GAW/METEO-FRANCE NETWORK
Chemistry composition measurements of precipitation samples

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Abstract

In the sixties, the World Meteorological Organization created several networks of pollution's survey.
All were integrated into the WMO's program Global Atmosphere Watch (GAW) in 1989.
In 1977, Météo France decided to participate in this network with six stations of precipitation sampling.
Since 1988, due to an internal reorganization of Météo France network, only three stations are operational: Abbeville, Carpentras, Gourdon.
The chemical composition of rain samples (pH, conductivity and principal mineral ions) collected in our network is measured by a subcontracting laboratory.
We will show first the main technical characteristics of our network such as precipitation sampling, analytics measurements of laboratory, quality assurance program, and methodology assessment of the quality of chemical precipitation data.
Precipitation chemistry data at GAW/BAPMoN sites for the [1980-2006] period will be exposed and statistics tests will be employed on these data to detect monotonic trends.
The results will be exposed and discussed.

Introduction:

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 (figure 1).
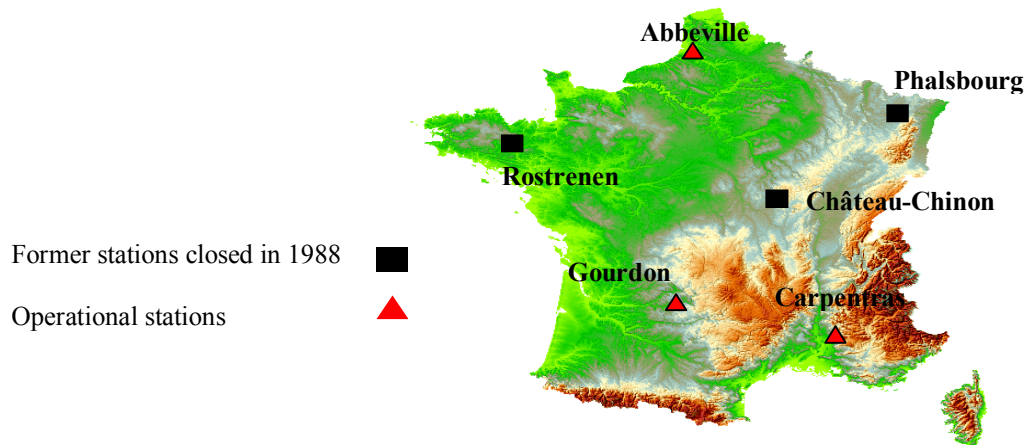

Fig.1*: French GAW Network*

Operational Stations	Latitude	Longitude	Altitude (m)	Topology
Abbeville	50°08'N	01°50' E	70 m	Plain
Carpentras	44°05'N	05°03' E	99 m	Plain
Gourdon	44°45'N	01°24' E	259 m	Plateau

Table 1. *Description of GAW Network stations*

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

A French GAW Network

1. Objective
The goal of the French GAW Network is the survey of the chemical composition of precipitation samples (pH, electric conductivity, Cl^-, SO_4^{2-}, NO_3^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Acidity/Alkalinity) in order to assess trends and spatial variability at a regional scale.

2. Precipitation Samples Collection

2.1 Rain Gauge

Fig.2 *: Old Collector*   **Fig.3** *: New Collector*

From 1977 until 2004, a rain gauge (fig.2) developed by Meteo-France has been used for sample collection. The main technical characteristics are:
- height of sample collection: 1m;
- lead acid battery of 24 V for the power supply;
- a reception cone (area=400 cm^2) with a lid driven by the precipitation sensor and a motorized;
- a precipitation sensor for the beginning and end of precipitation.

Since January 2005, a new collector (fig.3) was operational for the sampling collection.
Differences with the old collector are:
- a best precipitation sensor;
- a bigger reception cone (area=580 cm^2);
- a higher height of sample collection: 1,30 m.

The reception cone is bigger to collect light rains in sufficient quantity.

