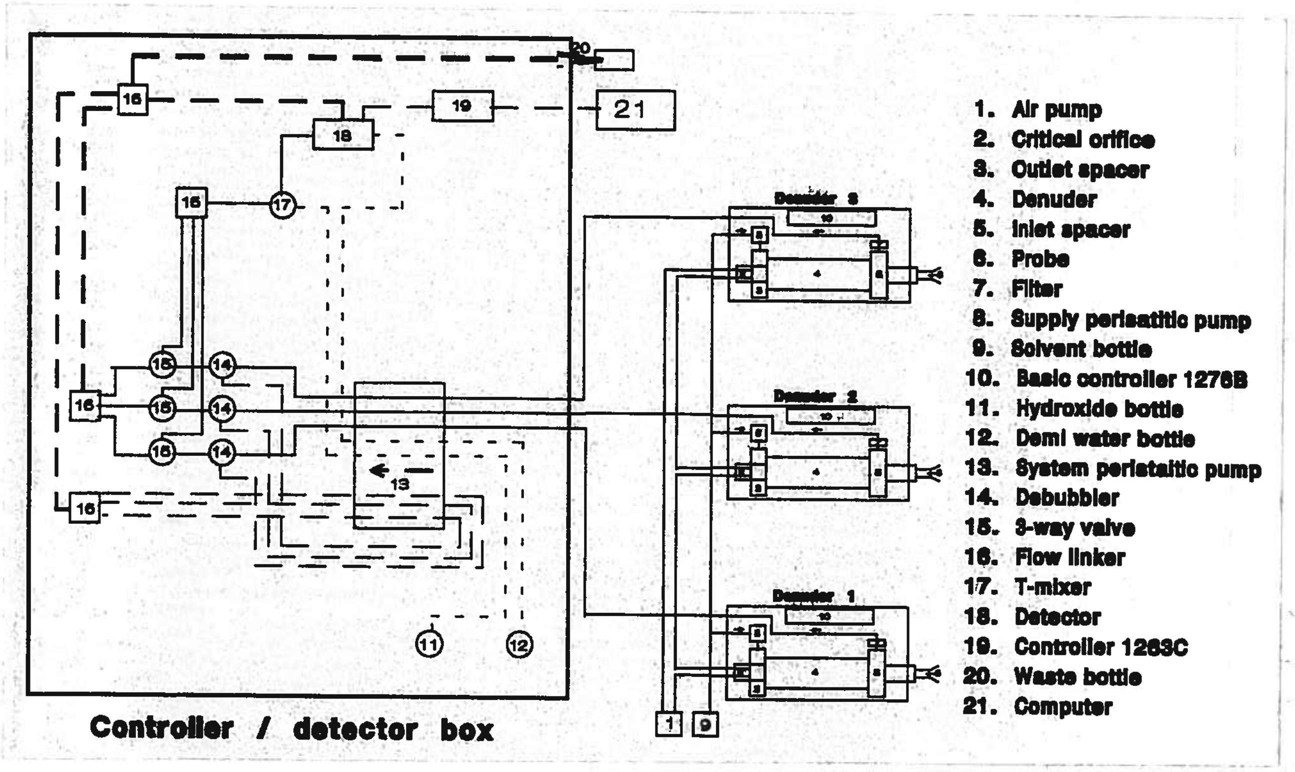


Figure 2 *The ammonia gradient system (see appendix 1 for more details).*

Table 2 provides an overview of the selected instrumentation. Table 2b lists the run parameters for the different gases.

Table 2a *Proposed set for monitoring the deposition of nitrogen oxides and sulphur dioxide.*

Meteorology	
windspeed x,y,u,w and Temperature	Solent Research anemometer
Radiation	Li-Cor LI200SZ Global-radiation
Gradient system 4 heights	
Valve System	4 Galtek 3 Way electronic valves PTFE 4 Tubes apr. 6 to 8 metres outer diameter 1/4". 4 Inlet filters PTFE (5 m pore size) Massflow Controller (Inacom)
Nitrogen oxides	Thermo Environmental Instruments 42S
Sulphur dioxide	Thermo Environmental Instruments 43W
Ammonia NH_3 Gradient system	ECN
Humidity/temperature	Vaisala HMP35AC
System Pressure	Brand DVR1
Data Acquisition	
Main system	Campbell 21XL Logger with interface and PC208 software
Extra features	SM 192 data storage with interface. 16 channels multiplexer
Housing and Masts	
Housing (NO_x, SO_2, O_3)	Zarges 22056 construction Airco (Seifert)
Mast Sonic Anemometer 6 metre	(low vegetation)
Mast Gradient (in sonic mast or:)	Clark QTM9M Construction for booms
Additional	
Campbell Bowen Ratio system	

Table 2b *Run parameters for the proposed set for NO_x and O_3.*

Sample frequency Eddy Correlation	2 Hz
Averaging Time	20 min.
Switching time valves	60 sec.
Flushing the intake tubes	48 sec.
Measuring heights (low vegetation example)	
Sonic Anemometer	5.5 m
Gradient Sample inlets and thermometers	4 m
	2 m
	1 m
	0.5 m
Flow trough tubes during measurement	3 l/min

Table 2c *Run parameters for the proposed set for SO_2.*

Averaging Time	30 min.
Switching time valves	180 sec.
Flushing the intake tubes	120 sec.
Measuring heights (forest example)	
Sonic Anemometer	36 m
Gradient Sample inlets and thermometers	36 m
	32 m
	28 m
	24 m
Flow trough tubes during measurement	3 l/min

3.1.3 Location of equipment

The mast on which the sonic anemometer is mounted should be located in such a way that flow distortion by large obstacles such as instrument housing, cabins etc. is limited. In the upwind fetch of the sonic mast a distance of several hundred meters is required. Downwind of the sonic mast a distance equal to two to three times the scale of these obstacles should be sufficient. The same rules apply to the location of the gradient mast with the intake lines. It is often of practical use to exclude one wind sector from the measurements and place bulky equipment in that area.

3.1.4 Data acquisition and control

The Bowen Ratio system works as a stand alone system with dedicated data-logging. All other data are logged using a Campbell 21X logger. A program was

designed and developed at TNO. It is described in more detail in Duyzer *et al.* (1996).
The Campbell logger is the heart of the system taking care of all data logging and control of valve switching. All magnitudes are logged with a frequency of 2Hz. Finally all results can be presented as hourly values. For NO_x and O_3 in a twenty minute period five independent measurements (48 seconds sampling) of the air concentration at every level are obtained. For SO_2 fifteen minute periods were used. For NH_3 ten 6 min measurements are averaged to hourly values.
Data is stored in the logger and needs to downloaded every 2 weeks. After this period data is transferred to a personal computer for further treatment. The logger stores only twenty minute average results in physical units including standard deviations. Covariances of the three components of the windspeed and air temperature are stored as well. A more detailed description of the sampling programme in the Campbell datalogger and the stored variables are given in Duyzer *et al.*, (1996). The system run by ITE used a 30 minute averaging time.
Data acquisition of the ammonia gradient unit is performed using a dedicated BASIC-programmable data logger.

