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J. Y. Cabon^a; A. Le Bihan^a

^a Laboratoire de Chimie Analytique, Brest, Cedex, France

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ANALYSIS AND TEMPORAL VARIATIONS OF TRACE METALS IN PRECIPITATION AT AN ATLANTIC STATION

J. Y. CABON* and A. LE BIHAN

*Laboratoire de Chimie Analytique, URA CNRS 322-UBO 6, Avenue Le Corgeu, BP 809,
29285 Brest-Cedex, France*

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Weekly and half-monthly bulk samples have been collected over one year at an Atlantic station and routinely analysed for 0.08 M HNO₃-leachable trace metals Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn by direct electrothermal atomic absorption spectrometry. In the presence of sea salt, interference effects may lead to important erroneous metal concentrations if peak height measurements and direct calibration with aqueous standards are used. Interference effects are minimized (to about 5%) by using integrated absorbance measurements for sea salt solutions having $C_{Na} < 100$ mg/l and using standards prepared in the presence of sea salt (20 mg/l in Na). The variability of trace-metal determinations obtained for six bulk collectors for each sampling event shows that our entire analytical protocol, sampling and analysis, permits to follow their temporal variations at a coastal station for weekly or half-monthly sampling periods. A high correlation is obtained for anthropogenic metals Cd, Cu, Ni, Pb and Zn. For Cr, Fe and Mn, significant correlations with anthropogenic metals indicate both anthropogenic and crustal sources. No correlation with Na is observed. At this Atlantic station, trace-metal concentrations and annual deposition densities are significantly lower than at European stations around the North Sea which are more subject to industrial emissions.

KEY WORDS: Precipitation, Atlantic, trace metals, sampling, analysis, variability, metal correlations.

INTRODUCTION

Atmospheric input represents one of the major sources of trace metals to the world ocean¹. They may be also in the same order of magnitude as inputs by rivers, dumping and discharges, as for example the North Sea^{2,3}. The dominant removal mechanism for atmospheric trace metals to the ocean⁴ and to the European continent⁴ is by wet deposition. However, reports of trace metals in precipitation are few in number due to the difficulties of collecting precipitation samples and to contamination problems at the low concentration levels which may be encountered at oceanic stations^{6,7}. This may partially explain the difficulties to estimate trace-metal deposits and to correlate them to model calculations from emission data⁸.

Among the various analytical methods used for determining trace metals in precipitation, atomic absorption spectrometry is the most widely used, with or without a preconcentration step, depending on the metal concentration level to be determined. Preconcentration is generally achieved by evaporation or by organic solvent extraction

* To whom all correspondence should be addressed.

with a complexing agent. This preconcentration step is obviously more prone to contamination problems and is also more time consuming than direct determination.

The aim of this paper is to evaluate the potential of direct electrothermal atomic absorption spectrometry to obtain representative data to estimate trace-metal deposition and to follow temporal trace-metal variations in precipitation samples of oceanic or continental origin, at a coastal station.

In non-polluted oceanic sites, sea salt is the major part of the rainwater saline matrix. Therefore, as a first step, we have examined the influence of sea salt at the concentrations level encountered at our sampling site on the atomization signals of trace metals. Data were obtained with a new electrothermal atomic absorption spectrometer which utilizes a transversely heated furnace and a longitudinal Zeeman-effect background correction system. This allowed the estimation of sea salt interference and the evaluation of the accuracy of trace-metal determinations in saline rainwaters, without the need to resort to the time-consuming standard addition method.

In the second part of this paper, we have tested our analytical protocol for sampling and analysis by determining the variability of 0.08 M HNO_3 -leachable trace metal concentrations in rainwater for weekly or half-monthly periods using six bulk deposition samplers over a one-year period. This has allowed an analysis of correlations between metal concentrations in precipitation.

EXPERIMENTAL SECTION

Site

Figure 1 gives the location of the sampling station. This site is part of the ATMOS pilot project on atmospheric inputs to Convention waters where wet deposition is monitored for trace metals. Porspoder site (F1) is situated 30 km north-west of Brest at about 500 m from the ocean and about 30 m above sea level. The sampling site is located in a field covered with low vegetation. This site is far from any important industrial sources, vehicular traffic or intensive agriculture. The major part of the precipitation is generally advected from the west and south-west and has an Atlantic origin.