The sampler has a lid opening and closing over the sample container orifice in order to collect representative samples. Besides, the precipitation sample container is chemically inert for the constituents measured and is decontaminated before each use.

2.2 Collection
The precipitation samples collection was monthly from 1977 to 1983, after it was weekly.
The weekly sample collection is made each Tuesday morning, according the GAW's requirements (GAW N°160, p19-21).
Precipitation samples are characterized by low ionic concentrations, they are very susceptible to contamination. So, the most important steps to respect the integrity of the precipitation samples are:
- sample handling;
- sample storage, because of the potential for chemical changes: the storage is made in a fridge as soon as collection has been realized;
- sample shipping: the samples are shipped in isothermal boxes as quickly as possible.

Furthermore a cooling system integrated to the collector is in test this year in order to maintain the precipitation samples between four and eight degrees.
The final goal is to have a complete cold chain throughout the measurement process (GAW N°160, p21-22).

3. Chemical analysis

Samples are firstly analyzed in Metrology Laboratory of Météo-France, before being sent to an external chemical laboratory to achieve all analysis.

3.1 Analysis in Metrology Laboratory of Météo-France

Samples are first sent to our laboratory where we check:
- aspect of samples (insect, dust presence etc….);
- weight;
- pH and conductivity (if there is enough precipitation >200 ml or 3.5 mm of rain).

We use, for our (pH, conductivity) measurements, certified reference materials of pH = 4 or 7 and of conductivity = 20, 50 or 100 μS.cm^{-1}, to calibrate respectively our pH-meter and conductimeter.
Our measurements are based on the WMO requirements (GAW N°160, p41-45).

3.2 Analysis in the subcontractor laboratory

Météo-France 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.

Parameters (units)	Methods
pH (pH unit)	Glass electrode
γ (μS/cm)	Conductivity cell
(Cl^-, SO_4^{2-}, NO_3^-) (mg.l^{-1})	Ion Chromatography
NH_4^+ (mg.l^{-1})	Colorimetry
(Na^+, K^+, Mg^{2+}, Ca^{2+}) (mg.l^{-1})	Inductively Coupled Plasma Spectrometry
Acidity/Alkalinity (μeq/l)	Titration

Table 2. *Methods used by laboratory*

4. Control quality and assessment of precipitation chemistry data

In order to ensure high quality GAW precipitation measurements, every network should provide elements of Quality Assurance (QA) defined in GAW N°160, p87-90.
These quality assurance elements are: accuracy, precision, completeness, representativeness and comparability. Activities realized by Météo France to assess those quality assurance elements are described below (Table 3).

Table 3. *WMO definition of QA elements and associated actions realized by Météo-France*

QA Elements	WMO Definition of Terms (GAW N°160, p xi)	Météo France Actions
Accuracy	Degree of agreement between an observed value and an accepted reference value.	-routine collection of field information for use in validating chemistry data, -routine inspections of the field, laboratory and data management systems, **-submission of blind samples** to the laboratory.
Precision[1]	Degree of agreement of repeated measurements of a homogenous sample by a specific measurement procedure, expressed in terms of dispersion of the values obtained about the mean value. It is often reported as the sample standard deviation of the sample set.	We send to laboratory **blind samples** and **replicate analysis** (about 20% of samples analyzed in a year) to asses the laboratory precision. The laboratory precision is measured by running duplicate analyses of the same samples (both within and between analytical runs). Furthermore comparisons with our pH and conductivity measurements are realized.
Completeness[2]	Amount of valid data obtained, compared to the planned amount (i.e. number of rain samples collected versus number of rain samples that occurred), usually expressed as a percentage.	There are two data completeness criteria : **-%PCL: Percent precipitation Coverage Length** It is the portion of the data summary period (season or year) with complete records of the amount of precipitation that fell. **-%TP: Percent Total Precipitation** That is the potion of the precipitation associated with valid chemical analysis and valid sample collection.
Representativeness (of site and sample)	Degree to which data accurately and precisely represent a characteristic in the population, e.g., spatial or temporal representativeness.	**Site representativeness** is assured and controlled by inspecting sites and their surrounding at regular intervals. **Sample representativeness** can be assured by minimizing sample contamination. Regular missions, at the field French sites, are carried out.
Comparability	Measure of the degree to which methods and data sets can be represented as similar.	Météo-France participates to intercomparison of WMO/GAW Precipitation Chemistry Laboratories.