3.1.5 Maintenance and quality control of the gradient system

The gradient valve system hardly needs any maintenance. The frequency by which filters need to be replaced depends on local conditions (pollution level, moisture etc.). In any case periodical checking at least every week is needed. The functioning of the valves can be checked by examining the pressure in the tubes at regular intervals.
Calibration and checking of the performance of the monitors depends on several parameters. The reader is referred to the manual supplied with each instrument.
The anemometers and radiation sensors need calibrating and checking as prescribed by the manufacturer.
Weekly maintenance of the NH_3 gradient system includes replacement of the solutions ($NaHSO_4$ solution, NaOH solution and demineralised water), measurement of the air flow and calibration of the detector.
For proper operation it is recommended to place all monitors in a thermostatted environment.
An example of a quality control procedure is given in appendix 2.

3.1.6 Software package for data treatment in the gradient system.

A software package was developed to calculate dry deposition fluxes from the measurements.
The raw data files downloaded from the logger contain several parameters in physical units. The file can be down loaded from the logger using a simple PC (286 or upwards compatible). The file contains information on the period the measurement was carried out and average results on windspeeds, covariances, average concentrations on the different heights etc. The raw files need to be rewritten in a

specific format before it can serve as input for a software package which calculates deposition parameters and statistical results.
Appendix 3 contains a description of the file structure (LIFE.FTN).

To treat the data in a structural way a Fortran program was developed at TNO which uses these files to:

1) Calculate fluxes from raw data.
   In addition secondary parameters such as the deposition velocity, aerodynamic, boundary layer, stomatal and canopy resistances are calculated
2) Detrend raw data.
   A simple procedure is used to correct for linear trends in gas concentrations.
3) Correct fluxes for instationarity.
   When the concentration of a gas changes during the measurement the flux calculated from the raw data may be biased. This procedure corrects for these artifacts (see also Duyzer et al., 1996)
4) Correct fluxes of NO, NO_2 and O_3 for conversions in the sample lines.
   The concentration of for example NO observed by the monitor may differ from the actual concentration at the inlet due to the reaction between NO and O_3 in which NO_2 is formed. This procedure corrects the observed concentrations of NO, NO_2 and O_3 to obtain the actual concentrations in air.
5) Calculate a model based estimate of canopy resistance R_c for each component.
   Based on observed parameters such radiation intensity etc. an estimation of the canopy resistance is made for each half hour period using two parameterisation schemes as outlined by Erisman *et al.*, (1994).
6) Calculate corrections for the influence of chemical reactions between NO, NO_2 and O_3.
   A correction procedure as outlined in Duyzer et al.(1995) is implemented in the program. This procedure allows calculation of the surface flux of NO, NO_2 and O_3 from measured concentration profiles. The calculated surface flux is not biased by chemical corrections between these gases and sunlight.

Figure 3 gives an overview of the dataflow in the LIFE deposition monitoring project.

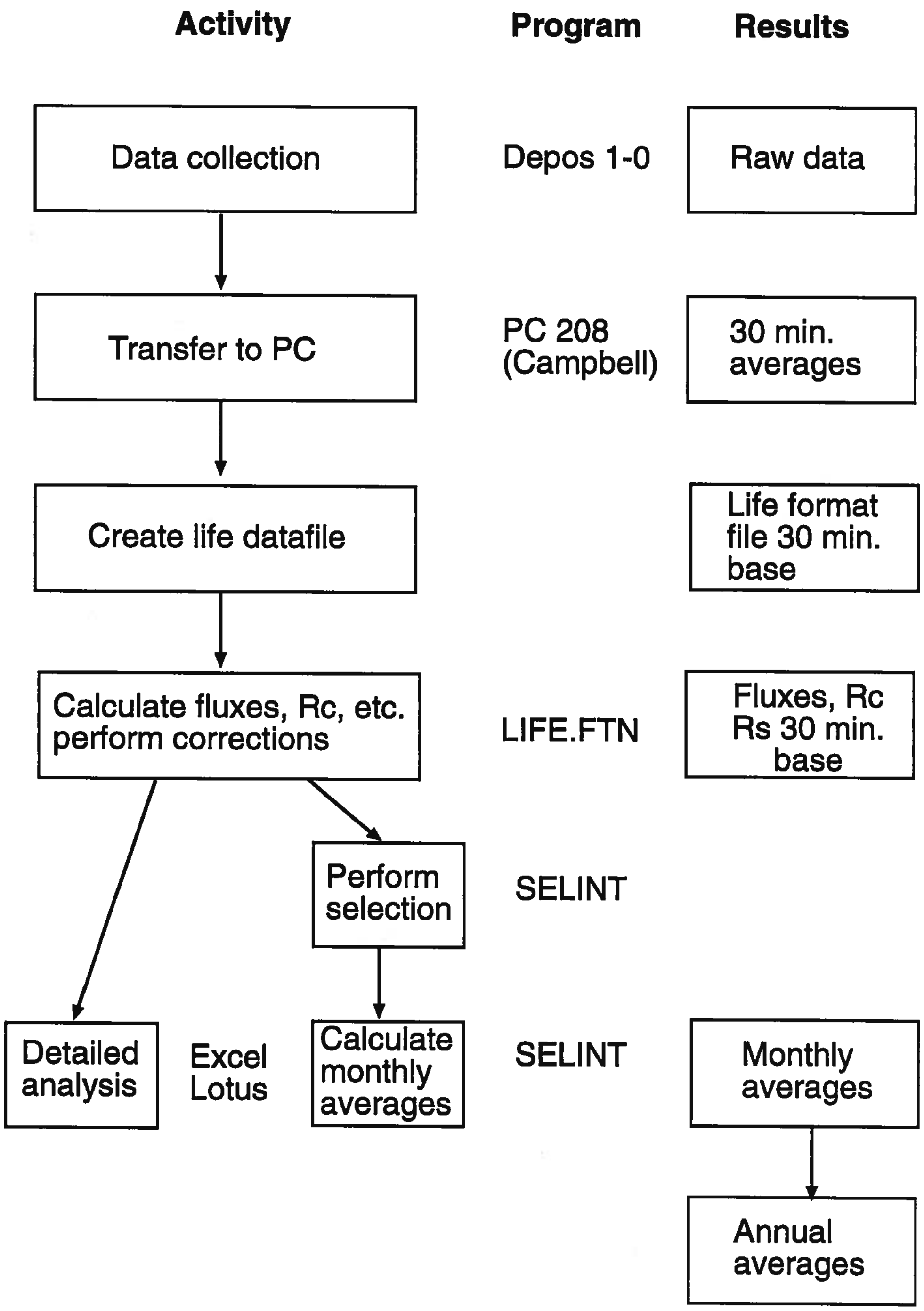


Figure 3 *Overview of dataflow in the LIFE project.*

The LIFE.FTN program can run on a PC or UNIX computer. The theory behind the correction methods and the effect of the various correction procedures and more detail about the programme are given in Duyzer *et al.* (1996).
Output of the program is a file in which each record corresponds to a half-hour (or twenty minute) measuring period. Each record contains the information given in table 3:

Table 3 *The uncertainty in the deposition fluxes estimated for the three sites in the LIFE program (after Erisman et al., 1996).*

Date and time,
Windspeed,
Air temperature,
Wind direction,
Bowenratio,
Sensible heat flux,
Latent heat flux,
Net radiation,
Dewpoint,
Soil temperature,
Soil heat flux,
Concentration at the second concentration level,
The square root of the variance of the concentration at this level,
The flux of the compound,
The error in the flux,
The deposition velocity,
The aerodynamic resistance,
The boundary layer resistance,
The canopy resistance (calculated from the measurements)
The canopy resistance (estimated from the model).

