Statistical Analysis of Piccardi Chemical Tests

by

F. De Meyer* and C. Capel-Boute**

ABSTRACT. — The numerical data collected daily for the longest series of inorganic chemical tests, carried out in Florence (Piccardi and co-workers, 1951-1972) and in Brussels (Capel-Boute, 1956-1978), have been submitted to a statistical analysis for the purpose of searching an answer to the questions which led to start the collection of long-term series of data with the Piccardi chemical tests in different places. The question was to study the variability in the course of time of various effects observed on aqueous systems, even in the most rigorously standardized conditions, for a chemical precipitation reaction. Since significant long-term perturbations and an annual variation are present in all data sets, the observations cannot be conceived as purely random fluctuations. No common long-term pattern is observed and the measurements are not unambiguously correlated with climatological effects or the solar cycle. The statistical information content of the chemical tests is time-dependent, which implies non-stationarity of the observations. These results suggest the necessity of search for disturbing geophysical and cosmological factors to understand the mechanisms of the interaction.

1. INTRODUCTION

Since the Piccardi chemical tests have started in Florence (1951) and in Brussels (1952), many publications have shown the strange fluctuations of their results in spite of the fact that these tests, based on simple precipitation reactions, are repeated in the course of time in so-called "identical conditions" for any chemist. The patterns of diurnal, annual and long-term variations observed in the data collected in Florence (till 1972) and in Brussels (till 1978) have suggested working hypotheses of some cyclic variations related respectively to the movements of the Earth or to solar-terrestrial relationships. Facts in favour of Piccardi's solar hypothesis have been reviewed in two interdisciplinary symposiums held in Brussels in 1958 and 1968 and in other international meetings.

The subject of this research is thus well-known already by many scientists from different disciplines all over the world, concerned like us with the origin and way of action of some usually uncontrolled environmental factors responsible for non-reproducible results in physical chemistry.

But this fact in itself seems still ignored or unacceptable for the major part of the

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scientific community as a challenge to the traditional methodology requiring that laboratory experiments could be repeated in any place or time with reproducible results.

In this view the following statistical analysis aimed at an answer to the basic questions which led to start the collection of long-term series of data in rigorously standardized conditions in different places of the world. The methods of statistical analysis chosen and the results for the data collected in Brussels and Florence are discussed.

2. METHODOLOGY AND SIGNIFICANCE OF THE PICCARDI TESTS

A. THE CHOICE OF THE LABORATORY METHOD. — Why and how were the Piccardi chemical tests devised? When C. Capel-Boute met G. Piccardi* for the first time, in October 1950, it appeared that they had encountered, quite independently, similar difficulties in studying various effects of different methods for physical treatment of water, used in industry to prevent scaling in boilers. In fact, many usual laboratory test-reactions and experimental conditions, that were tried also by other research workers, did not ensure reproducible results in view to characterize effects of treated (activated) water against untreated (normal) water, as the differences observed could vary considerably and even change from positive to negative results.

Such methods of "physical treatment of water", using controlled low-energy electric, magnetic or electromagnetic fields, suggested that some physical factors, possibly of similar nature, existing and varying in the environment could act, uncontrolled, in the same way on water itself with evident effects on the building of a new phase in a test reaction. This working hypothesis raised, for chemists and biologists, the fundamental question of an enlarged concept of possible control of our physical environment: it was tested since the first of March 1951 in Florence by the Piccardi chemical tests F and D.

The question was to study the variability in the course of time of any effect observed in the most rigorously standardized conditions concerning the internal parameters of the system itself. Although biological effects of some physical treatments of water had already been observed, with the same disturbing variability, it was clearly easier to standardize a sensitive physico-chemical process such as an inorganic precipitation reaction, so that it could be repeated daily in identical conditions, for sufficiently long periods of time to provide data for a statistical analysis.

A hydrolysis reaction (BiCl$_3$ + H$_2$O = BiOCl + 2 HCl), with either pretreated or untreated distilled water, was particularly adequate to observe the variability of the effect of a suitable physical treatment of the water on the germination, growth and sedimentation of the resulting precipitate, in otherwise identical laboratory conditions. This was called F-test (F = fuori = outside) by Piccardi.

The conditions of the experiment had to be chosen rigorously and had to be simple enough to enable a single operator to carry out simultaneously the couple of reactions to compare and to repeat the test in function of time in a statistically sufficient number of experiments. As much as ten couples of reactions at three fixed different hours were carried out daily in Florence from 1951 to 1972 (for technical details and full discussion of experimental conditions, see Piccardi, 1960 and Capel-Boute, 1960).

The anomalous variability observed on the sedimentation rates, even for the most

* Director of the Institute of Physical Chemistry of the University of Florence (died 1972).

rigorously standardized control conditions, led to characterize the effect only by the visible positive or negative sign of the difference in the level reached by the precipitates for each couple of reactions carried out simultaneously at room temperature, neglecting deliberately its absolute value.

The numerical result of a series of Piccardi chemical tests is thus expressed as the frequency of a positive result (accelerated sedimentation) obtained repeatedly as apparent effect of the controlled factor differentiating the two reactions compared. This numerical "variability index" may be given in function of time as percentage for the daily series of experiments or calculated as weekly, monthly or annual means of these daily percentages.

B. DIFFERENTIATING THE CONDITIONS OF THE ENVIRONMENT. — The question raised of possible disturbing factors in the environment of the same nature as those applied in different physical treatments of water led Piccardi to carry out the same test in a Faraday-cage (made of a 1 mm thick copper sheet) and he called it D-test (D = dentro = inside). The puzzling question of non-reproducibility of the controls (all precipitation reactions with untreated water) led him also to differentiate only the couple of reactions by their environmental conditions, that is, comparing precipitations carried out inside versus outside the Faraday-cage, studying with this P-test the variability of the screen-effect itself.

The different patterns of fluctuations observed in Florence and Brussels led us to organize systematically since 1956 in Brussels and other places of the world, the collection of data on four standardized tests: F-test and D'-test, similar to the D-test but using only a horizontal copper screen (0,1 mm thick) instead of a whole earthed Faraday-cage, to differentiate environmental conditions. This new type of screen-effect was observed on both reactions with untreated (normal) water (P_N-test) or with treated (activated) water (P_A-test), carried out simultaneously for either the F or D'-test with the Piccardi Synchronous Mixer (Capel-Boute, 1960, p. 91).

The numerical results, expressed in percentage, for the frequency of a positive effect observed daily on ten couples of reactions for each of these four tests have been subjected to a statistical analysis. Attention is focussed on the time variation of the monthly and weekly means.

C. RESULTS OF THE PICCARDI CHEMICAL TESTS. — The numerical results of all Piccardi chemical tests, collected in Brussels by C. Capel-Boute from 1952 to 1978, have been published in 7 volumes, containing monthly and weekly means, computed from daily values, and running means for 10 consecutive days*. Daily results from Florence, collected by Piccardi and co-workers from 1951 to 1972, have also been published in separate volumes.

Figure 1 shows the monthly means of the Piccardi chemical tests obtained in Brussels and Florence. Figure 2 displays the weekly means of the tests F, D', P_N and P_A (Brussels). As possible candidates for the description of the influences of external factors the time series of atmospheric temperature (TEMP), barometric pressure (PRES), the Wolf sunspot numbers (WOLF) and the 2800 MHz flux, measured at Ottawa (FLUX), are represented in Figure 3.

*Available from the International Committee for Research and Study of Environmental Factors, CIFA (ULB CP 196), Av. Roosevelt 50, 1050 Brussels.