Remarks:
[1] The Overall Precision is the precision of the complete precipitation chemistry measurement system including the field and laboratory components.
[2] Two supplemental criteria defined by Olsen (1990) exist, but are not requested by GAW:
%VSMP: the fraction of the total number of sampling periods (daily, weekly, monthly etc.) having valid concentration data.
%VSL: the percentage of time in the summary period represented by samples having valid concentrations.

B **Trends of precipitation chemistry data for the period 1980-2006**

1. **Data Definition**

   The data used for this study are the annual weighted mean concentrations in precipitation defined by:

   $$Cpw = \sum_{i=1}^{m}(Ci * Pi) / \sum_{i}^{m} Pi \quad \text{where:}$$

   - Cpw is the precipitation-weighted mean concentration for the year;
   - Ci is the analyte concentration of sample;
   - Pi is the standard gauge precipitation depth for each sample i (where i = 1 to m);
   - m is the total number of samples with valid, non-missing concentration values.

2. **Statistic Methodology**

   The nonparametric Mann-Kendall test (Gilbert, 1987) will be applied on the precipitation chemistry data to detect the existence of a monotonic increasing or decreasing trend, and the nonparametric Sen's method (Sen, 1968) will be used to estimate the slope of this trend. The test for the trend is based on ranks within the time series. Sen's slope estimator is the median of the slopes calculated from all pairs of values in the data series. These two tests are highly recommended by WMO (Sirois, 1998), and details of the method are also given by Salmi (Salmi, 2002).

   The data used for the trend analysis are the annual weighted mean concentrations in precipitation (i.e. Cpw).

3. **Main Results of the precipitation data trends**

   Rates of changes, for the [1980-2006] period, of average pH (unit pH.period^{-1}) and means concentrations in precipitation (%.period^{-1}) for hydrogen, sulfate, nitrate, and ammonium from are shown in table 4:

Stations	pH	H$^+$	SO$_4$$^{2-}$	NO$_3$$^-$	NH$_4$$^+$
Abbeville	***0.65	***-79	***-74	**-35	*-46
Carpentras	0.2	-32	***-69	14	*111
Gourdon	***0.52	***66	***-61	9	**56

Table 4: *Rate of changes over the [1980-2006] period for average pH (unit pH.period^{-1}) and means concentrations (%.period^{-1}) estimated by Mann–Kendall nonparametric Test.*
*Significance levels α = 0.001 ***, 0.01**, 0.05*, 0.1+, > 0.1*
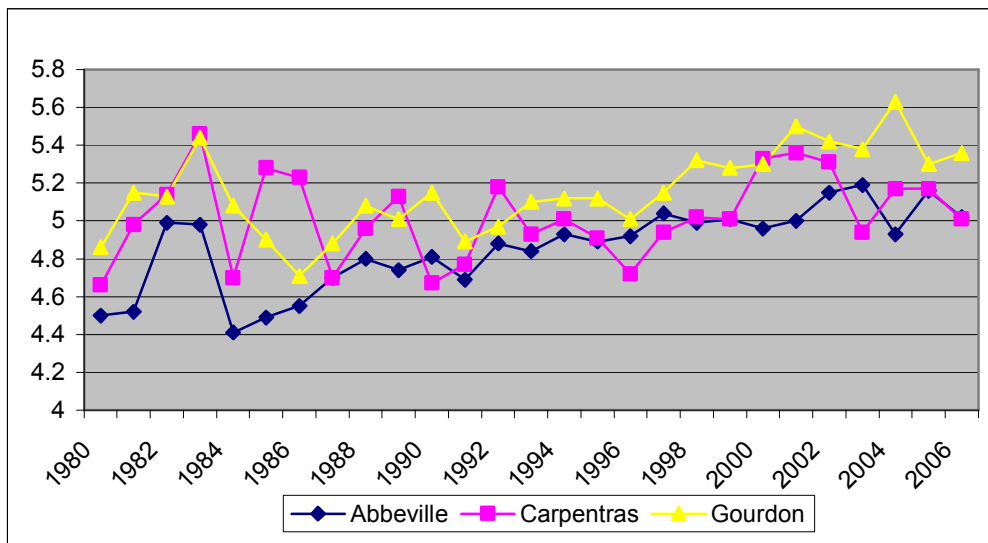
For pH