In principle one file is outputted by the program. When correction procedures are used two files can be delivered; one file contains the results without any corrections, the other contains the results with corrections. The difference between the two files depends on which corrections have been applied. Unavailable or faulty measurements are given a unique code. The output files can easily be incorporated in a spreadsheet file such as Excel or Lotus for further analysis.

In a second step a programme called SELINT can calculate average diurnal cycles of all of these parameters for each month. Selections can be made in order to reject measurements under certain conditions to obtain high accuracy deposition parameters. For example measurements during which the windspeed was below 1 m/s can be rejected. Important selection criteria could be

- Atmospheric stability
  The conditions for application of the method may be violated. Periods with extremely stable or unstable atmospheric conditions are excluded.
- Windspeed
  Periods with windspeeds less than, for example 1 m/s, can be excluded.
- Wind direction
  Specific wind sectors may be excluded because of limited fetch, obstacles etc.
- Detection limit
  When the gas concentration is below a certain threshold measurements of the deposition velocity may give unrealistic results. This criterion is quite dange-

rous to handle especially in cases where the deposition velocity depends on the air concentration. Measurements during which the concentration was low may easily be overlooked if this criterion is not handled with care.

With this package it is easy to obtain an overview of a month data in less then an hour. If the results are satisfactory they can be considered final.
In a more sophisticated procedure estimates can be made of the flux during the rejected periods by using the inference technique. In the rejected periods the canopy resistance may be estimated from measured quantities. Using the estimated canopy resistance the deposition velocity may be estimated and the flux can be calculated as:

$$Flux \;=\; v_d(estimated) * c_{measured}$$

Erisman *et al.* (1996) gives an overview of application of this method.

3.1.7 Concentration monitoring of acid gases for inference estimates

With the wet rotating denuder (Keuken et al., 1988) several atmospheric trace gases can be sampled automatically and simultaneously. In the current project this instrument is used for determination of hourly concentrations of HNO_3, HNO_2 and HCl. This denuder system is in many aspects similar to the continuous-flow denuder for ammonia described above. The main difference is that the denuder solution is not analyzed on-line, but collected in a fraction collector. The annular denuder tube has the same dimensions as the tube used in the continuous-flow denuder, see appendix 1. A small volume (10-18 mL) of a 1 mM K_2CO_3 solution containing 10 mg/L HCHO is present within the annular space. During sampling, air passes the denuder at a flow of 30 L/min, maintained by a critical orifice. Trace gases are collected in the absorption solution which is present as a thin layer on the walls of the annulus due to rotation of the denuder. After a sampling period of typically 40 min the air flow and rotation stop, the denuder is slightly tilted and the solution containing the absorbed trace gases is pumped out of the denuder to a fraction collector. Then the denuder is brought back to the horizontal position and filled with fresh absorption solution for a new sampling cycle. A multi-channel time switch controls the air pump, the rotation motor, the solution pump and the sample changer. In the current project this instrument is used to measure 40-minute-averaged concentrations of HNO_3, HNO_2 and HCl for one day (every Tuesday) per week during a full year. The samples are collected on the next day (Wednesday). The instrument is activated by a clock.

After sampling the samples are weighed and analyzed by ion chromatography for nitrate, nitrite and chloride. The time span between sampling and analysis should be kept as short as possible. The samples should be stored in a refrigerator until analysis. A detection limit of 10 μg/kg is necessary to obtain a detection limit in air of approximately 0.1 $\mu g/m^3$. The concentration of the gas is calculated from:

$$C = (c-b) * G * M / V$$

with:
C = gas concentration in $\mu g/m^3$
c = concentration in aqueous phase in $\mu mol/kg$
b = blanc in aqueous phase in $\mu mol/kg$
G = weight of sample solution in kg
M = molecular weight of the gas
V = Sampled air volume in m^3

NO in combination with NO_2 (a) and NO_2 in combination with SO_2 (b) may lead to artefact formation of nitrite in the absorption solution (Wyers et al., 1993b). Interference (a) results from the reaction $NO+NO_2+H_2O=2HNO_2$. Under ambient air conditions the NO concentration will be limiting this artefact formation. Laboratory experiments have shown that [artefact HNO_2]= 0.044*[NO] ($\mu g/m^3$). When necessary, the HNO_2 measurements should be corrected for this artefact. Significant uptake of NO_2 in the denuder can be expected in the presence of sulphite in the solution. This can be prevented by addition of formaldehyde (10 mg/l) to the absorption solution which converts sulphite to HMSA.

3.1.8 Aerosols

To determine the input of acid aerosols, base cations and heavy metals by dry deposition the LIFE monitoring station is equipped with a sampler for measuring the aerosol concentration in two size classes. The ambient concentrations of the following components are to be determined:

- acid aerosol: Cl, NO_3, SO_4 and NH_4
- base cations: Na, K, Mg and Ca
- heavy metals: Cd, Pb, Cu, Zn, Ni and Cr.

The instrument selected for the LIFE monitoring station is a so called Partisol Model 2000 Air sampler (Rupprecht & Patasnick Co., Inc.). The selection of this equipment was based on availability of modern control features for the sample flow, storage of information on preceding sampling periods and the robustness of the filter exchange mechanism. The Partisol sampler has been submitted for approval through a limited test programme. Main elements of this programme were reproducibility, intercomparison with a dichotomous sampler and a filter pack application to get insight in artifact effects. Results of these tests are given in:

- F.G. Römer and A.A. Veldkamp
  Test results of a selected aerosol sampler to be applied in the CEC LIFE project
  KEMA-report 63944-KES/MLU 94-3231.

Description of aerosol sampling equipment

The R&P Partisol Model 2000 Air sampler is a microprocessor-controlled sampler for measurements of total suspended matter, acid aerosols and other atmospheric constituents. The Partisol main unit is called "Hub" (H_1) and is equipped with one sampling head. It contains the microprocessor, sampling pump, mass flow control unit, sensors for ambient pressure and temperature and a filter exchange mechanism. A "Hub" can control up to three auxiliary units called "Satellites"(S_2, S_3 and S_4). The satellites only contain a sampling head and a filter exchange mechanism and are connected to the Hub by flow lines that are activated by solenoid valves inside the Hub.

Sampling flow must be appropriate for the inlet being used. The default value is 16.7 $l.min^{-1}$ (1 $m^3.h^{-1}$) but can be varied in a range from 0 up to 20 $l.min^{-1}$. Flow rates are expressed as mass-flow at defined standard pressure and temperature. Different sampling heads for particulate matter in size ranges <10 µm, < 2.5 µm and Total Suspended Particulate (referred to as PM-10, PM-2.5 and TSP) are available.

