

UNCERTAINTIES OF MEASUREMENTS IN METEO-FRANCE' S MONITORING OF THE CHEMICAL COMPOSITION OF PRECIPITATION

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ABSTRACT :

The World Meteorological Organization created in the sixties, several networks of pollution's survey including a worldwide network: BAPMoN, Background Air Pollution Monitoring Network.

In 1977, Météo France in association with a chemical analysis laboratory, decided to participate in this network with six stations of precipitation sampling. Nowadays, three stations are measuring pH, conductivity and chemical composition in principal mineral ions, through weekly samples. The Météo France's network was integrated into the WMO's program Global Atmosphere Watch (GAW) in 1989. Météo France developed a quality assurance plan, according to the GAW's requirements, which has been managing the Météo France's activities since 1993.

Today, the database is 25 years old.

In a first part, the results of chemical composition of precipitation in France of the last 25 years and the methods of chemical analysis are presented. Then, different problems concerning sampling, sample's storage, handling and transporting are analyzed.

In a second part, we will deal with the protocols chosen by Météo France in order to fulfill GAW's requirements concerning:

- internal controls of the samples (visual, pH and conductivity);
 - monitoring of our measuring apparatus, control of material;
 - methods of analysis and the associated uncertainties;
 - intercomparisons organized by the WMO twice a year to evaluate the fiability of the measurements;
 - "testing samples";
 - reanalysis according some selection criteria to test some methods.
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INTRODUCTION:

In front of the increase of pollution in the world, the WMO decided to create in the sixties several networks of pollution survey, among them BAPMoN (Background Air Pollution Monitoring Network). The WMO combined them to form the GAW (Global Atmosphere Watch) in 1989. Nowadays, there are 400 GAW stations in the world, global and regional sites. The GAW programme (www.wmo.ch) coordinates global monitoring of aerosols, ozone, greenhouse gases, ultraviolet radiation, selected reactive gases and precipitation chemistry.

Our French network for the GAW dedicated to monitor the chemical composition of precipitation began in 1977 with six regional stations. Today only three of them are still working (see figure 1).

The stations in Abbeville and Gourdon are under oceanic influence, whereas Carpentras is under Mediterranean influence.

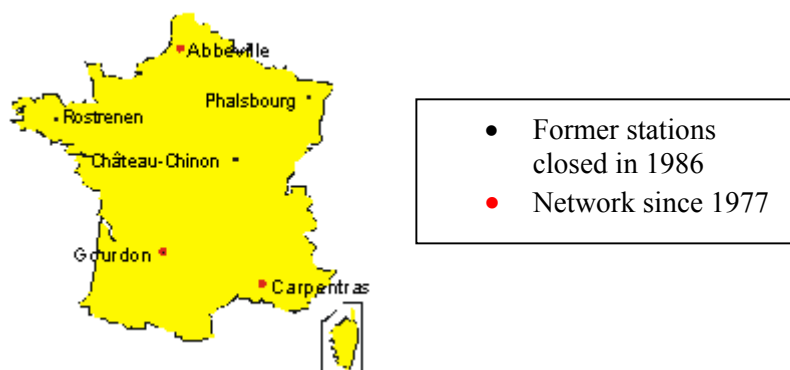
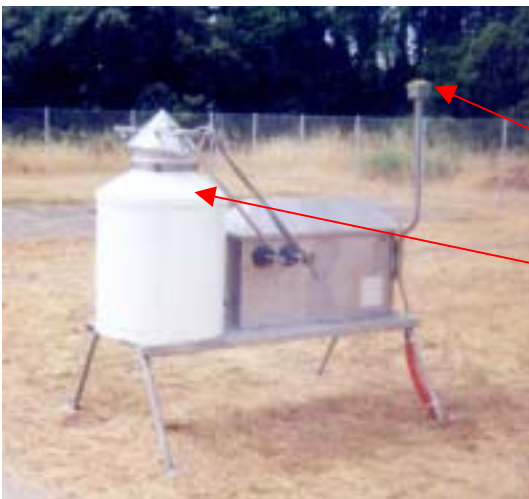


Fig.1: GAW French network

In a first part, we will deal with the sample collection and the chemical analysis, which are the main uncertainty components. In a second part, the main results obtained by Météo France for France over the last 25 years are presented. Finally, in a last part, the uncertainty balance is presented.

1. Sample collection

1.1. Rain Gauge



Sampling collection is made by a special rain gauge developed in the DSO (Direction des Systèmes d'Observation/Direction of Observing Systems) for Météo France. Main technical characteristics are:

- a precipitation sensor for the beginning and end of precipitation;
- a reception cone (area=580 cm²) with a lid driven by the precipitation sensor and a motorized mechanism;
- lead acid battery of 24 V for the power supply;
- height of sample collection: 1,30 m.