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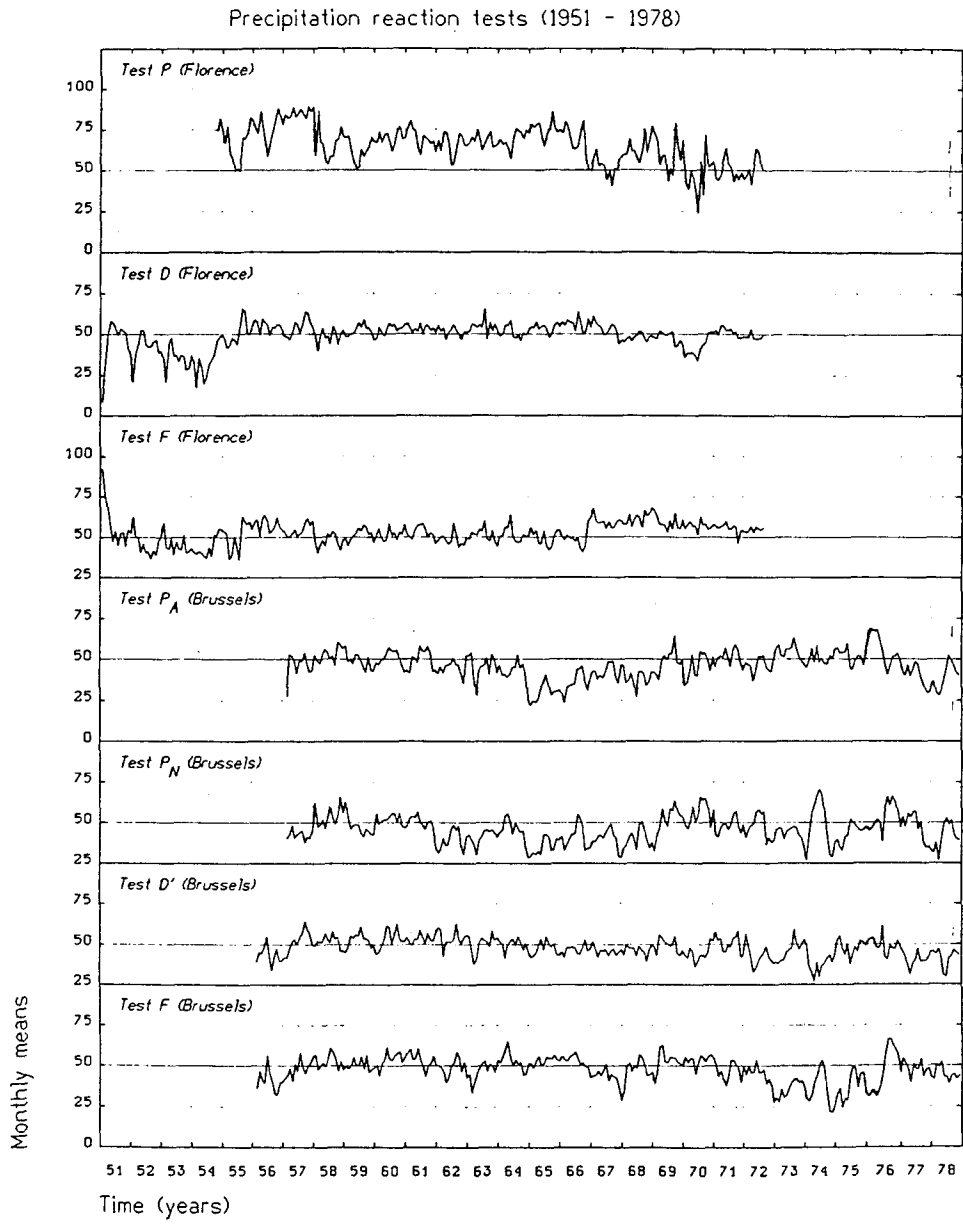Fig. 1. Monthly means of the chemical tests F, D′, P_N and P_A (Brussels) and F, D and P (Florence).
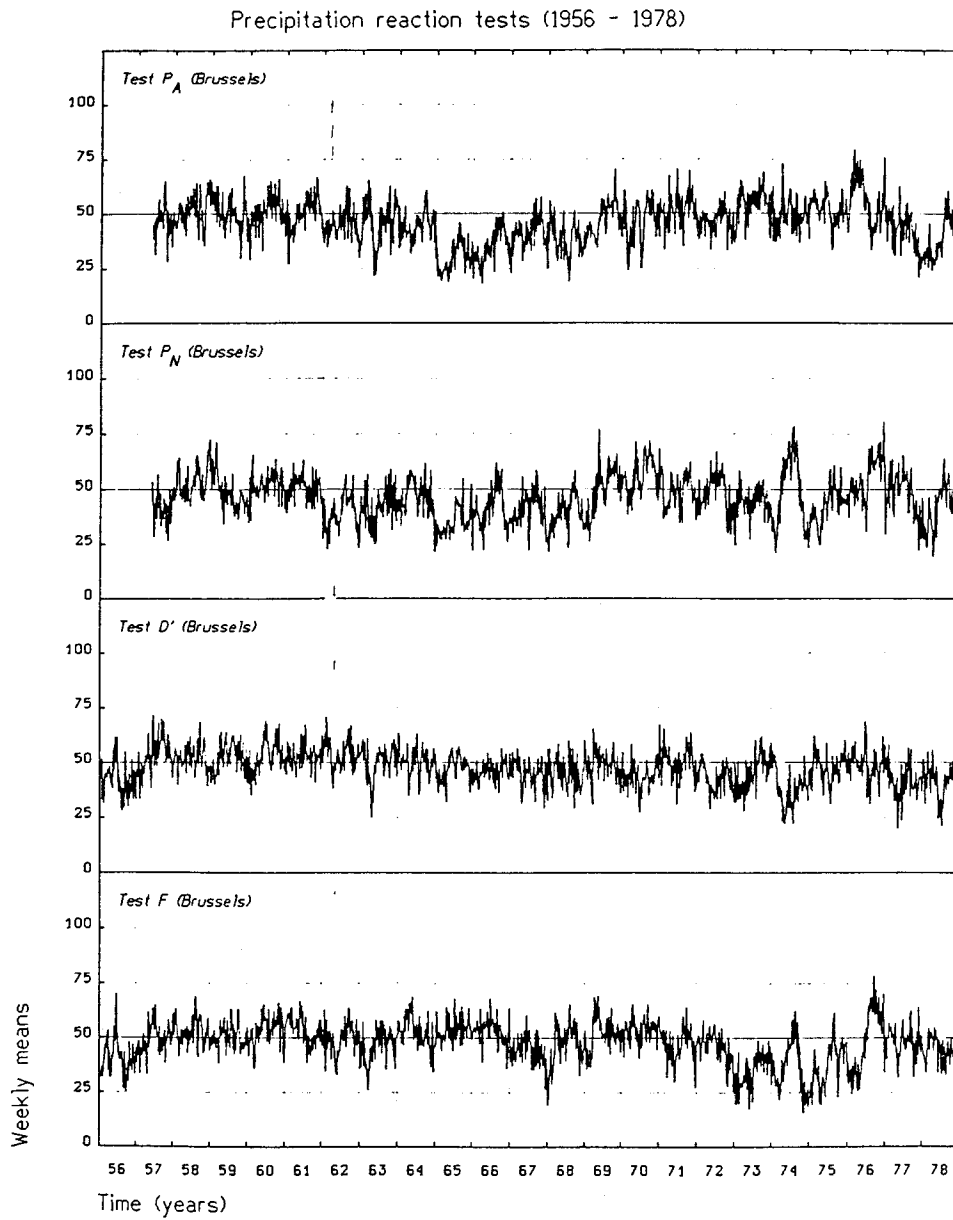
Precipitation reaction tests (1956 - 1978)

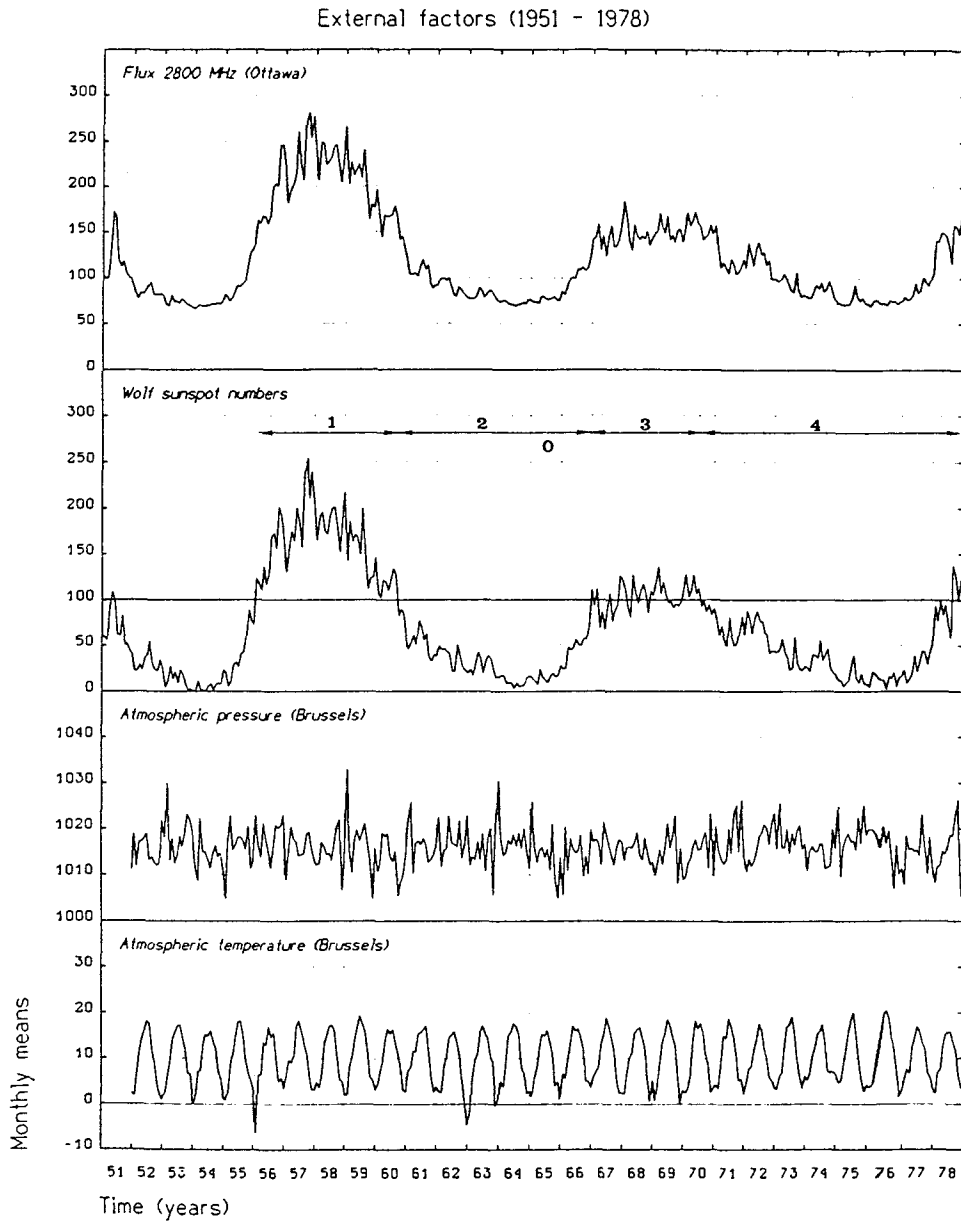Fig. 2. Weekly means of the chemical tests F, D', P_N and P_A (Brussels).