The LIFE monitoring station uses one hub and three satellites equipped with two PM-10 and two PM-2.5 sampling heads. The default flow rate of 16.7 $l.min^{-1}$ was used. In wind tunnel tests D_{50} values (50 % cutpoint of particle aerodynamic diameter distribution curve) of 9.8 µm at 2 km/h and 9.6 µm at 24 km/h were found at this flow rate (VanOsdell, 1991). A test report for the PM-2.5 is not yet available. The sampling head to be used at a flow rate of 16.7 l/min was developed according to a design (URG-2000 cyclone, University of Minnesota, Particle Technique Laboratory, Minneapolis, USA) that was tested at a flow rate of 10 l/min (ENI, 1994)
An extensive operating manual is shipped with each sampler.

Proposed sampling schedule

The Partisol 2000 Hub has a large number of program features to make dedicated sampling schedules. The preconditions of the aerosol sampling strategy in the LIFE project are to discriminate between two size fractions as well as between day and night time. A timing schedule that fully meets these preconditions and can yet be programmed and used with a minimum of effort was used. For details the reader is referred to Römer and Veldkamp (1994)

To simplify the handling of data of analytical results, all participants used the same sampling schedule and exactly the same start / end dates of weekly sampling periods. For the same reason the following set up of the Partisol equipment is proposed:

- Hub_1 PM-10 sampling head; day time
- Sat_2 PM-2.5 sampling head; day time
- Sat_3 PM-10 sampling head; night time
- Sat_4 PM-2.5 sampling head; night time.

Filter materials

Based upon blank values for metals and following recommendations from literature, the Fluoropore FS filter type 3 m (Millipore Corp.) is recommended for use in the monitoring equipment.

Extraction

After sampling, all filters were analyzed for both acid aerosols and heavy metals. Filters have to be divided into halves prior to extraction:

1 one half of the filter is used for analysis of aerosol sampled on Cl^-, NO_3^-, SO_4^{2-} and NH_4^+

2 the other half of the filter is used for analysis of the aerosol sampled on heavy metals.

Filters (or halves) were transferred into 25 ml polyethylene sealable sample vessels and 20 ml extraction liquid was added:

1 demineralized water for acid aerosols

2 0.1 M HNO_3 ultrapure for heavy metals

Extraction is forced using ultrasonic vibration during 15 minutes.

Several analytical methods can be used to determine the quantities on the filters. In this project all chemical analysis were carried out at ECN.

3.2 Wet deposition unit

The precipitation collectors used in this project are wet-only collectors designed by ECN (Slanina, 1983) and manufactured by Van Essen Instruments BV in Delft. With a wet-only sampler, contamination of the precipitation sample by dry deposition or bird droppings is prevented by means of a tight-fitting lid, which covers the collecting surface of the sampler in absence of precipitation. All parts of the collector in contact with the sample are made of polythene, selected for its inertness to trace elements, and in addition prewashed with 0.1 M HNO_3. The cross section of the funnel is 0.040 m^2. The sample is stored in a 5L polythene bottle inside the collector housing, protected from light, to minimize biological activity in the sample. The opening and closing of the lid is automatically controlled by a heated rain sensor. This sensor consists of chromium strips on a PVC layer and detects precipitation as a change in conductivity. It has a pyramidal shape and a large surface area of 80 cm^2. The sensor causes opening of the lid at a rain intensity of 0.1 mm/h or higher. The samples are collected every week and analyzed for SO_4, NO_3, NH_4, Cl, Na, Ca, Mg, K, Zn, Pb, Cd, Cu, Ni and Cr by ion chromatography, ICP-AES, AAS and graphite-furnace-AAS. In the laboratory the sample is split into two fractions. The fraction for heavy metal analysis is acidified with 100 µL concentrated HNO_3 per 50 mL sample. Maintenance is limited to weekly cleaning of funnel and rain sensor with double demineralized water.

3.3 Fog sampler

The fog sampler is made up of a fog detector, an active cloud water collector and a fractionating device. The water fractionating device and the control unit are built in a frost protected housing.

The fog detector is based on the light scattering effect that occurs on fog droplets. The detection level is defined (and calibrated) on a fog density corresponding to a visibility less than 200 meters which is a water content of 50-60 mg/m^3. If fog density exceeds the detection level for an uninterrupted period of 8 seconds the control unit starts up the cloud water collector and the fractionating device.

The construction of the cloud water collector has been designed by KEMA based on a description by Dauble et al. (1987). The sampler is constructed as a square shaped tube (dimensions 132•23•23 cm l•w•h) with an air inlet at the front bottom side and a ventilator on the rear side. Air is drawn through the tube (air speed 3.5 m/s) and fog droplets are impacted on teflon strings. A total number of 732 teflon strands are placed on three changeable holders. Due to gravity the impacted droplets are gathered, and further transported to the fractionating device by means of a peristaltic pump.

In the fractionating device the collected water is stored in glass tubes. The total volume of water per tube can be preset. The minimum amount required should allow a sufficient sample amount to perform all chemical analyses. The control unit of the whole system provides event signals for external use :

- when the fog detector is activated
- each time a filled tube is replaced by an empty one in the fractionating device.

The system runs without attention as long as empty tubes are present in the fractionating device. An operating manual is available with each sampler.

4 Concluding remarks

Sites

After the system is assembled a suitable site to operate the equipment location where the system will be operated needs to be selected. There are numerous arguments of completely different order to select or reject a specific site. Scientific specifications need to be considered first. For an introduction the reader is referred to for example Businger (1986) or Fowler and Duyzer (1989). A general rule is that the site must consist of several hundreds of meters of homogeneous, flat terrain in the direction of the most important wind sector. It is also important to be at a reasonable distance (several kilometres) from important sources.

Wind may have an impact on the amount of precipitation collected by precipitation collectors. It is relevant to place them in an situation with no specific wind flows. With respect to the fog collectors the location is extremely relevant. It is important to have some knowledge of the occurrence of fog at the site before a collector is installed. In Erisman *et al.*, (1996a), A measurement strategy for Europe using this equipment is proposed.