Fig. 2: new rain gauge (since the end of 2004)

A lid opens and closes over the sample container orifice. So, only the constituents of precipitation are collected. The precipitation measurements made by the rain gauge are then representative.

Precipitation sample container is chemically inert for the constituents measured and is decontaminated before each use.

1.2. Sample collection

The weekly sample collection is made each Tuesday morning, according to a rigorous protocol, based on the GAW's requirements. As a matter of fact, precipitation samples are characterized by low ionic concentrations and are very susceptible to contamination.

The most important steps are:

- sample handling, for example only one sweat droplet may double the NaCl concentration;
- sample storage, because of the potential for chemical changes, especially because of temperature. The storage is also made in a fridge and the samples are transported in isothermal boxes as quickly as possible.

2. Chemical analysis

Before being sent to an external laboratory to achieve all the chemical analysis, the samples are firstly analyzed by Météo France at DSO.

2.1. Analysis in the DSO

Samples are first sent to the DSO where:

- aspect;
- weight;
- pH and conductivity (if there is enough precipitation >200 ml or 3.5 mm of rain) are checked.

Our pH and conductivity measurements follow of course a rigorous protocol based on the WMO requirements. Certified reference materials of pH = 4 or 7 and of conductivity = 20, 50 or 100 $\mu\text{S}\cdot\text{cm}^{-1}$ are used to calibrate our pH-meter and conductimeter.

2.2. Analysis in the subcontractor laboratory

DSO has been subcontracting the measurements of pH, conductivity and main ions to the same laboratory of chemical analysis since 1977.

Their protocols follow the WMO requirements according to a quality assurance plan, which describes the sample handling and storage, the analytical measurements and the results supplied to Météo France.

Besides, the laboratory is checked by:

- comparison with our pH and conductivity measurements;
- blind samples;
- replicate analysis;
- intercomparisons planned by the WMO twice a year.

The analytical precision (S_i) of the laboratory can be calculated from duplicate analysis of the same precipitation samples to estimate the contribution of analytical variability:

$$S_i = \left(\frac{\sum di^2}{2.N_i} \right)^{1/2}$$

where di is the difference between the two analyses and N_i the number of sample pairs.

Recently, we use the methodology *M.MAD* (Modified Median Absolute Difference) developed in the last GAW Report to calculate the precision of measurements made by our laboratory (see [1], Appendix A p91).

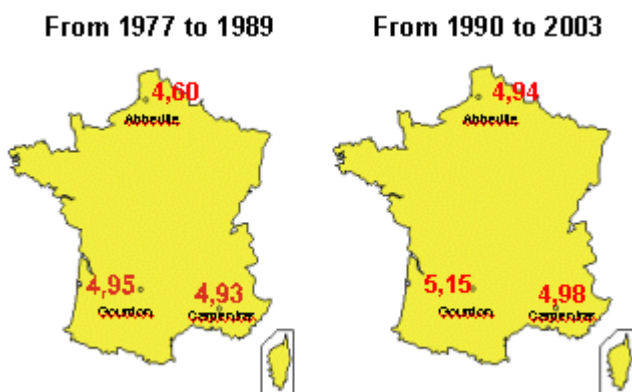
$$M.MAD = \frac{1}{0.6745} \times Median(|xi - Median(xi)|)$$

where xi is the variable of interest (in our case, the sampler error for each set of paired concentration data obtained from replicate analysis).

The different intercomparisons give the laboratory accuracy and assess the inter-laboratory bias.

3. Major results in France over the last 25 years

3.1. pH



The comparison between the two maps on figure 3 shows a real increase of pH for the three stations especially for the North of France, in Abbeville, where the pH is also the lowest.

Fig.3: Average pH^l in France

Cumulative distributions of pH frequency are shown on fig.4. Period of three years have been chosen to demonstrate the pH evolution.