Sampling

Precipitation was collected in six bulk collectors on a half-monthly basis and on a weekly basis during important precipitation periods. 1 l polyethylene bottles and 160-mm diameter polyethylene funnels from the Nalge company were used. The funnels were sealed onto polyethylene caps, then screwed onto the bottles; 230- μm mesh polyethylene macro filters were sealed in the lower part of the funnels to prevent ingress of insects. The bottles and funnels were all cleaned by soaking in 1 M HNO_3 for at least one week and then rinsed three times with ultrapure water (Milli-ro-Milli-Q Millipore system). Funnels were rinsed with ultrapure water between each sampling period to minimize propagation effects of eventual contaminations; visually contaminated funnels were changed. The six samplers were installed on three PVC supporting posts separated by about 10 m. Sampling bottles were placed 2 m above the ground and protected from light in PVC tubes. All the collectors were protected from birds which may cause severe contamination problems⁹ and surrounded with nylon strings separated by about 5 cm.

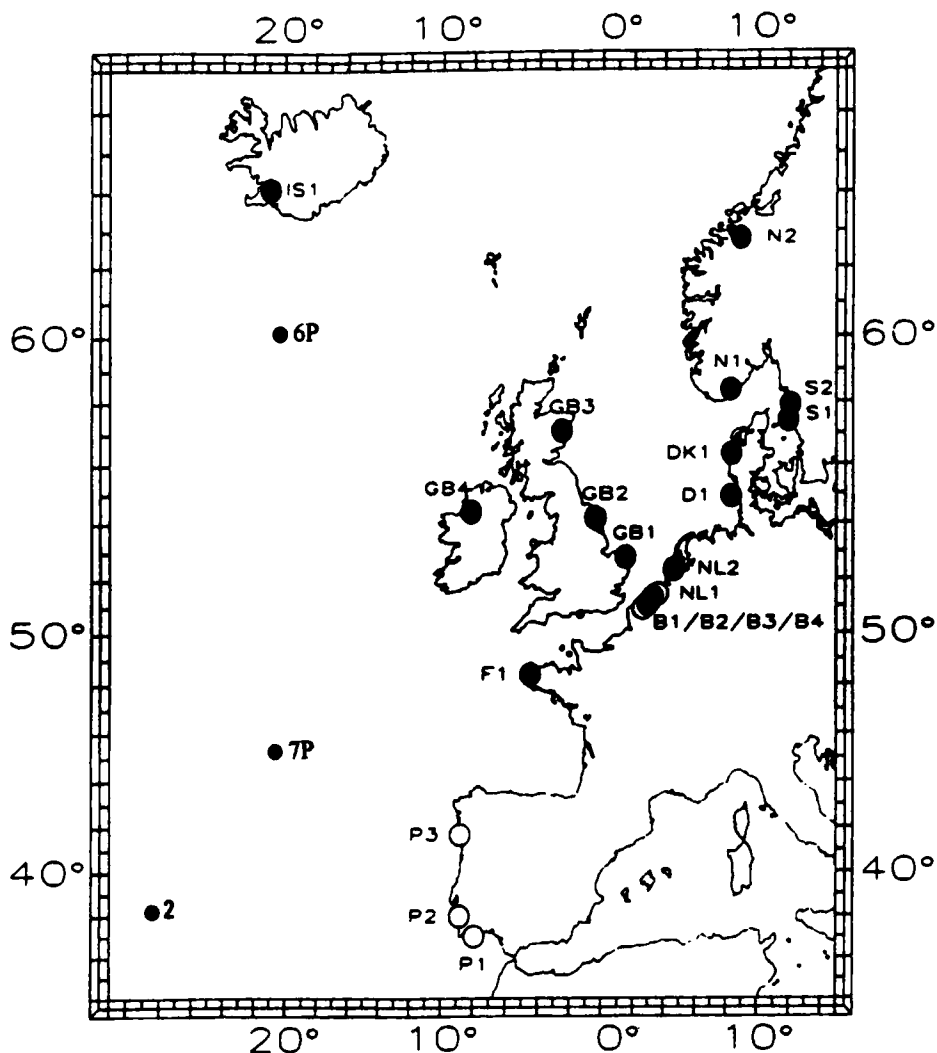


Figure 1 Location of ATMOS stations.