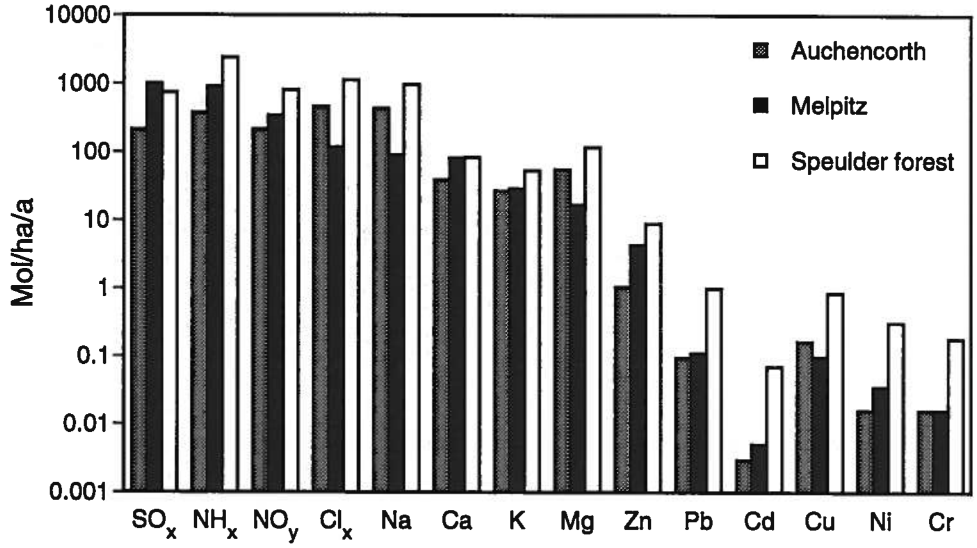
Performance

The deposition monitoring system described here has been used on three sites in Europe for nearly a year continuously. Although the pollution climates on the three sites in Scotland over moorland (clean site), the Netherlands over forest (moderately polluted site) and Germany over grassland (polluted site) differed strongly the systems operated with great success. Annual fluxes could be derived with good reliability for SO_2, NH_3 and O_3. For NO_x the results were not clear. Chemical reactions between NO, NO_2 and O_3 may have caused the unexpected results obtained for NO and NO_2 at the site in Scotland. NO deposition and NO_2 emission was observed in many conditions. However the correction procedures did not change the results considerably. This means that the results cannot be explained with current knowledge.

Wet deposition fluxes could be derived with great accuracy for acid species, base cations and heavy metals.

The low frequency of fog events at most sites makes reevaluation of the set up for fog necessary.

Figure 4 (after Erisman *et al.*, 1996) gives an example of the results from the LIFE sites for 1995. The difference in the deposition fluxes observed on the three sites is large, sometimes up to a factor of 10. Ammonia dominates the flux at Speulderbos and Auchenchorth whereas Sulphur dioxides dominate flux at Melpitz.



Figuur 4 *Deposition of acidifying species on Auchenchorth, Melpitz and Speulderforest (after Erisman at al., 1996)*

Table 4 displays the uncertainty estimated in the obtained deposition estimates. The major sources of uncertainty are also listed. As can be seen in this table large uncertainties are still present for NO_X and aerosols. It is important to note that these numbers are estimates and sometimes "educated guesses" only.

A more comprehensive overview of the results obtained with the monitoring system is given in Erisman *et al.*(1996a).

Costs

The total investment in durable equipment for one site is Hfl. 375 000 (or approximately 170 000 ECUs). These prizes were valid in 1994 in the Netherlands. The manpower required to run a station is estimated at 0.5 manyear per year. Running costs are dominated by chemical analysis and amount to approximately Hfl. 125 000 (60 000 ECU) per year. Analysis of heavy metals is dominating these costs.

Table 4 *The uncertainty in the deposition fluxes estimate for the three sites in the LIFE program (after Erisman et al., 1996).*

	Auchencorth Moss	Melpitz	Speulder forest	Major source of error
1-Dry deposition Trace gases				
SO_2	30	50	40	
NH_3	30	40	30	NH_3 concentration
O_3	20	30	–	Air chemistry ?
NO	80	60	50	NO concentration
NO_2	50	50	50	Air chemistry
HNO_3	50	30	40	HNO_3 concentration
HNO_2	90	50	40	HNO_2 concentration
HCl	90	40	40	HCl concentration
1-Dry deposition Aerosols				
SO_4-S, NO_3-N	90	40	40	Vd formulation
NH_4-N	90	40	40	Vd formulation
Cl, K, Mg, Ca, Na	90	40	40	Vd formulation
Pb, Cu, Zn	90	40	50	Vd formulation
Ni, Cd, Cr	90	45	50	low concentrations
2-Wet deposition Ions				
SO_4-S, NO_3-N	10-20	10-20	15-20	Rain collection efficiency
NH_4-N	10-20	10-20	25	Rain collection efficiency
Cl, K, Mg, Ca, Na	10-20	10-20	25	Rain collection efficiency
Pb, Cu, Zn	10-20	10-20	30	Rain collection efficiency
Ni, Cd, Cr	10-20	10-20	30	low concentrations

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Authentication

Name and address of the sponsor

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Names and functions of the contributing personnel

Dr J.H. Duyzer — Project leader

Names of establishments to which parts of this research were sub-contracted

–

Period in which the research took place

January 1994 – April 1997

Signatures

Dr J.H. Duyzer
Project leader
Date: 16/4/96

Approved by

Ir H.P. Baars
Head of Department Environmental Quality
Date: 16/4/96

Appendix 1 The Ammonia gradient system

The vertical concentration gradient of ammonia is measured with continuous-flow denuders. A continuous-flow denuder (see Wyers et al., 1993a for more detail) is an annular denuder for sampling of atmospheric ammonia, connected to an in-line ammonium detector (Figure A1).

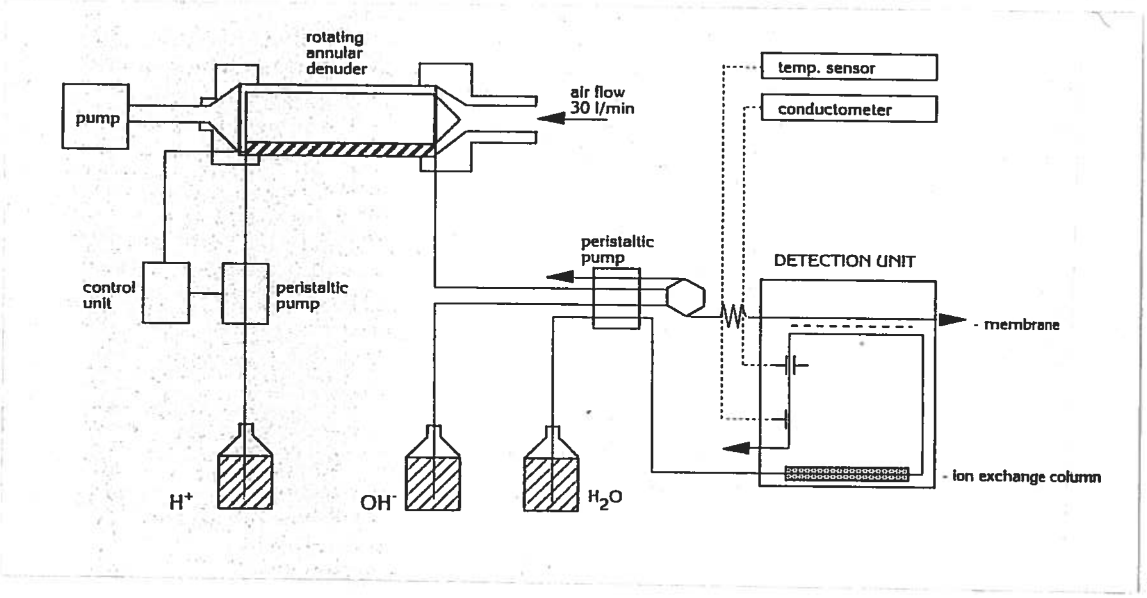

Figure A1 Schematic diagram of the continuous-flow denuder.