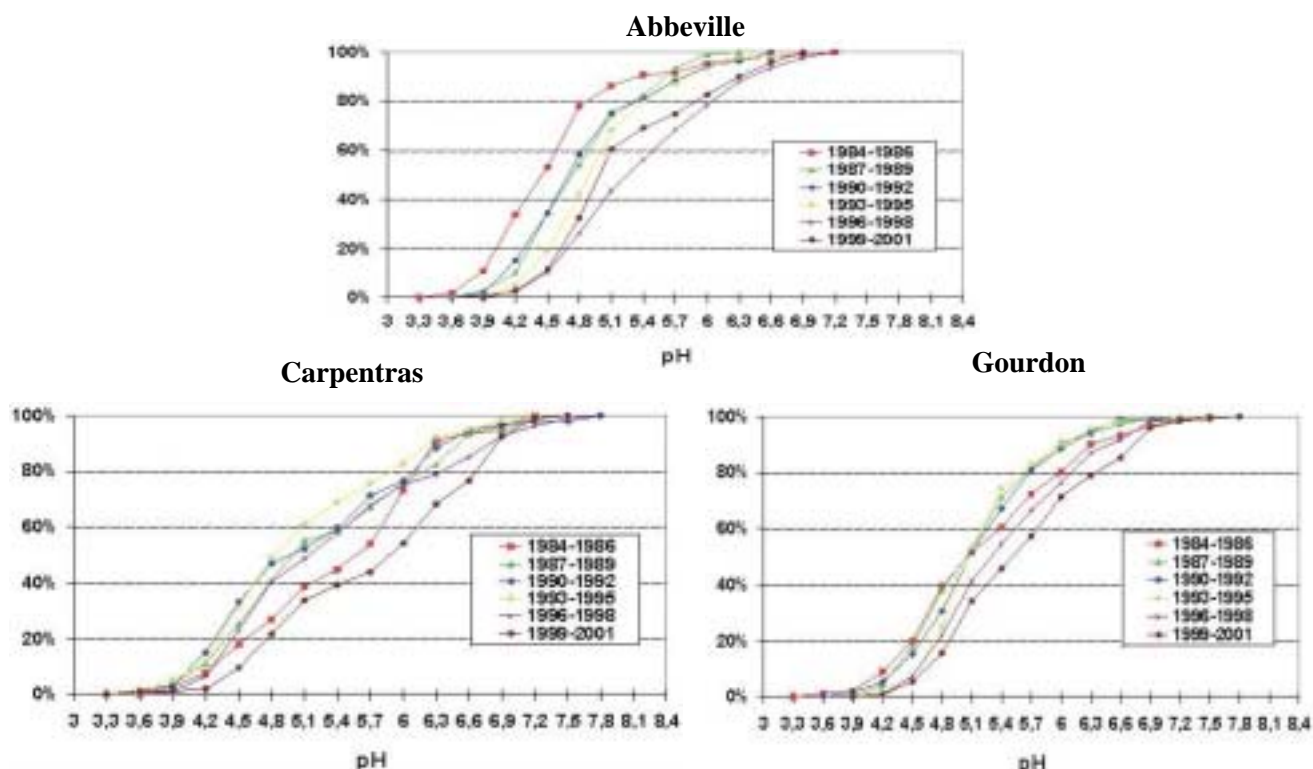


Fig. 4: Cumulative distributions of pH-frequency in Abbeville, Carpentras and Gourdon from 1984 to 2001

In Abbeville, between 1990-1992 and 1999-2001, the 50th percentile (median) increased of 0.4 pH-unit, in spite of an acidification between the two last periods 1996-1998 and 1999-2001, probably due to a deposit of sulphate.

We also observe for the two others stations, between 1990-1992 and 1999-2001, an increase of pH, with more intensity in Carpentras.

The difference of pH between Abbeville and Carpentras was nearly 1.1 pH-unit for the period 1984-1986 and decreased to 0.3 pH-unit in 1990-1992 until 1993-1995. Then, this difference increased and for the period 1999-2001, this difference was nearly about 0.6 pH-unit.

In Gourdon, pH has been remaining at a constant level since 1984; the little acidification of precipitation with pH > 5 observed between the periods 1984-1986 and 1990-1992 (see [3]) stopped in 1995.

Nowadays, the average pH in France is 5.13 pH-unit.

3.2. Ratio $\frac{NO_3^-}{SO_4^{2-}}$

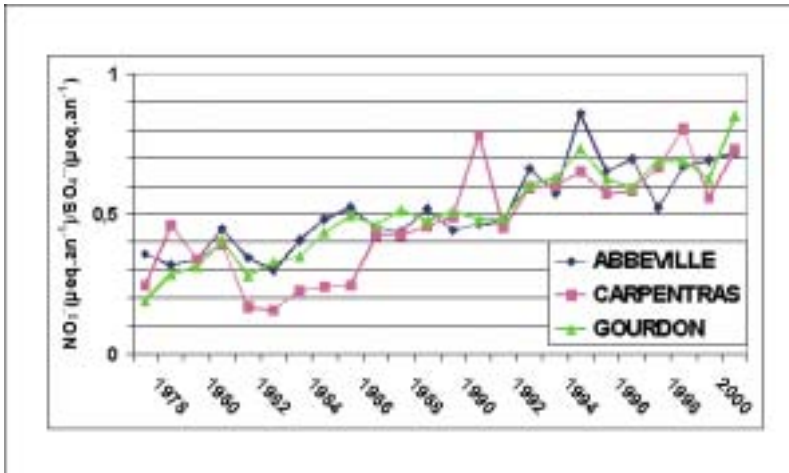


Fig. 5: Ratio nitrogen/sulphur

The ratio $\frac{NO_3^-}{SO_4^{2-}}$ on the figure 5 tends to increase in the same extent for the three stations. An explanation could be that nitrogenous pollution, mainly from cars, is becoming more important.