Fig. 3. External factors

3. STATISTICAL ANALYSIS

At the outset it is imperative to investigate the homogeneity of the observations. Table 1 summarizes the main statistical characteristics using n monthly means.

For each of the data sets, visualized in Figure 1, a Gaussian distribution is fitted to the empirical distribution function. Figure 4 shows the histograms obtained from the monthly means of the measurements. The dotted curve represents the normal probability density resulting from the arithmetical mean m and the sample standard deviation s in Table 1. To test the null hypothesis H_0 that the sample is drawn from a population obeying a normal probability law with mean m and standard deviation s, the Kolmogorov-Smirnov test (Sneyers, 1975) computes the probability α_K of being incorrect that H_0 may be rejected. In a way the result of this parametric test may be interpreted as the probability of correctness of the null hypothesis.

Table 1. Statistical analysis of the monthly means of the chemical tests

Brussels	n	α_k	m	s	t_μ	r_s	α_s	$u(\tau)$	α_M	Trend
F	274	0.04	47.59	8.21	4.86	-0.27	0.00	-4.35	0.00	D*
D′	274	0.80	47.59	6.53	6.11	-0.42	0.00	-7.17	0.00	D
P_N	262	0.58	45.96	8.83	7.41	0.02	0.72	0.36	0.72	N
P_A	262	0.30	45.96	8.65	7.56	0.00	0.97	0.13	0.90	N
Florence	n	α_k	m	s	t_μ	r_s	α_s	$u(\tau)$	α_M	Trend
F	260	0.73	52.53	7.31	5.58	0.39	0.00	6.06	0.00	I
D	260	0.00	49.23	8.22	1.51	0.14	0.02	2.18	0.03	I
P	215	0.31	65.05	12.13	18.19	-0.53	0.00	-7.88	0.00	D

t_δ-values for comparison of means						
Brussels	D′	P_N	P_A	Florence	D	P
F	0.00	2.22	2.25	F	4.83	13.87
D′		2.44	2.48	D		16.86
P_N			0.00			

F-values for variance of ratio test						
Brussels	D′	P_N	P_A	Florence	D	P
F	1.58	1.16	1.11	F	1.26	2.75
D′		1.83	1.75	D		2.18
P_N			1.04			

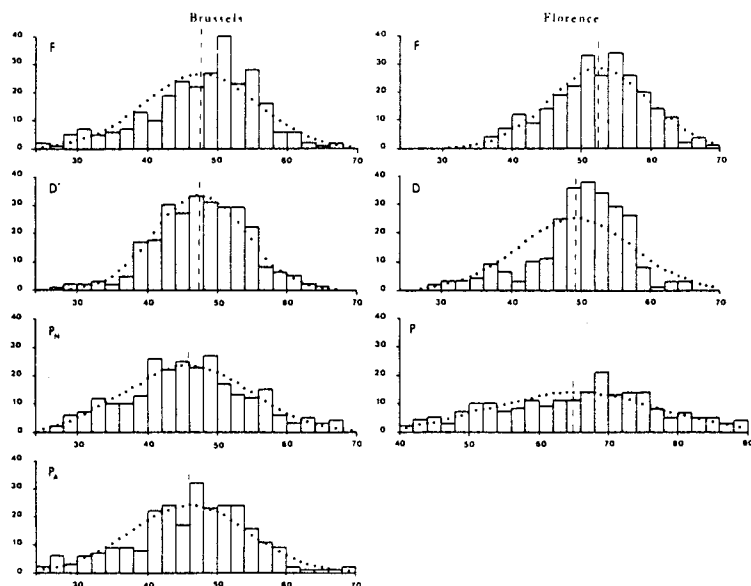* I = increasing trend, D = decreasing trend, N = no trend

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Fig. 4. Histograms chemical tests.

From a pure statistical point of view it follows from Table 1 that, in a strict sence, the null hypothesis cannot be rejected at the 80% confidence level for the test D' (Brussels) only, whereas it cannot be accepted for the other chemical tests. Nevertheless it is concluded from Figure 4 that the histograms are reasonably well approximated by a Gaussian probability density.

The Student's t-test (Brandt, 1973) is used to verify the hypothesis of an expectation value $\mu = 50$ for all chemical tests. Table 1 gives the computed t-values $t_\mu = (|m-\mu| \sqrt{n})/s$, with $\mu = 50$, which are to be compared with the α-fractile $t_{1-\alpha/2}$ of the t-distribution with n-1 degrees of freedom. For $\alpha = 0.01$ and $n > 200$ we have that $t_{0.995} \approx 2.86$. Therefore it is concluded from the values t_μ in Table 1 that the null hypothesis $H_0 : \mu = 50$ is rejected at the confidence level of 99% for all chemical tests, except for D (Florence), where rejection of H_0 only corresponds to a confidence level of 85%. Perhaps with exception of the test D (Florence) the arithmetical averages of the chemical tests may consequently be interpreted to be significantly different from the *a priori* expected value $\mu = 50$.

The equality of sample means can be validated by Student's difference test (Brandt, 1973). Suppose that from two independent samples of sizes n_1 and n_2 the arithmetical means m_1 and m_2, which are estimates of their respective population means μ_1 and μ_2, and standard deviations s_1 and s_2 are obtained. Denoting by $s^2 = [(n_1-1)s^2_1 + (n_2-1)s^2_2] (n_1 + n_2 - 1)$ the pooled estimate of variance, the null hypothesis $H_0 : \mu_1 = \mu_2$ may be tested by comparing the computed t-value $t_\delta = \delta/s_\delta$, with $\delta = |m_1 - m_2|$ and $s_\delta^2 = (n_1 + n_2)s^2/n_1 n_2$, with the fractile $t_{1-\alpha/2}$ of Student's t-distribution with $n_1 + n_2 - 2$ degrees of freedom, corresponding to the significance level α. If $t_\delta > t_{1-\alpha/2}$ the hypothesis of equal sample means has to be rejected at the confidence level $1 - \alpha$.

The values t_δ in Table 1 are compared with the theoretical value $t_{1-\alpha/2} \cong 1.97$ for $\alpha = 0.1$ and $n_1 + n_2 - 2 > 500$ degrees of freedom. It is concluded that the sample means of F and D', P_N and P_A (Brussels) cannot be considered to be different at the confidence level 95%, whereas the sample means of the other combinations may be regarded as being unequal. In an analogous way it follows from Table 1 that the sample means of F and D, F and P, D and P (Florence) are definitely different, since $t_{1-\alpha/2} \cong 3.31$ for $\alpha = 0.001$ and $n_1 + n_2 - 2 > 500$ degrees of freedom.