The annular denuder consists of two concentric glass tubes with a length of 30 cm. The inner tube has an outer diameter of 42 mm and the outer tube has an inner diameter of 45 mm, leaving an annular space between the tubes of 1.5 mm. At the recommended air flow of 30 L/min, maintained by a critical orifice, the flow inside the annular denuder is laminar. A small volume (9 mL) of a 3.6 mM $NaHSO_4$ absorption solution is present within this annular space. During sampling the denuder is rotated around its axis. This rotation causes the absorption solution to form an aqueous layer on the surfaces of the annular space, in which ammonia from the sample air is collected. The absorption solution is continuously pumped into and out of the denuder by two peristaltic pumps, in counterflow with the sampled air. The resistance of the solution film inside the denuder is measured and used to adjust the flow rate of solution into the denuder in order to maintain a constant volume of solution in the annular space. The solution is pumped out of the denuder at a fixed rate of 1.5 mL/min. Downstream of the denuder a 0.5 M NaOH solution containing 60 ppb NH_4^+ is merged with the absorption solution in a mixing chamber/debubbler, which results in the formation of gaseous ammonia. The solution then passes a semi-permeable membrane. Approximately 30% of the ammonia permeates the membrane and is dissolved in a stream of double-demineralized water, that has received additional purification on an ion exchange column. The ammonium concentration in the water stream is determined conductometrically. The temperature of the stream is measured by a thermistor and used to correct the analysis for temperature effects. The detector is calibrated with solutions containing 50 and 500 µg/l NH_4^+ and a blank solution.

For measurement of vertical concentration gradients of ammonia, three continuous-flow denuders placed at different heights are connected to a common detector (Figure 3). A peristaltic pump continuously leads the solutions from each of the three denuders to a three-way valve. Every two minutes one of the flows at the three-way valves is led to the detection system while its flow rate is measured; the two other flows are led to the waste. At the detector the conductivity is measured for 1 min, starting after a 1-min pause to avoid memory effects. Thus, the analysis of the effluents of the three denuders will be completed in 6 min. The precision of the measurements is 1-2% for 30-min averages; the bias between the three denuders is below 1%. The detection limit is 10 ng NH_3/m^3.

Figure A2 gives a schematic overview of the denuder used to collect samples for determination of gases such as HNO, HNO_2 and HCl.

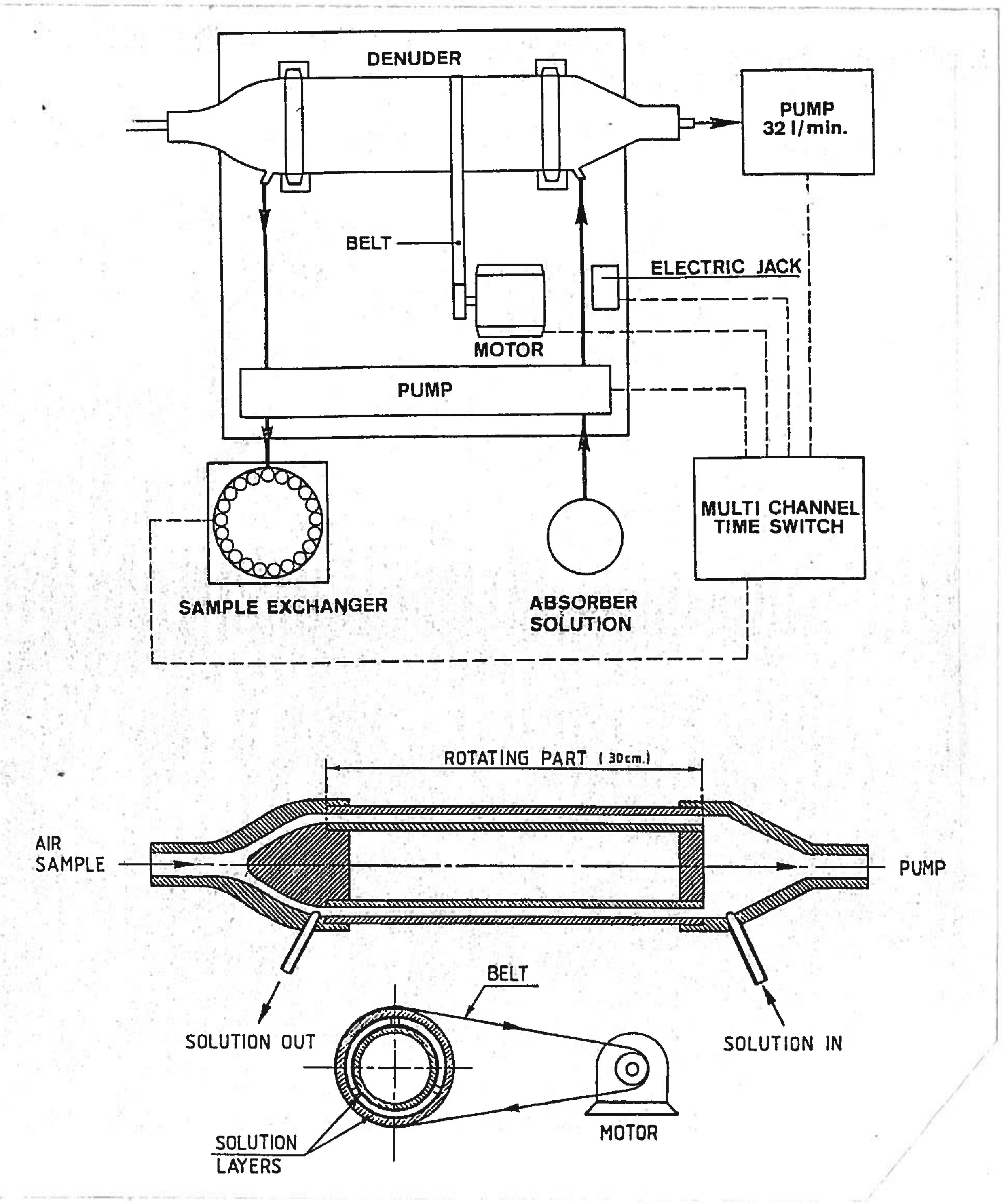

Figure A2 Schematic diagram of the wet rotating denuder

Appendix 2 Quality Control procedures

Here the protocol for the LIFE system is listed.