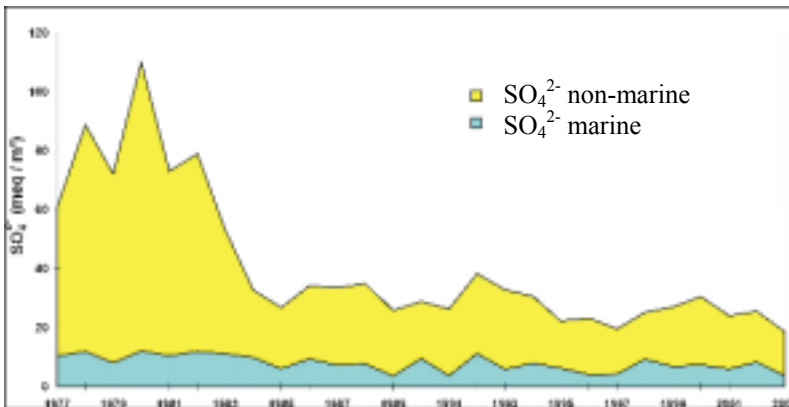


Fig. 6: Non-marine versus marine sulphates in Abbeville

Whereas the ratio of marine sulphates is almost at a constant level, the ratio of non-marine sulphates has been decreasing for 25 years, because of the closing down of a lot of heavy industries in the North of France and because of the stop of the thermal power stations. The decrease of non-marine sulphates is the more significant in Abbeville than in the other towns.

4. Measurements uncertainties

4.1. General description

The main components of the uncertainties for the monitoring of the chemical composition of precipitation are linked with:

- sample collection;
- analysis.

The sampling collection uncertainties are very difficult to estimate; however the precision of the whole precipitation chemistry measurement system (*overall precision*) may be determined by comparing the results obtained by two rain gauges located in the same place and working together during one year. The laboratory precision, which refers to the precision of the analytical measurements made by GAW Laboratories, could also be estimated. This calculation has been demonstrated by Sirois and Vet. Their publication in 1999 [4] was concerning the network CAPMoN (Canadian Air Pollution Monitoring Network). Then GAW fixed the Data Quality Objectives (DQO) (see [1], Appendix A p99).

The uncertainties of the laboratory that achieves the analysis are divided into:

- uncertainty of the measurement protocol;
- uncertainty of the sample matrix, which is quite difficult to determine because it depends on each sample. The only solution is to deal with the sample: replicate analysis, comparison with other measurement protocols...This solution is too expensive and so it is impossible to do it for each analysis.

4.2. Laboratory performance

The laboratory uncertainty* linked to the measurement protocol has been established for stable synthetic samples and is summarized for each component of precipitation in the following worksheet 1.

In this worksheet, the precision Li^{**} of the analytical measurements made by our laboratory was calculated from precipitation samples of 2002 and 2003, which are composed of blind samples and of about 10% of routinely analyzed samples (see [2], p23).

					DQO
COMPONENT (UNIT)	MEASUREMENT PROTOCOL	RANGE	LABORATORY UNCERTAINTY*	LI**	LABORATORY PRECISION***
pH (pH-unit)	Glass electrode	3 -7.5	±0.05	±0.34 at pH >5 ± 0.13 at pH < 5	± 0.04 at pH >5 ± 0.02 at pH < 5
γ (μS/cm)	Conductivity cell	0-150	<5%	/	/
Cl ⁻ mg.l ⁻¹	Ion Chromatography	0.02-50	<5%	0.05	0.02
SO ₄ ²⁻ mg.l ⁻¹	Ion Chromatography	0.02-30	<5%	0.03	0.03
NO ₃ ⁻ mg.l ⁻¹	Ion Chromatography	0.02-30	<5%	0.04	0.03
NH ₄ ⁺ mg.l ⁻¹	Automatic Colorimetry	0.01-20	<10%	0.12	0.01
Ca ²⁺ mg.l ⁻¹	Inductively Coupled Plasma	0.01-10	<10%	0.07	0.01
K ⁺ mg.l ⁻¹	Inductively Coupled Plasma	0.01-10	<10%	0.01	0.01
Na ⁺ mg.l ⁻¹	Inductively Coupled Plasma	0.01-20	<10%	0.06	0.01
Mg ²⁺ mg.l ⁻¹	Inductively Coupled Plasma	0.01-5	<10%	0.01	0.01
Acidity/Alcalinity (μeq/l)	Titration	±200	/	/	/