For the test of equality of two variances the null hypothesis is $H_0 : s_1^2$ and s_2^2 are from independent random samples following a normal probability law with the same variance. The variance ratio test (Snedecor and Cochran, 1978), uses the criterion $F = s_1^2 / s_2^2$ (where s_1^2 is the larger variance), which is compared with the $(1 - \alpha)th$ percentile $F_{1-\alpha}$ (n_1, n_2) of Fisher's F-distribution with (n_1, n_2) degrees of freedom. If $F > F_{1-\alpha}(n_1, n_2)$ the null hypothesis is rejected at the confidence level $100 (1 - \alpha)$ percent.

Since $F_{1-\alpha}(n_1, n_2) \cong 1.25$ for $\alpha = 0.05$ and $n_1 = n_2 = 250$ it follows from Table 1 that the variances of F and P_N, F and P_A, P_N and P_A (Brussels) cannot be considered as being different at the 95% confidence level, whereas the variances for the combinations F and D', D' and P_N, D' and P_A are definitely different. The last conclusion also holds for the combinations F and D, F and P, D and P (Florence).

To examine the random characteristics of a series of observations the null hypothesis consists of the assumption that the data are drawn from the same population and that they are independent. Two non-parameteric statistical tests can be used to elucidate a possible trend in the measurements (Sneyers, 1975).

Using a table of the normal distribution the Spearman test determines the probability $\alpha_s = \text{Prob} \{|u| > |u(r_s)|\}$, with r_s the Spearman rank correlation coefficient and $u(r_s) = r_s\sqrt{n-1}$. The null hypothesis is accepted or rejected at the significance level α whether $\alpha_s > \alpha$ or $\alpha_s < \alpha$. For significant values of r_s an increasing (I) or decreasing (D) trend is concluded according to $r_s > 0$ or $r_s < 0$.

Under the null hypothesis the probability law of the Kendall rank correlation coefficient τ is asymptotically a normal distribution with mean $E\{\tau\} = n(n-1)/4$ and variance $\sigma^2(\tau) = n(n-1)(2n+5)/72$. In the Mann test the probability $\alpha_M = \text{Prob} \{|u| > |u(\tau)|\}$ is determined by using a table of the normal distribution, where $u(\tau) = [\tau - E\{\tau\}]/\sigma(\tau)$. The null hypothesis is then accepted or rejected at the confidence level $1-\alpha$ whether $\alpha_M > \alpha$ or $\alpha_M < \alpha$. For significant values of $u(\tau)$ an increasing (I) or decreasing (D) trend is concluded according to $u(\tau) > 0$ or $u(\tau) < 0$.

Table 1 includes the statistics r_s and $u(\tau)$, as well as the associated probabilities α_s and α_M. From the Spearman and Mann tests it is remarked that no trend (N) can be detected for the chemical tests P_N and P_A (Brussels), whereas the null hypothesis of random behaviour can be rejected for the other chemical tests, for which an overall positive or negative trend is concluded.

Table 2 compiles the results of a trend analysis of the monthly means of the four tests at Brussels, selecting for each sample 262 observations covering the same observing interval (March 1957–December 1978). Each data set as a whole, indicated by the index 0 in Table 2, is subdivided *a priori* into three consecutive and non-overlapping intervals (numbered 1, 2 and 3), containing 87, 87 and 88 measurements, respectively. These three subsamples refer to the epochs March 1957–May 1964, June 1964–August 1971 and September 1971–December 1978.

From Table 2 it is obvious that the mean value m of each chemical test varies considerably in time, as particularly indicated in $(F)_3$, $(D')_3$, $(P_N)_2$ and $(P_A)_2$. The same

Table 2. Trend analysis of the monthly means of the chemical tests (Brussels)

Test	n	m	s	r_s	α_s	$u(\tau)$	α_M	Trend
$(F)_0$	262	47.90	8.16	−0.37	0.00	−5.84	0.00	D
$(F)_1$	87	51.09	5.51	0.01	0.92	0.33	0.74	N
$(F)_2$	87	50.07	5.95	−0.05	0.63	−0.47	0.64	N
$(F)_3$	88	42.60	9.55	0.20	0.06	1.85	0.12	N
$(D')_0$	262	47.80	6.51	−0.52	0.00	−8.65	0.00	D
$(D')_1$	87	52.31	5.09	−0.07	0.60	−0.53	0.60	N
$(D')_2$	87	47.11	4.26	−0.09	0.38	−0.88	0.38	N
$(D')_3$	88	44.03	6.97	−0.09	0.44	−0.84	0.40	N
$(P_N)_0$	262	45.96	8.83	0.02	0.72	0.36	0.72	N
$(P_N)_1$	87	46.80	7.17	−0.24	0.03	−1.97	0.00	D
$(P_N)_2$	87	44.14	9.24	0.53	0.00	5.05	0.00	I
$(P_N)_3$	88	46.93	9.67	−0.07	0.54	−0.47	0.64	N
$(P_A)_0$	262	45.96	8.65	0.00	0.98	0.13	0.90	N
$(P_A)_1$	87	48.10	6.33	−0.30	0.01	−2.69	0.01	D
$(P_A)_2$	87	41.17	8.82	0.56	0.00	5.72	0.00	I
$(P_A)_3$	88	48.58	8.58	−0.38	0.00	−3.43	0.00	D

conclusion can be advanced for the standard deviation s. It appears that the mean values of F and D' decrease towards the end of the observing interval, whereas the mean values of P_N and P_A are lower for the second subdivision. As for the trend statistic it is interesting to note that it changes sign over the whole observing interval in a significant way, so that the trend detected seems to be dependent on the time interval chosen. Because the statistical information content of each chemical test is time-dependent this implies that the time sequences of observations are non-stationary in time.

In an attempt to correlate this irregular trend behaviour of the precipitation reaction tests with the external factor of solar activity the time series from March 1957 till November 1978, indicated by the index 0 in Table 3, is now divided into four subsamples. Subsets 1 (March 1957 – September 1960) and 3 (January 1967 – July 1970) refer to the time intervals when the sunspot number R > 100, while subsets 2 (October 1960 –December 1966) and 4 (August 1970 – November 1978) cover the epochs of the minimum of the solar cycle when R < 100. This subdivision is clearly chosen in relation with the periods of different intensity of the solar activity as shown in Figure 3. Table 3 summarizes the associated trend analysis. Note that the trends, indicated in Tables 1, 2 and 3, are considered to be statistically significant whenever $\alpha_M \leqslant 0.05$.

4. SPECTRAL ANALYSIS

The identification of fundamental periodicities in a time series plays an important part in understanding the sources of the fluctuations. For this purpose the method of power spectrum analysis is a valuable tool because the inherent periodicities appear as relatively

Table 3. Trend analysis of the monthly means of the chemical tests (Brussels)

Test	n	m	s	r_s	α_s	$u(\tau)$	α_M	Trend
$(F)_0$	261	47.92	8.17	-0.37	0.00	-5.78	0.00	D
$(F)_1$	43	51.15	4.61	0.23	0.14	1.73	0.08	N
$(F)_2$	75	51.65	5.30	0.06	0.59	0.83	0.41	N
$(F)_3$	43	48.36	6.75	0.59	0.00	3.57	0.00	I
$(F)_4$	100	43.54	9.55	-0.02	0.83	-0.50	0.62	N
$(D')_0$	261	47.81	6.52	-0.51	0.00	-8.60	0.00	D
$(D')_1$	43	52.33	5.08	0.02	0.89	0.24	0.81	N
$(D')_2$	75	50.43	5.16	-0.54	0.00	-4.67	0.00	D
$(D')_3$	43	46.22	4.15	-0.05	0.76	-0.12	0.91	N
$(D')_4$	100	44.60	6.92	-0.20	0.05	-1.84	0.07	N
$(P_N)_0$	261	45.99	8.83	0.03	0.63	0.47	0.64	N
$(P_N)_1$	43	49.06	6.59	0.41	0.01	2.86	0.00	I
$(P_N)_2$	75	42.53	7.58	-0.39	0.00	-3.28	0.00	D
$(P_N)_3$	43	44.92	8.77	0.64	0.00	4.09	0.00	I
$(P_N)_4$	100	47.72	9.70	-0.15	0.14	-1.45	0.15	N
$(P_A)_0$	261	45.98	8.66	0.01	0.88	0.24	0.81	N
$(P_A)_1$	43	49.74	5.96	0.16	0.31	1.02	0.31	N
$(P_A)_2$	75	41.77	9.12	-0.64	0.00	-5.43	0.00	D
$(P_A)_3$	43	42.73	6.96	0.23	0.14	1.48	0.14	N
$(P_A)_4$	100	48.98	8.17	-0.31	0.00	-2.97	0.00	D

sharp peaks in the spectral curves, rising above a continuous background generated by the coloured noise. It is obvious that the only guarantee that the lines detected correspond to real physical mechanisms is a high signal-to-noise ratio in the spectral peaks. Any definite interpretation of a power spectrum is generally thwarted by the presence of the subharmonics of the fundamental periodicities, which is a consequence of the circumstance that most cyclic variations are not strictly sinusoidal. Moreover, pseudoperiodicity tends to broaden the spectral lines.