Measurement

wet-only sampler : one week average
- wet deposition : SO_4, NO_3, NH_4, Cl, Na, Ca, Mg, K, Zn, Pb, Cd, Cu, Cu, Ni, Cr

string collector : sequential samples combined to one pooled sample for each event, dependent on occurence and droplet size
- fog/cloud deposition : SO_4, NO_3, NH_4, Cl, Na, Ca, Mg, K, Zn, Pb, Cd, Cu, Ni, Cr

gradient systems : 30 min averages
- SO_2
- NH_3
- NOy NO, NO_2, (HNO_3,HNO_2, PAN, ..?)

aerosol sampling system : day and night weekly averages, diameter classes: < 10μ and < 2.5 μm, and blank filter
- aerosol SO_4, NO_3, NH_4, Cl, Na, Mg, K, Zn, Pb, Cd, Cu, Ni, Cr

rotating wet denuder : one hour averages during one day a week. To suppress the costs of analysis, and/or to detect very low concentrations, every two sequential samples may be combined to two-hour samples, yielding a total of twelve samples and one blank per week
- HNO_3, HNO_2, HCl

meteorological equipment : 30 min averages
- u_*, H_0, u, T, Rn, dd, rh

Sampling heights:

	low vegetation	Speulder forest
NH_3	1, 2, 4 m	24, 28, 34 m
SO_2	0.5, 1, (2), 4 m	24, 28, 32, 36 m
NOy	0.5, 1, 2, 4 m	14, 28, 32, 36 m
HNO_2, HNO_3, HCl	2 m	28 m
aerosol	2 m	28 m
fog	2 m	28 m
sonic	4 m	36.5 m
bowen ratio	1,4 m	28,36 m

Measuring protocols

wet deposition : one week
sampling time : see manual
storage of samples : in the dark at 4°. Acid has to be added to one half of the sample for heavy metal analysis[1]
collection of samples : Wednesday
components : H^+ and conductivity in the field; in the lab: SO_4, NO_3, NH_4, Cl, Na, Ca, Mg, K by the institutes themselves
Zn, Pb, Cd, Cu, Ni, Cr; sent to ECN every week[1]

- **fog/cloud deposition**

sampling time : one week sequential sampling during events (maximum)
cleaning : every week with demineralized water; strings; sampling tubes and optical fog detector, see also the manual
storage of samples : in the dark at 4°
collection of samples : Wednesday
components : H^+ and conductivity in the field; in the lab: SO_4, NO_3, NO_2^-, NH_4, Cl, Na, Ca, Mg, K by the institutes themselves
Zn, Pb, Cd, Cu, Ni, Cr; send to ECN every week[1]

- **SO_2**

sampling time : 30 min
maintenance : every week: replacement of filters; inspection of tubes; valves, etc calibration of SO_2 monitors (see manuals)
data collection : once a week: Wednesday

- **NH_3**

sampling time : 6 min. averaged over 30 min.
maintenance : see manual
data collection : once week: Wednesday

- **NOy**

sampling time : 30 min.
maintenance : every week: replacement of filters; inspection of tubes; valves, etc. calibration of NO_x monitors (see manuals)
data collection : once a week: Wednesday

---

[1] for heavy metal analysis add 100 µl concentrated HNO_3 to 50 ml sample. Minimum sample required is **2 ml**, if sample is less than 2 ml, dilute with demineralized water

• aerosol
sampling time : one week: as daily and nightly averages
cleaning : see manual
storage of samples : the filters will be cut in two halves and stored in dry light-tight botles at 4°. Filters for heavy metal analyses have to be shipped under dry conditions in bottles to ECN
collection of samples : Wednesday; installing new filters
components : SO_4, NO_3, NH_4, Cl, Na, Ca, Mg, K by the institutes themselves
Zn, Pb, Cd, Cu, Ni, Cr; send to ECN every week[1]

• HNO_3, HNO_2, HCl
sampling time : one day in the week as one or two hour averages
cleaning : see manual
storage of samples : in the dark at 4°
collection of samples : sampling on Tuesday, collection on Wednesday
components : SO_4, NO_3, NO_2^-, Cl by the institutes themselves

• meteorology
sampling time : recorded as 30 min. averages
maintenance : see manuals
data collection : on a week: on Wednesday

Golden (ECN) rule:
'small samples in small storage bottles!'

As an example of a quality control procedure the procedure used for the IfT site in Leipzig is listed.

---

[1] for heavy metal analysis add 100 µl concentrated HNO_3 to 50 ml sample. Minimum sample required is **2 ml,** if sampls is less than 2 ml, dilute with demi-water

Quality control procedures

During the test measurments (end of 1994) and the year of measurements (1995) different strategies for the maintenance and calibration have been developed for the used equipment. The measuring place in Melpitz was visited twice a week. In the following text the maintenance and calibration are described:

1 Analyzers for chemical trace gases

NO_x-Analyzer
producer : Thermo Environmental Instruments Incorporation
type : Model 42 s
principle : Chemoluminescence
range : NO 0 to 50 ppb
NO_2 0 to 50 ppb
NO_x 0 to 50 ppb
time of integration : 40 s
detection limit : 0.2 ppb
calibration gas : 50.7 ppb NO in nitrogen producer : Messer Griessheim
zero air : adsorption producer : Zander
procedure : Gas-phase-titration type : Sycos-GPT

This Analyzer is extremely sensitive for inconstances in the electrical power supply. Every week the analyzer was checked by integrated NO-simulation function.

SO_2-Analyzer (2 Analyzers)
producer : Thermo Environmental Instruments Incorporation
type : Model 43 s
principle : UV-Luminescence
range : 0 0 to 50 ppb
time of integration : 10 s
detection limit : 0.1 ppb
calibration gas : 10.4 ppb SO_2 in nitrogen producer : Messer Griessheim
gas mixing : with zero air by mass flow controllers in a gas mixer
procedure : producer : Zellweger Ecosystem
type : S 2000

The simultaneous measuring results from the two analyzers were checked weekly.

O_3-Analyzer

The O_3-gradient-measurements are not direct integrated in the "IIFE"-instrumentation, some results from measurements on Melpitz site are integrated.

producer : Environment, France; ANSYCO, Karlsruhe, Germany
type : 41 M
principle : UV-adsorption
range : 0 0 to 200 ppb
time of integration : 30 s
detection limit : 1 ppb
calibration gas : by O_3-generator (Calibrator)
producer: Thermo Environmental Instruments Incorporation
Messer
type: 49 PS

NH_3-gradient-system

producer : ECN, Petten, Netherlands
type : AMANDA-AS-gradient-system
principle : continuous flow, conductivity
resolution : 6 minutes for one profile (3 heights)
dection limit : 10 ng/m^3
calibration : with calibration solutios
1. blanc adsorption solution
2. blanc adsorption solutions with 50 µg/kg NH_4^+
3. blanc adsorption solution with 500 µg/kg NH_4^+

used chemicals : ethyleneglycol1) Fa. MERC 822329
NH_4Cl Fa RIEDEL-DE HAEN 31107
$NaHSO_4$ Fa. MERC 63520500
formaldehyde Fa. MERC 104003
NaOH Fa. RIEDEL-DE HAEN Fixanal

water is used from central station in IfT
producer: Fa. Wilhelm Werner GmbH, Germany

The air flow was inspected and measured by a gasometer every week. The glass tubes were cleaned every two weeks. The detector membrane need to be changed if it was necessary (new calibration had to be done after this).