Fig.4. *Temporal variations in annual average pH for the period 1980-2006. (The average pH is obtained from precipitation-weighted mean concentration of H$^+$)*

As shown in figure 4, increase trend of average pH for Abbeville and Gourdon stations, was detected. We see, for Abbeville, a clear increase of average pH from 4.4 in 1984 to 5.2 in 2003, this site stays the

most acidic among the three stations. The magnitude of the increase trend for this site is significant (+0.65***pH unit on the period) while it is slightly less for Gourdon (+0.52*** pH unit on the period). We observe at Gourdon, a continuous positive trend, particularly pronounced since 1986 (no value is below 5 since 1992), this site remains the most basic.

For Carpentras station, no significant trend is found, in spite of a relatively marked increase observed between 1996 and 2001.
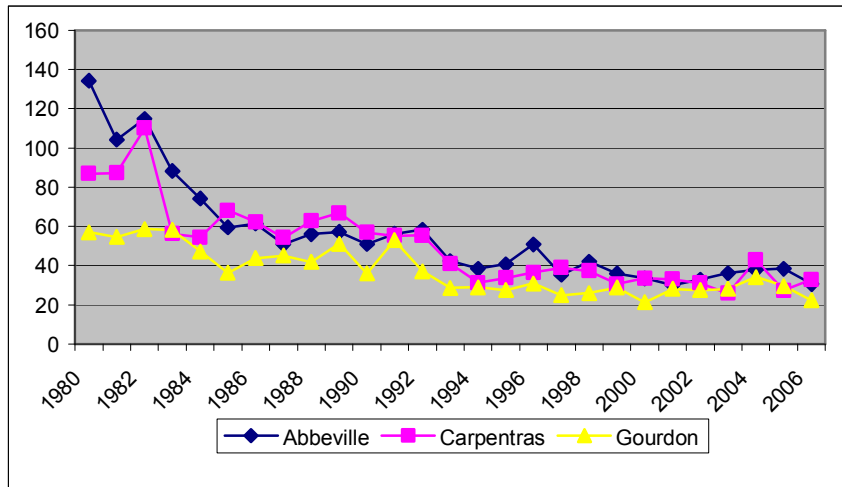
For Sulfate (SO$_4$$^{2-}$)

Fig 5 . *Temporal variations in Cpw of SO$_4$$^{2-}$ (µeq/l) at GAW stations for the period 1980-2006*

The decrease of Cpw of SO$_4$$^{2-}$ (Fig.5) happened, for all stations, mainly in the beginning of the eighties corresponding also to the decrease of sulfur emission in France (decrease of 86% between 1980 et 2005; CITEPA 2007). The magnitude of the trend of sulfate concentration varies from -61%*** (Gourdon), -71%*** (Carpentras) to -74%*** (Abbeville).

This decrease trend is as well observed by the French EMEP network (Sicard, 2006) and also in many countries such as Spain (Avila, 1996), Austria (Puxbaum, 1998), Germany (Zimmerman, 2003).