The computation of the least squares periodogram in the form of the F-spectrum (De Meyer, 1986) is a straightforward and unsophisticated numerical method for detection of hidden periodicities in time series. To avoid as much as possible the personal bias this relatively simple technique is preferred in this context, also because it validates the statistical significance of the spectral peaks detected.

Let $\tilde{y}_1,...,\tilde{y}_n$ be n ordinates of a continuous time function y(t), which is sampled at the time instants $t_1,..., t_n$. Assuming that the polynomial trend is linear and writing $\tilde{y}_j = y_j + \beta t_j$ the majorities of the trend contributions, which are not interesting in terms of periodicities, are reduced by removing a least squares line from the observations $\tilde{y}_j$. This procedure of trend reduction acts as a high-pass filter and it must be clearly stated that the influence of removing any trend from the data can have a drastic effect in the low-frequency range. It is now the intention to examine the residuals $y_j = \tilde{y}_j - \hat{\beta} t_j$ for

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periodic behaviour, where $\hat{\beta}$ denotes the least squares estimate of the trend coefficient β. Hereafter the term "observations" will stand for the detrended data y_j.

As a model of periodic behaviour a cosine function of an *a priori* chosen frequency $f = 1/T$ can be fitted to the observations

$$y_j = M + a \cos 2\pi f t_j + b \sin 2\pi f t_j + \epsilon_j , \qquad (1)$$

where ϵ_j denotes the model error at time t_j. Writing $(\hat{M}, \hat{a}, \hat{b})$ for the least squares estimate of the model parameters (M, a, b), the null hypothesis $H_0 : a = b = 0$ is rejected at the confidence level $1-\alpha$ if $F > F_{1-\alpha}(2, n-3)$, where

$$F = \frac{1}{2(1 - r^2_{ab})} \left[\left(\frac{\hat{a}}{s_a}\right)^2 - 2r_{ab}\left(\frac{\hat{a}}{s_a}\right)\left(\frac{\hat{b}}{s_b}\right) + \left(\frac{\hat{b}}{s_b}\right)^2 \right] ,$$

(Anderson, 1971), which may then be interpreted in the sense that a periodic oscillation with frequency f is significantly detected in the observations. In equation (1), s_a and s_b are the estimated standard errors of $\hat{a}$ and $\hat{b}$, $r_{ab} = s_{ab} / (s_a s_b)$ is the correlation coefficient of $\hat{a}$ and $\hat{b}$ and s_{ab} is their covariance. These quantities are obtained from the diagonal and off-diagonal elements of the covariance matrix of the least squares estimate.

Taking f at a number of points in a given frequency interval, estimates of the model parameters, associated with the cosine model of arbitrary frequency, are obtained by the least squares technique, as well as s_a, s_b and s_{ab}. Accordingly, the quantity F in equation (2) becomes a function of frequency, representing in this manner the F-spectrum $F(f)$ of the observations (De Meyer, 1986).

If the data contain a true harmonic wave with frequency f_0, the F-spectrum reveals the location of the matching period $T_0 = 1/f_0$ in the shape of a sharp peak centered at $f = f_0$, rising significantly above the level, defined by the theoretical threshold $F_{1-\alpha}(2, n-3)$ for the chosen α and indicating that the cosine model with frequency $f = f_0$ is significant at the confidence level $1-\alpha$.

This numerical technique essentially searches for hidden periodicities in a time series on a probabilistic base. Since the data sets in question comprise only observations of a relatively limited extent, period identification at high-resolution in the low-frequency interval evidently becomes unreliable. The fact that the time series of the chemical tests have a strong stochastic characteristic entails that the spectral curves will have a disturbed appearance, which implies that a number of small spurious peaks can be created by the noise fluctuations.

Because the observing interval is inevitably finite, side lobe effects are evidently expected to show up in the computed spectra, but at least we are familiar with this inconvenience, since the side lobes, accompanying a strong peak, can be exactly located in frequency (Jenkins and Watts, 1968). When the fundamental lines are closely spaced, the side lobes of each spectral peak become superimposed upon some of the other lines and introduce period, amplitude and phase errors. This effect is particularly important when a strong line is present.

These disagreeable properties are common to all power spectrum techniques but an advantage of the F-spectrum is that it is less sensitive to the coloured noise inherent in the data, because it is in principle impossible to fit a harmonic model significantly to a random sequence. Moreover, rather realistic confidence limits for the F-spectrum are provided, although the presence of residual autocorrelation tends to underestimate the theoretical rejection level $F_{1-\alpha}(2, n-3)$.

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Figures 5 and 6 respectively illustrate the F-spectra of the monthly means of the data
sets for Brussels and Florence. The frequency f is in cycles/year (cpy) and the matching
periods, corresponding to the spectral peaks rising significantly above the theoretical
threshold $F_{0.95}$, are indicated in years.
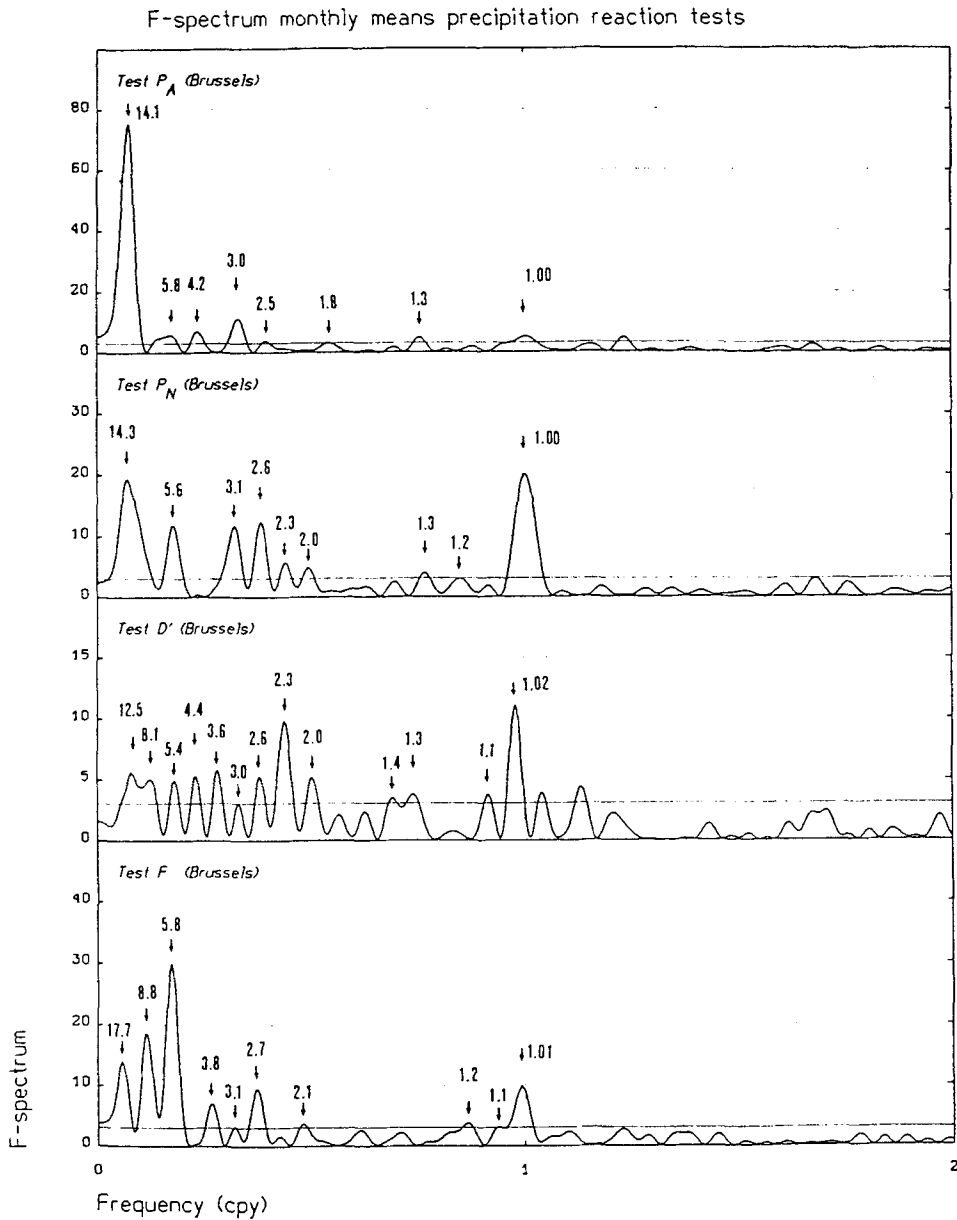
F-spectrum monthly means precipitation reaction tests