HCl, HNO_2 and HNO_3 off-line wet anular denuder

producer : ECN, Petten, Netherlands
type : AMANDA-100
principle : off-line denuder with sampling system

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1) only during wintertime (January to March and November, December)

resolution : 1 hour (measuring 40 minutes)
dection limit : 0,2 µg/m^3
analyse : Ion chromatograph
used chemicals : K_2CO_3 Fa. MERC 4928.0500
water is used from central station in IfT
producer: Fa. Wilhelm Werner GmbH, Germany

The air flow was checked and measured by a gasometer every week. The glass tubers were cleaned every two weeks. Ionchromatographical analyse was done latest the next day in IfT laboratory.

2. Meteorological measurements

Bowen ratio system

producer : Campbell, U.K.
type : Bowen ratio system with added wetness sensor

Every week inspection of air pumps and filters and check of dew point sensor with integrated function. The dew point mirrow was cleaned every two weeks or if required. The radiation sensors were inspected twice a week.
One thermocouple had to be changed in the summertime.

Gill-anemometer

producer : Gill-Instruments Ltd.
type : Solent Research Ultrasonic Anemometer (Issue 4.1)

Visuell inspection of sensor and cleaning if necessary, especially in the summer time (cobwebs)

3. Rain, fog and aerosols collectors

precipitation collector

producer : van Essen Instruments, NL
type : Precipitation collector Type PR 1400

Test of the sensor function (wet only sampler) and clean up of the sampling funnels with clean water.

Fog-sampler

producer : KEMA, NL

type : Fog sampling system K94-85092-1

Test of the stand by function, the sensor function and clean up of the teflon-threads.

Aerosol sampling system

producer	: Rupprecht & Patashnick Co., Inc., USA
type	: Partisol Model 2000, Air sampler

Function test every week, every month test of the gas tightness.

Appendix 3 Structure of data files to be distributed in the LIFE project

Introduction
Below follows a description of the format for files used to exchange data within the LIFE project.

Two file types are discussed : Raw data files and files containing results.

1 RAW DATA FILES

1.1 FILENAMES

* For every month :

- one SON-file (Sonic),
- one BRS-file (Bowen Ratio System),
- one MOI-file (Rain)
- one COM-file for each chemical component (fluxes etc.),
- one AER-file (aerosol constituents)

* Filenames : RMMMINS.COM

- R is for raw data
- MMM stands for Jan, Feb, Mar, Apr, May, Jun, Jul, Aug, Sep, Oct, Nov, Dec
- INS could be a three letter word for each institute (eg. ITE, IFT, RIVM)
- COM is SO_2, NO_2 etc. or SON for the sonic information, BRS for the Bowen Ratio information and MOI for additional rain and fog information, AER for aerosol constituents

* Examples
RJANITE.SO$_2$ for the raw data for SO_2 from January from ITE.
RFEBIFT.SON sonic data from IFT for February

1.1 CONTENTS OF FILES

1.1.2 The chemical components

The chemical components in question are NO, NO_2, NO_x, SO_2, NH_3, O_3.

For each gas every month one file needs to be made with :

* In the first 2 records:

1) The measuring heights z_1, z_2, z_3, z_4 (if not available it should be indicated by a zero)

2a : a digit which indicates wether the time given is the start of the period or the end (1 for start, -1 for end).
2b : the time : GMT (0), local-time (1), local-wintertime (2) throughout the year. Don't use local time it gives a lot of confusion.
2c : the Units $\mu g/m^3$ (0), ppb (1) use only $\mu g/m^3$!

Two digits for heights in m, starting times given in GMT, all concentrations in $\mu g/m^3$
record 1 : z_1, z_2, z_3, z_4, example : *0.5 ,2.0, 0.0, 0.0* (reals in meters)
record 2 : start, GMT, UNIT Example : *1, 0, 0* (integers)

* In every other record :

First information of the sampling period the month, the day, the hour, the minute, all in integer format. Then the concentrations at the indicated heights in E format. There must be a record for every half hour that month.
so :

Imonth, Iday, Ihour, Iminute, $4C_z$, $4_\sigma C_z$
Format, I2,I2,I2,I2,4Eformat,4Eformat
for the E format 3 significant digits.
Unavailable data would get a value of -9.99E+99

An example 14:00 to 14:30 3 March 1995

so record 3 and all the rest :
3,3,14,0,1.01E+01,1.02E+01,1.03E+01,-
9.99E+99,1.00E+00,1.10E+00,1.20E+00,-9.99E+99

3,3,14,30,1.20E+01,1.22E+01,1.23E+01,-
9.99E+99,1.00E+00,1.10E+00,1.20E+00,-9.99E+99
etc.

The file RMARITE.SO_2 could look like:
0.5 ,2., 0., 0.
1, 0, 0
3,3,14,0,1.01E+01,1.02E+01,1.03E+01,-
9.99E+99,1.00E+00,1.10E+00,1.20E+00,-9.99E+99
3,3,14,30,1.20E+01,1.22E+01,1.23E+01,-
9.99E+99,1.00E+00,1.10E+00,1.20E+00,-9.99E+99
etc.

1.2.2 Sonic

For the **SON**, **MOI** and **BRS** data the first part of each record should be similar to the chemical component file.
Use m/s, °C, wind direction in degrees, W/m^2

first record : Zson, start, GMT, Example : *5, 1, 0*
All other records

For .SON files :
Imonth, Iday, Ihour, Iminute, U, T, H, U*, W_{dir}, σ_{dir}
EXAMPLE *1, 2, 10, 10, 5.00E+01, 2.00E+01, 2.00E+02, 5.00E-01, 2.00E+02, 2.00E+01*

1.2.3 Bowen ratio system

For .BRS files :
Imonth, Iday, Ihour, Iminute, R_n T, H_{soil1}, H_{soil2} T_{s1}, T_{s2}, T_{air1}, T_{air2}, $Dewp_1$, P_{H2O1}, $Dewp_2$, P_{H2O2},Q_{global},wetness

All variables have the name used in the CAMPBELL system.

1.2.4 The rain information

For .MOI files :
The wet denuder results are included here.
IMonth, Iday, Ihour, Iminute, Rain (frequency), Rain (quantity), Fog, HNO_3, HNO_2, HCL

1.2.5 The aerosol constituents

For .AER files :

Three records per sample

record 1 start and stop

Imonth, Iday, Ihour, Iminute, Imonth, Iday, Ihour, Iminute,

record 2

first diameter information :
1 means *dia* < 2.5 _m
2 means 2.5 < *dia* < 10 _m

so : (Use E format as above)
1, SO_4, NO_3, NH_4, CL, Na, Ca, K, Mg, Zn, Pb, Cd, Cu, Ni, Cr
2, SO_4, NO_3, NH_4, CL, Na, Ca, K, Mg, Zn, Pb, Cd, Cu, Ni, Cr

2 OUTPUT FILES

The LIFE fortran computer programme will produce files which look like :

Output file names PMMMINS.com
P -processed
MMM -month
INS -institute
com -component

and make for each component a file which looks like :

Imonth, Iday, Ihour, Iminute, U, T, Wdir, U*, β, H, LE, Qnet, L, RH, Tsoil, Hsoil, C_1, σ_C, F, σ_F, v_d, R_a, R_b, R_c,
R_c (estimated according to Erisman *et al.,* 1994)

File name for example PJANITE.SO_2