Since 2000, Cpw values of SO$_4$$^{2-}$, for French GAW stations, are between 20 µeq/l and 40 µeq/l.

Unlike trend of sulfate concentration, different trends are observed among stations concerning the azote elements (NO$_3$$^-$ on Fig6.(a) and NH$_4$$^+$ on Fig6.(b))
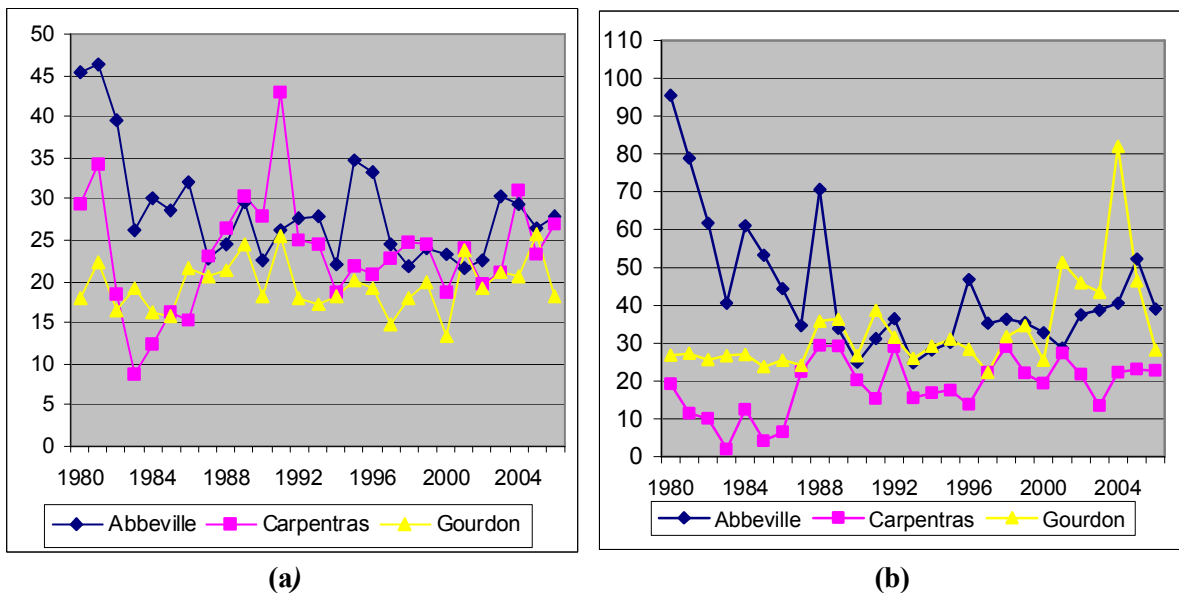

(a)   (b)

Fig 6 . *Temporal variations in Cpw of NO$_3$$^-$ (µeq/l) (a) and in Cpw of NH$_4$$^+$ (µeq/l) (b) at GAW stations for the period 1980-2006*

In Abbeville station**, <u>significant decrease</u> trend for NO$_3$$^-$ and NH$_4$$^+$ have been found (respectively -35%** and -46%*).

The precipitation-weighted mean concentration of NO_3^- and of NH_4^+ remain the highest over the complete period, except two moments:
- for NO_3^- at Carpentras station, high values occurred in 1991,
- for NH_4^+ at Gourdon station, high values are observed since 2001.

Similar results from Carpentras and Gourdon are found for NO_3^- and NH_4^+:
No significant trend for NO_3^- was detected at Gourdon and neither at Carpentras, although an important increase of the Cpw of NO_3^- occurred at this site from 1984 until 1991, followed then by a decrease at values about 25 µeq/l.
Significant increase trend have been found for NH_4^+ at Carpentras and Gourdon:
Carpentras has significant increase trend (111%* over the period), the values are the lowest of the three stations (around 20 µeq/l).
At Gourdon station, a significant increase trend was also detected with the magnitude of 56%**.