Fig. 5. F-spectrum of the monthly means of the precipitation reaction tests (Brussels).
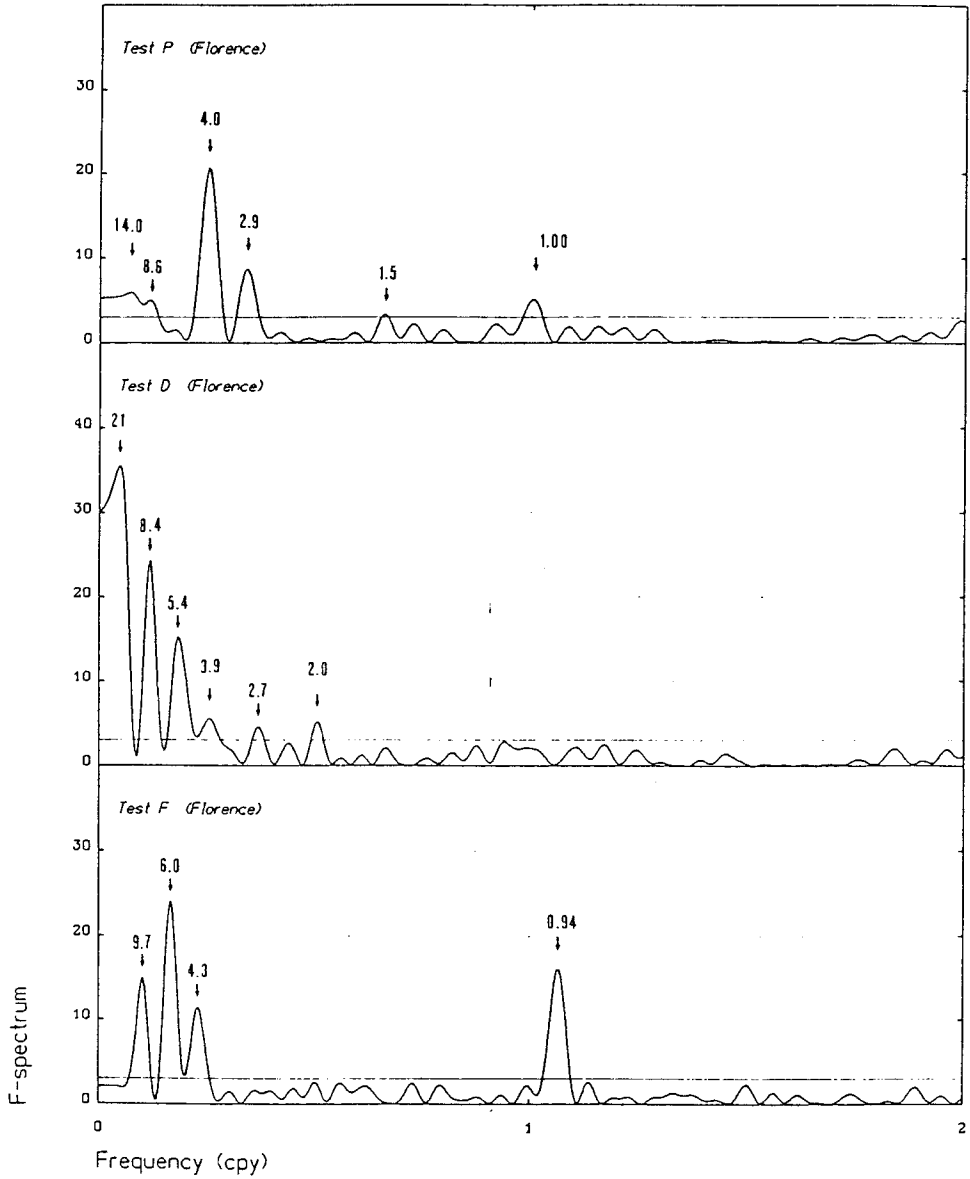
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Fig. 6. F-spectrum of the monthly means of the precipitation reaction tests (Florence).

For the observations obtained at Brussels the test P_N reveals an important annual line, whereas it is less pronounced in D', F and P_A. In consequence it is concluded that a significant annual variation is present in the four chemical tests. A marked peak near 14.2 years appears in P_N and P_A, but the morphological features of the spectrum of F and D' are less plain at the very low frequencies although the existence of a long-period cyclic variation is suggested.

It is important to consider that the precipitation reaction tests, collected at Brussels and Florence, do not refer to the same observing interval. In Figure 6 a nearly annual peak (period 0.94 year) is striking in F and to a less degree in P, but is absent in D. Lines are present in the vicinity of the period of the solar cycle, but it must be remarked that period identification at this resolution is inaccurate. Also a contribution near 5.5 years (second harmonic of the solar cycle) is noted in F and D, but it is almost inexistent in P.

The F-spectra in Figure 5 are confirmed by the diagrams in Figure 7, which are obtained from the weekly means of the chemical tests at Brussels. Lines at the same periods as in Figure 5 are relevant. Again a significant annual variation is stressed and P_N and P_A demonstrates a strong line at about 14.2 years. This result is a strong indication that the long-term peaks are not artefacts of the numerical technique used and that they are no by-product of an aliasing effect introduced by oversampling of the measurements. As could be expected the procedure of taking monthly means only performs a low-pass filtering of the daily values.

It is remarked that the records in Figure 3 are subjected to the very same numerical treatment by first subtracting a least squares linear trend from these observations. Considering the F-spectra of the external factors in Figure 8 an important peak is evidently present at one year in the atmospheric temperature, whereas the line is less plain in the barometric pressure, which on the contrary reveals an important peak at 1.15 years. In addition the latter time series exhibits apparent variations at 3.8, 2.8 and 0.82 years. In the Wolf sunspot numbers and the solar flux data the mean solar cycle period at 11.0 years stands out clearly, while the peak at 5.4 years is interpreted as its second harmonic. The two small peaks close to the 11.0 years period are concluded to be the first side lobes of this line.

5. HARMONIC ANALYSIS

Once a number of frequencies $f_1,...,f_p$ are identified in a given time series by the apparent peaks in the F-spectrum, the amplitudes A_k and phases Φ_k of the associated variations with periods $T_k = 1/f_k$, $k = 1, ...,p$, are estimated by fitting a trigonometric model

$$\bar{y}_j = M + \beta t + \sum_{k=t}^{p} A_k \cos(2\pi f_k t_j + \Phi_k) + \epsilon_j \tag{3}$$

to the observations. Estimates of the model parameters $M, \beta, a_k = A_k \cos \Phi_k, b_k = -A_k \sin \Phi_k$ are again obtained by the least squares algorithm. A zero amplitude test for each frequency f_k can be performed by comparing the computed F-value F_k with the theoretical rejection value $F_{1-\alpha}(2, n - 2p - 2)$ for the significance level α considered (De Meyer, 1986).

A measure of goodness of fit of the linear regression model (3) is the multiple correlation coefficient R, with $R^2 = SSR/TSS$, where TSS is the total sum of squares of the observations and SSR is the sum of squares due to the regression. A value $R^2 = 1$