After collection, the samples were visually inspected for the presence of bird droppings. The samples considered as contaminated were rejected. Using this protocol only 1% of the samples were rejected. At the laboratory, the bulk precipitation samples were weighed to determine the amount of precipitation and, under laminar-flow clean-bench class-100 conditions, acidified to 0.08 M with 'suprapur' nitric acid (Merck). Blank values for a 0.08 M nitric acid water solution are given in Table 1.

Analysis

A Perkin-Elmer 4100ZL was used for the electrothermal atomic absorption measurements. Perkin-Elmer pyrolytic graphite-coated tubes equipped with pyrolytic-

Table 1 Detection limits, blank values and trace-metal concentrations (all in $\mu\text{g l}^{-1}$) at station F1 in 1992.

	<i>Cd</i>	<i>Cr</i>	<i>Cu</i>	<i>Fe</i>	<i>Mn</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>
Detection limit	0.003	0.030	0.045	0.030	0.01	0.090	0.06	0.010
Blank	< DL	< DL	< DL	0.1	< DL	< DL	< DL	< DL
C_{\min}	0.002	0.02	0.13	3.3	0.32	0.15	0.2	0.4
C_{\max}	2.4	7.6	55	2191	275	26.6	89.9	423
C_{mean}	0.022	0.11	0.58	47.7	2.42	0.43	1.15	4.13

coated platforms were used. Acidified rainwater samples were stored in acid-washed polypropylene cups prior to injection. 30 μl of rainwater samples were directly delivered to the furnace using a Perkin-Elmer autosampler AS-70. For the volatile elements Cd, Pb and Zn, after a charring step at 300°C (10 s), atomization occurred at 1800°C using a max-power ramp. For Cu, Cr, Fe, Mn and Ni, after a charring step at 900°C (10 s), atomization occurred at 2300°C using a max-power ramp. The gas flow (argon 250 ml/min) was interrupted at the atomization stage. Only integrated absorbance measurements were used.

Sodium concentrations were determined by atomic emission spectrometry using a Varian AA-10 spectrometer.

Dilutions were made with calibrated Gilson Pipetman pneumatic syringes. Merck metallic standard solutions were 1 g l^{-1} in 0.5 mole l^{-1} HNO_3 . Merck suprapur nitric acid was used. Seawater used for preparing sea salt solutions was collected near the sampling site. Sodium concentrations were taken as reference for sea salt solutions.

RESULTS AND DISCUSSION

Atomic absorption spectrometry

For non-polluted coastal sampling locations, the major part of the saline matrix of rainwater samples is essentially sea salt. At relatively low concentration levels, sea salt may induce important interference effects on the atomization signals of metals thereby leading to erroneous concentrations values if direct calibration with standards prepared in water is used (10–14). The importance of these interference effects is dependent on sea salt concentration level, the measurement mode (peak area or peak height) and the experimental conditions (nature of the chemical modifier, type of atomizer, nature of the graphite, tube or platform, electrothermal conditions). Due to the high variability of sea salt concentrations in rainwater samples, the most accurate way for trace-metal determinations is the method of standard additions. Unfortunately, this method increases risks of contamination and is time consuming when numerous and diverse precipitation samples have to be analysed. It therefore appeared necessary when using a new electrothermal atomic absorption spectrometer (transversal heating and longitudinal-effect background correction spectrometer with platform atomization) to examine the influence of the seawater matrix on the atomization signals of metals and to estimate the induced error when using direct calibration with aqueous standards for trace-metal determinations in oceanic rainwater samples.

In this study, as recommended by the Paris Commission¹⁵, all the bulk rainwater samples were acidified with nitric acid (0.5%). This acid plays an important role by avoiding trace-metal adsorption on container walls, dissolving particulate trace metals and modifying seawater matrix in atomic absorption spectrometry determinations. We therefore examined the influence of sea salt, at concentration levels encountered at our sampling location, on the atomization signals of Cd, Cr, Cu, Mn, Fe, Ni, Pb and Zn in 0.5% HNO₃.

In the presence of such an excess of nitric acid (0.08 M) as compared to the sea salt concentration levels encountered in our rainwater samples ($\text{Cl}^- < 0.005 \text{ M}$), interference effects induced by the chloride matrix (NaCl, MgCl₂) are generally suppressed and only the resulting nitrate and sulphate matrix may modify the atomization mechanisms of metals and induce an interference effect.

For Ni, the atomization signal shape is not modified in the presence of sea salt for Na concentrations lower than 100 mg l⁻¹ and no interference effect is observed (Figure 2).