Conclusion:
The main characteristics of the GAW French measurement system have been described.
We have seen that, in order to provide high quality precipitation measurements, we must particularly take care of:
- sampling collection: the starting point of the measurement chain;
- measurement protocols in the laboratory (traceability, calibration, quality control…);
- assessment of precipitation chemistry data.

Besides, trends of the series were detected by the use of the Mann Kendall Test, slopes of trends were calculated by Sen's Method. The main results for the french GAW data on the period 1980-2006 are:
- significant increase of pH for two stations (Abbeville and Gourdon);
- significant decrease of sulfate for all stations (from -60% to -75%).

About azote components, differences are observed between the stations:
- In Abbeville, significant decrease trend for NO_3^- and NH_4^+ have been detected (respectively -35%** and -46%*).
- Similar trends at Carpentras and Gourdon have been observed for NO_3^- and NH_4^+:
  - no significant trend for NO_3^-
  - significant increase trend for NH_4^+ (111%*, 56%** respectively at Carpentras and Gourdon station.).

The reduction of sulfur emissions due to the abatement regulations at an European scale, has clearly had a significant decrease effect of sulfate in precipitation for the French GAW stations.
However, we must continue to monitor the chemistry composition of precipitation to assess particularly the contribution of azote elements that seem to be in increase.

Bibliography

- Avila, A., (1996). Time trends in the precipitation chemistry at a montane site in northeastern Spain for the period 1983-1994. Atmospheric Environment 30, 1363-1373.
- Cénac N., M. Zéphoris et C. Thibord (1995). Précipitations Acides en France : Bilan et Tendances après 15 ans de mesures - 10 ème Congrès Mondial sur l'Air Pur, Espoo, Finlande (28 Mai - 2 Juin 1995), IUAPPA & FAPPS, vol.2, p. 269.
- CITEPA (2007). Rapport d'Inventaire National: Inventaire des émissions atmosphériques en France,
- GAW N°160 (2004). GAW Precipitation Chemistry Science Advisory Group, GAW: Manual for the GAW Precipitation Chemistry Programme.
- Gilbert, R.O, (1987). Statistical methods for environmental pollution monitoring. Van Nostrand Reinhold , New York.
- Olsen, A. R., Voldner E. C., Bigelow D. S., Chan W. H., Clark T. L., Lusis M. A., Misra P. K. and Vet R. J. (1990). Unified wet deposition data summaries for North America: data summary procedures and results for 1980-1986. Atmos. Environ. 24A(3), 661-672.
- Puxbaum, H., Simeonov, V., Kalina, M.F., (1998). Ten years trends (1984–1993) in the precipitation chemistry in central Austria. Atmospheric Environment 32, 193–202.
- Salmi T., (2002).Detecting trends of annual values of atmospheric pollutants by the Mann-Kendall test and Sen's slope estimates. Publications on air quality 31, Finnish Meteorological Institute, Helsinki.

- Sen P.K., (1968). Estimates of the regression coefficient based on Kendall's tau. J. of the American Statistical Association 63, 1379-1389.
- Sicard P., (2006). Caractérisation des retombées atmosphériques en France en zone rurale sous forme de précipitations, gaz et aérosols. Analyse des tendances spatio-temporelles et des séries chronologiques. Thèse de doctorat. Université des Sciences et Technologies de Lille.
- Sirois, Allan, (1998). A Brief and Biased Overview of Time Series Analysis or How to Find that Evasive Trend. In WMO report No. 133: WMO/EMEP workshop on Advanced Statistical methods and their Application to Air Quality Data sets (Helsinki, 14-18 September 1998).
- Zimmermann F.; Lux H.; Maenhaut W.; Matschullat J.; Plessow K.; Reuter F.; Wienhaus O. (2003). A review of air pollution and atmospheric deposition dynamics in southern Saxony, Germany, Central Europe.Atmospheric Environment, Volume 37, Number 5, February 2003 , pp. 671-691(21).