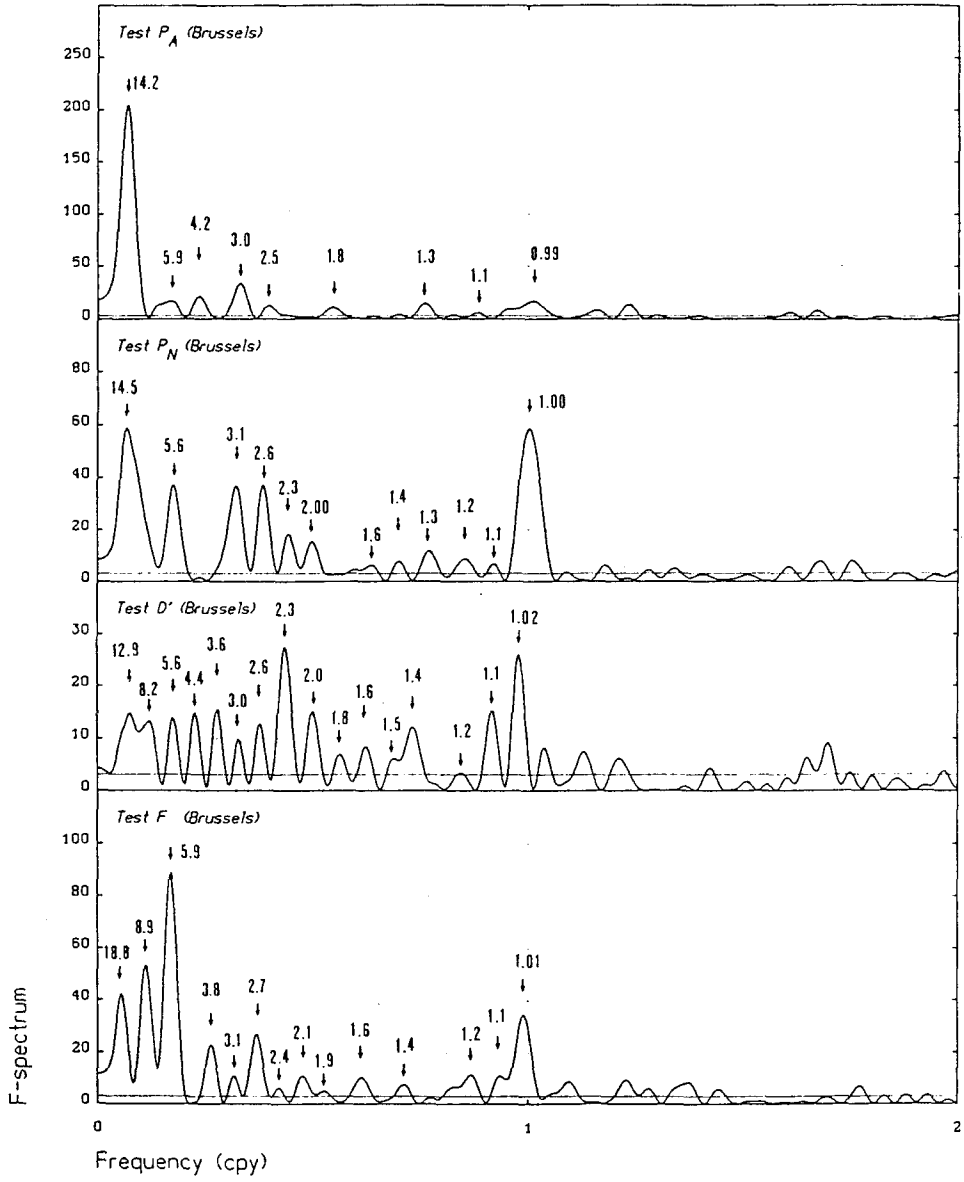F-spectrum weekly means precipitation reaction tests

Fig. 7. F-spectrum of the weekly means of the precipitation reaction tests (Brussels).
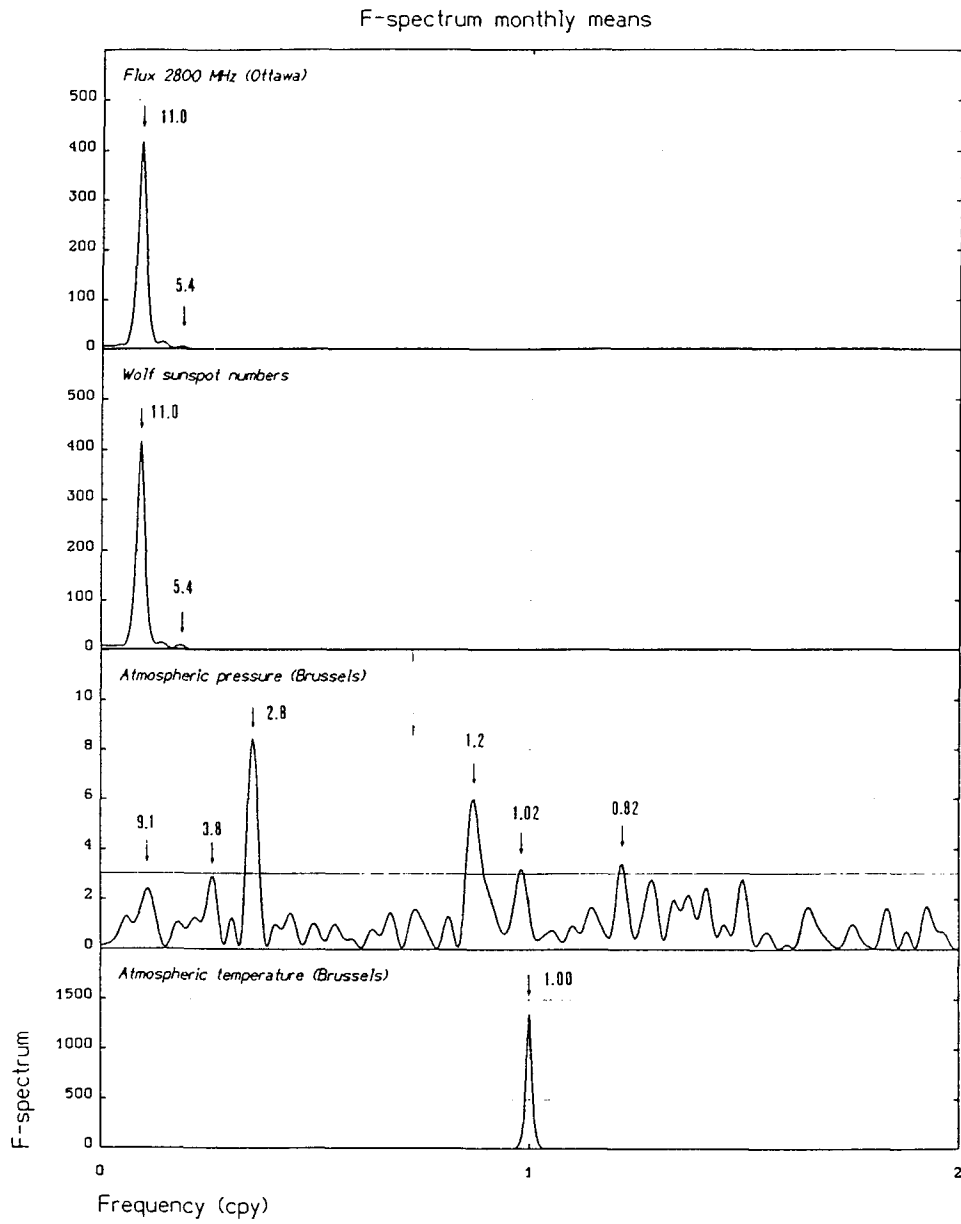
Fig. 8. F-spectrum of the monthly means of the external factors.

indicates a perfect fit of the trigonometric constituents to the measurements, whereas a value $R^2 = 0$ implies that the model gives a completely inefficient description of the data. The quantity $ESS = 100\ R^2$ (explained sum of squares) may therefore be interpreted as the percentage of the variance of the observations, explained by the trigonometric model as a whole.

Since the periods of the apparent lines in the F-spectra of Figures 5, 6 and 8 are reasonably well defined, the amplitudes and phases of the attendant periodic oscillations are obtained by fitting a harmonic model of the form (3) to the observations. The estimated trend coefficients $\hat{\beta}$, together with their standard deviations s_β and t-values $t_\beta = \hat{\beta}/s_\beta$, are summarized in Table 4, whereas the results of the harmonic analysis are compiled in Tables 5 and 6. The periods T_k are expressed in years, F_k denotes the computed F-value for the harmonic wave with period T_k and $F_{0.95}$ is the theoretical F-level for $\alpha = 0.05$. The phases Φ_k are expressed in degrees.

Table 4 shows that, except for the chemical test P_N (Brussels), the estimated trend coefficients $\hat{\beta}$ are significantly different from zero at the confidence level of 95% since the computed t_β-values are larger than the theoretical t-value $t_{0.98} \cong 1.97$ for more than 200 degrees of freedom. Moreover it is concluded from Table 5 and 6 that almost all periodic variations detected are significantly resolved at the 95% confidence level, but it must be considered that the low-frequency components in the harmonic models are inaccurately established in period.

The phase Φ_k determines the dates of the extrema of the model constituent with period T_k at the time instants

$$t_{extr} = \frac{1}{2}\ T_k\left(n - \frac{\Phi_k}{180}\right), \quad n = 0, \pm 1, \pm 2, \ldots \tag{4}$$

with Φ_k in degrees. A maximum results at the time t_{max} whenever the integer n is even and a minimum at t_{min} is found for n odd. For example, taking $n = 2$ in equation (4) and $\Phi = 174°$ (Table 5) for the phase of the annual component of the atmospheric temperature, the maximum at $t_{max} = 6.20$ months follows. Since the origin $t = 0$ refers to January 15, 1951 this date corresponds to July 23, which evidently coincides with the date of the maximum of the annual variation in atmospheric temperature. Since the standard deviation of Φ is $1°$ the standard error of t_{max} is estimated to be 1 day.