For Cr, Cu and Fe, the atomization signals are only slightly modified in the presence of sea salt and are not very different from the atomization signals observed in water (Figure 2). However, an important increase of the peak height of Cr in the presence of the highest sea salt concentration (100 mg l⁻¹ Na) is noted. For these three elements, the interference effects induced by the presence of sea salt on their respective integrated absorbances is lower than 5% for Na concentrations less than 100 mg l⁻¹ (Figure 2).

For Mn, we can note an important modification of the atomization signal shape in nitric medium with increasing sea salt concentration whereas the peak height increases by about 50% in the presence of sea salt, the integrated absorbance decreases slowly with increasing sea salt concentrations, the depressing effect being about 10% for a 100 mg l⁻¹ Na concentration (Figure 3).

For Cd, Pb and Zn the atomization signal shapes are strongly modified in nitric medium in the presence of sea salt. One notes a severe depression of the peak height with increasing sea salt concentrations (about 70% for Cd, 50% for Pb and 40% for Zn); metallic oxides (NaO, MgO, CaO) resulting from the decomposition of their corresponding nitrates stabilize Cd, Pb and Zn and modify the atomization mechanisms leading to multiple-peak atomization signals. Moreover, one notes a delaying effect; consequently the integration windows used for trace-metal determinations as compared to the atomization signals observed in water have to be modified. By using integrated absorbance measurements for Cd and Pb, the depressive interference effect induced by sea salt ($\text{Na} < 100 \text{ mg l}^{-1}$) is less than 10%; for Zn the stabilizing effect induced by sea salt may induce a positive interference effect of about 10% (Figure 3).

These results confirm the necessity for using integrated absorbance measurements instead of peak height measurements, particularly to determine Mn, Cd, Pb and Zn in marine rainwater samples. Moreover, for such media, it appears from Figures 2 and 3 that interference effects may be diminished by using standards prepared in a sea salt solution instead of ultrapure water. So, by using a sea salt solution (20 mg l⁻¹ in Na; 0.08 M in HNO₃) as a standard medium, the interference is reduced to about 5% for all the metallic elements in sea salt solutions having Na concentrations of less than 100 mg l⁻¹. This precision is generally sufficient to follow the temporal variations of trace-metal concentrations in precipitation.

The detection limits obtained for Cd, Cr, Cu, Fe, Mn, Ni and Zn using our experimental conditions and a 30-μl sample injection are given in Table 1. These detection limits are obtained by optimizing the time integration window closely to the atomization signals of metals obtained in a sea salt solution 20 mg l⁻¹ in Na. If necessary,