Worksheet 1: Uncertainties, precision of laboratory, and DQO

The precision of our laboratory was calculated here in 2002-2003 for 35 samples, which 16 had a pH<5. Over these 35 samples, 9 had a high conductivity (>30 μS.cm⁻¹): six of them were collected in Abbeville, a station under marine influence.

Some analytical precision exceeds the Data Quality Objectives (pH, Cl⁻, NO₃⁻, NH₄⁺, Ca²⁺ and Na⁺). In fact, the laboratory precision *** is calculated over more than 30 samples, as usual, but they cover the whole measurement range.

4.3. Intercomparisons

Twice a year, the WMO organizes an intercomparison for all the GAW members. It enables the laboratories to check if they meet the Data Quality Objectives (DQO) fixed by WMO, according to the laboratory bias:

$$bias = 100 \times \frac{Clab - MedianC}{MedianC}$$

where *Clab* is the laboratory's reported concentration and *MedianC* is the median concentration of all laboratories.

The worksheet 3 sums up the results obtained by Météo France in the intercomparisons organized by the WMO in 2003 (28th and 29th). For the two intercomparisons in 2003, our measurement bias is calculated and compared with the inter-laboratory bias:

		SAMPLE 1	SAMPLE 2	SAMPLE 3	DQO
pH	29th	O	O	O	± 0.07 pH-unit
	28th	N (0.1 pH-unit)	O	O	
γ	29th	O	O	O	± 7 %
	28th	O	O	O	
Cl ⁻	29th	O	N (-27.54%)	O	± 10 %
	28th	O	O	O	
SO ₄ ²⁻	29th	O	O	O	± 7 %
	28th	O	O	O	
NO ₃ ⁻	29th	O	O	O	± 7 %
	28th	O	O	O	
NH ₄ ⁺	29th	N (-7.21%)	N (-14.63%)	O	± 7 %
	28th	N (-10.83%)	O	N (-10.15%)	
Ca ²⁺	29th	N (19.04%)	N (56.86%)	O	± 15 %
	28th	O	N (-18.92%)	O	
K ⁺	29th	O	N (57.89%)	O	± 20 %
	28th	O	N ⁽¹⁾	O	
Na ⁺	29th	O	O	O	± 10 %
	28th	O	O	O	
Mg ⁺	29th	O	N (-37.5%)	O	± 10 %
	28th	N (11.11%)	O	N (11.57%)	
Acidity-Alcalinity	29th	N (88.03%)	N (116.98%)	O	± 25 %
	28th	O	N (29.41%)	O	

N⁽¹⁾: value was below the detection limit (<0.01mg.l⁻¹)

O: bias meets the DQO

N: bias doesn't meet the DQO

Worksheet : Intercomparisons in 2003

In one hand, the results for pH and anions meet the quality objectives most of the time. On the other hand, results do not match for the cations, which exceeded the objectives, particularly for Ca^{2+} and Mg^+ and NH_4^+ . So we are working about the measurement protocol with the laboratory, to choose between chromatography and ICP (Inductively Coupled Plasma).

To conclude, to improve the measurement system of chemical composition of precipitation, we have to take care about:

- sampling collection, starting point of the measurement chain, in order not to provide contaminated samples;
- measurement protocols in the laboratory, especially traceability, calibration.

Thanks to the use of new rain gauges at the end of 2004, the DSO would be able to calculate the uncertainty of sample collection according to the WMO protocol (see [1], Appendix A p91-98).

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- [1] GAW Precipitation Chemistry Science Advisory Group, GAW: Manual for the GAW Precipitation Chemistry Programme, *Report No. 160*, 2004
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- [3] Nadine Cenac et al., 1995: Précipitations Acides en France : Bilan et Tendances après 15 ans de mesures -10ème Congrès Mondial sur l'Air Pur, Espoo, Finlande (28 Mai- 2 Juin 1995), *IUAPPA & FAPPS*, vol.2, p.269
- [4] Sirois, A. and Vet. R. (1999): The precision of precipitation chemistry measurements in Canadian Air and Precipitation Monitoring Network (CAPMon). *Environ. Monitor and Assess.* 57, 301-329.