In an analoguous way the dates t_{min} and t_{max} of the annual and cyclic variations in Tables 5 and 6 are computed from the phases and are compiled in Table 7. The time series F, D' P_N and P_A (Brussels) show maxima of the annual variation at the time instants August 13, October 26, August 10 and September 3, respectively, with a standard error of

Table 4. Trend coefficients of the chemical tests

Brussels				Florence			
Test	$\hat{\beta}$	s_β	t_β	Test	$\hat{\beta}$	s_β	t_β
F	−0.0355	0.0042	8.45	F	0.0303	0.0047	6.45
D'	−0.0436	0.0037	11.78	D	0.0345	0.0076	4.54
P_N	0.0091	0.0049	1.86	P	−0.1057	0.0097	10.90
P_A	0.0142	0.0046	3.09				

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Table 5. Harmonic analysis precipitation reaction tests (Brussels)

F				D'				P_N				P_A			
T_k	A_k	Φ_k	F_k	T_k	A_k	Φ_k	F_k	T_k	A_k	Φ_k	F_k	T_k	A_k	Φ_k	F_k
17.65	2.8	58	19.4	12.54	1.6	38	8.3	14.32	4.5	171	38.1	14.14	7.5	144	114.0
8.78	3.0	308	22.6	8.07	1.8	253	11.6	5.62	3.2	167	19.9	5.81	1.7	313	6.2
5.81	4.2	194	42.8	5.75	1.1	203	4.0	3.09	3.0	268	16.7	4.24	1.9	34	7.4
3.75	1.9	33	9.2	4.35	1.1	97	4.0	2.59	3.0	332	16.0	3.02	2.9	224	16.3
2.68	2.3	85	13.2	3.55	1.3	354	5.5	2.25	1.6	186	4.9	2.52	1.5	284	4.6
2.07	1.7	234	7.3	2.62	1.3	80	5.7	2.01	2.2	107	9.1	1.83	1.7	287	6.4
1.62	1.6	315	6.7	2.27	2.1	355	14.4	1.57	0.9	113	1.9	1.32	2.1	340	9.1
1.40	1.4	212	5.3	1.98	1.5	218	7.6	1.43	1.3	237	3.0	1.13	1.6	241	5.2
1.15	1.8	224	7.9	1.77	0.9	148	3.0	1.30	1.9	302	6.8	1.00	2.4	133	12.4
1.06	1.7	223	7.0	1.44	1.5	58	7.6	1.17	1.9	349	6.6	0.88	1.4	172	4.4
1.00	3.0	154	22.6	1.35	1.4	49	6.7	1.09	1.3	224	2.9				
				1.18	0.8	233	2.2	1.00	4.7	156	42.9				
				1.09	1.2	40	5.2								
				1.00	1.5	81	8.6								
				0.96	1.6	7	8.4								
				0.88	1.5	129	8.0								

$F_{0.95}$	3.03		3.01		3.03		3.00
ESS	66%		63%		63%		64%

TEMP				PRES				WOLF				FLUX			
T_k	A_k	Φ_k	F_k	T_k	A_k	Φ_k	F_k	T_k	A_k	Φ_k	F_k	T_k	A_k	Φ_k	F_k
7.60	0.5	314	6.5	9.08	0.8	195	2.9	10.97	68.5	111	651	10.96	61.9	111	610
2.50	0.4	260	3.8	3.81	0.7	179	2.3	5.43	18.8	274	49.0	5.38	14.3	259	32.4
1.00	7.5	174	1688	2.81	1.3	39	8.0								
0.50	0.3	281	2.9	1.15	1.1	332	6.1								
				1.00	0.5	160	1.1								
				0.82	0.8	174	3.6								

Table 6. Harmonic analysis precipitation reaction tests (Florence)

	F				D				P		
T_k	A_k	Φ_k	F_k	T_k	A_k	Φ_k	F_k	T_k	A_k	Φ_k	F_k
9.74	2.8	54	14.3	20.95	4.8	182	44.1	14.02	3.2	11	10.2
5.96	3.2	18	20.8	8.37	2.9	70	14.1	8.55	3.2	107	6.8
4.33	2.1	316	9.1	5.39	2.9	350	15.8	3.96	6.2	136	37.3
0.94	3.4	301	29.6	3.88	2.0	251	7.5	2.93	3.8	317	13.9
				2.70	2.0	122	8.4	1.51	2.9	230	8.9
				1.97	2.3	249	10.8	1.00	3.7	8	14.7
				1.00	1.4	140	4.3				
$F_{0.95}$	3.00				3.00						3.00
ESS	48%				57%						67%

approximately 15 days, whereas the maximum in the time series TEMP is situated at July 23 with a standard error of 1 day. For the test P (Florence) a significant annual variation is detected, whereas its maximum is located at January 8, while the maximum of the annual variation in the F and D tests occurs on March 6 and August 27, respectively. Because the periods of the cyclic variations in the solar cycle data and the chemical tests are so different, no reliable conclusion can be advanced concerning a relationship between the epochs of the maxima of these oscillations.

From Tables 5 and 6 it is seen that the values of the explained sum of squares EES for all chemical tests range between 48% and 67%, which means that the harmonic models proposed explain an important part of the variance of the respective variations. In consequence it is concluded that the long-term behaviour of the observations of the chemical tests can be significantly approximated by deterministic harmonic models with relatively few numbers of constituents.

6. CONCLUSIONS

This study contributes to answer by appropriate statistical methods the two fundamental questions which led to start the long-term series of Piccardi chemical tests, carried out daily in Florence (Piccardi and co-workers, 1951-1972) and Brussels (Capel-Boute, 1956-1978).

The purpose was to investigate the anomalous variability in the course of time observed in the effects of a physical treatment of water, even in the most rigorously standardized conditions for a chemical inorganic precipitation reaction in an aqueous medium (F-test). Secondly, the intention was to test the hypothesis of possible disturbing factors of external origin, by executing the same test in different places and in differently screened environmental conditions (D,D'-tests) and to investigate simultaneously the fluctuations observed on the screen-effect itself (tests P, P_N, P_A).

It is apparent that the time variability of the observed effects in Piccardi's precipitation reaction tests cannot be considered as being purely random, in the sense of a purely white noise fluctuation, because the statistical information content changes in time, which implies non-stationarity of all time series considered.

Table 7. Dates of the extrema of the harmonic variations

	F T	F t_{min}	F t_{max}	D' T	D' t_{min}	D' t_{max}	P_N T	P_N t_{min}	P_N t_{max}	P_A T	P_A t_{min}	P_A t_{max}
	1.0	11 Feb	13 Aug	1.0	26 Apr	26 Oct	1.0	9 Feb	10 Aug	1.0	4 Mar	3 Sep
	8.8	Jun '65	Dec '69	12.5	Jul '68	Apr '62	14.3	Sep '65	Nov '72	14.2	Aug '66	Aug '73

	F T	F t_{min}	F t_{max}	D T	D t_{min}	D t_{max}	P T	P t_{min}	P t_{max}
	0.94	15 Sep	6 Mar	1.0	25 Feb	27 Aug	1.0	9 Jul	8 Jan
	9.7	Mar '64	Jan '69	8.4	Sep '67	Jul '63	14.0	Aug '71	Aug '64

	TEMP T	TEMP t_{min}	TEMP t_{max}	PRES T	PRES t_{min}	PRES t_{max}	WOLF T	WOLF t_{min}	WOLF t_{max}	FLUX T	FLUX t_{min}	FLUX t_{max}
	1.0	22 Jan	23 Jul	1.0	5 Feb	6 Aug	1.0	Feb '64	Aug '69	1.0	Feb '64	Aug '69
	9.1			9.1	Oct '68	Apr '64	11.0			11.0		

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The sample means of either treatment-effect tests (F and D') versus screen-effect tests (P_N and P_A) are almost certainly unequal and the sample means of all three tests in Florence (F, D and P) are definitively different. For all chemical tests mean values and standard deviations are significantly different for successive subdivisions in the observing interval.

Different significant trends, changing sign, appear in all tests in Florence and Brussels. They seem to be dependent on the time interval chosen, whether *a priori* or in function of periods of different intensity of the solar activity.

Significant annual and long-term variations are present in all data sets, but no common long-term pattern is observed. The observations of atmospheric temperature, barometric pressure, EM flux and Wolf sunspot numbers are included *a priori* in the analysis as possible candidates for the representation of environmental factors, but no unambiguous results point to a single or dominant cause.

Nevertheless it is concluded that at least a part of the influences responsible for non-reproducible results in space and time, in such physico-chemical processes in aqueous media, must come from physical factors of external origin. These results stress the necessity of search for disturbing geophysical, climatological and cosmological factors to understand the mechanisms of their interaction in aqueous media.

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