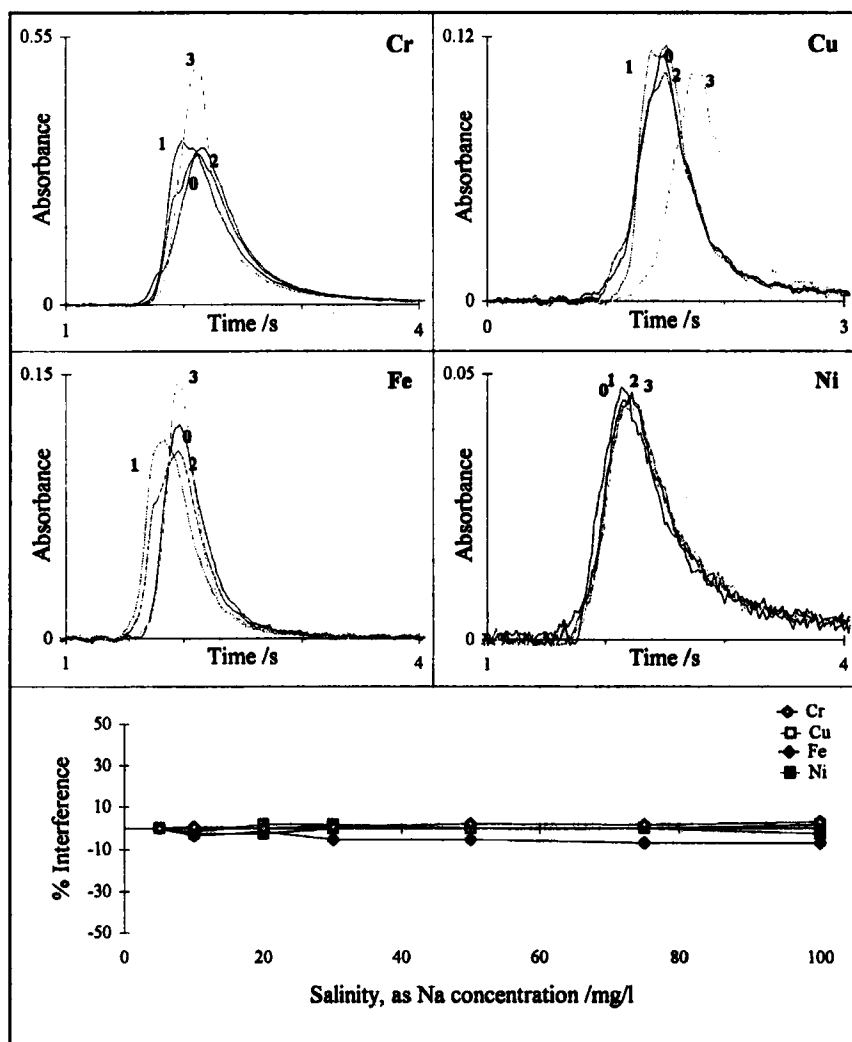


Figure 2 Influence of sea salt on the atomization signals of Cr, Cu, Fe and Ni; 0: MQ water; 1: 0.05% seawater; 2: 0.1% seawater; 3: 1% seawater and variation of the percent interference with the sea salt concentration expressed as Na concentration on the integrated absorbance of Cr, Cu, Fe and Ni.

they may be improved by increasing the injection volume by multiple injections into the furnace.

Measurement variability

Figures 4 and 5 present the variability of trace-metal determinations in rainwater samples obtained in routine analysis for six collectors for each period of sampling (32 periods) over one year, less than 1% rainwater samples being rejected due to visual contaminations by bird droppings. As observed, the variability increases with

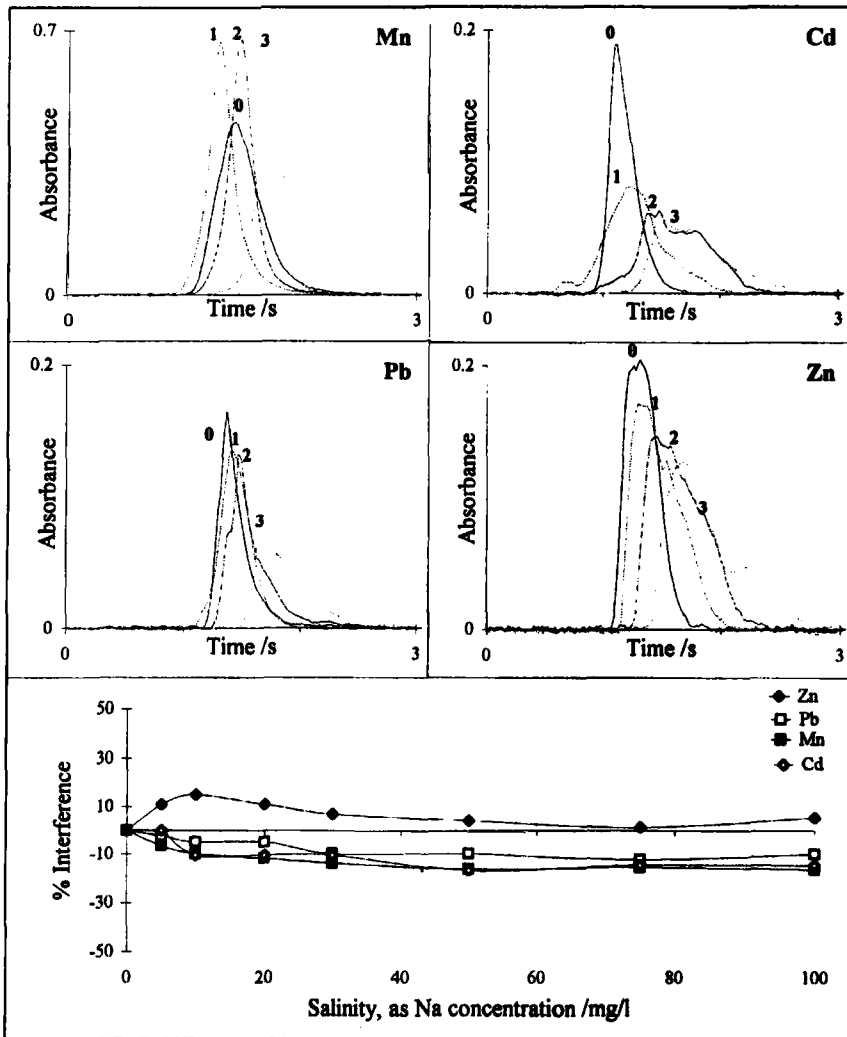


Figure 3 Influence of sea salt on the atomization signals of Cd, Mn, Pb and Zn; 0: MQ water; 1: 0.05% seawater; 2: 0.1% seawater; 3: 1% seawater and variation of the percent interference with the sea salt concentration expressed as Na concentration on the integrated absorbance of Cd, Mn, Pb and Zn.

decreasing concentrations, particularly for Cd and Cr and to a lesser degree for Cu, Ni and Pb.

The variability of trace-metal determinations obtained for the six collectors is a general parameter which reflects the entire analytical protocol, sampling and analysis. Therefore, this parameter includes various factors:

– a precision term related to the analytical method used. In Figures 4 and 5 for each metallic element the curves are plotted which represent the limit of precision of direct electrothermal atomic absorption spectrometry defined as:

$$\% \text{ precision} = \text{detection limit} / \text{metal concentration} * 100 \quad (1)$$

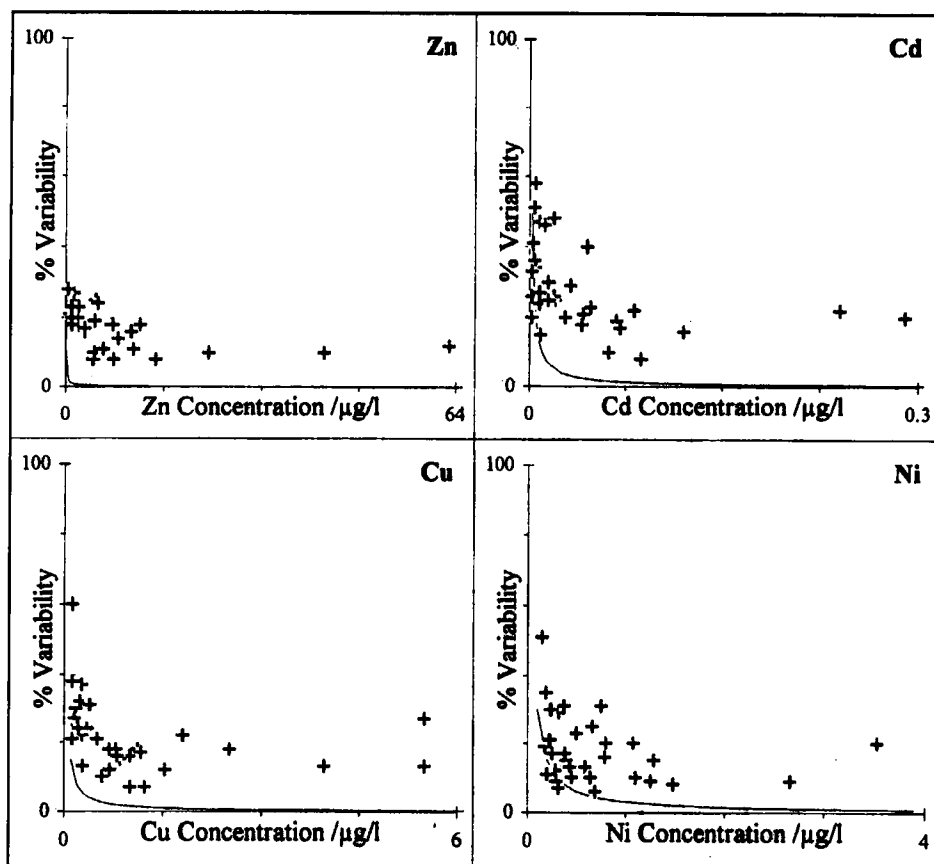


Figure 4 Percent variability of Zn, Cd, Cu and Ni determinations with concentration level in six bulk collectors for each sampling period (+ signs) and limit of precision of the analytical method (full line).

As expected, the variability is higher when the metal concentrations to be determined are closer to the detection limit. From these curves, it appears that the precision term is an important part of the variability (about 20%) in the case of Cd, Cu, Ni, Pb and Cr at the lowest concentration levels.

- the trace metal concentration errors (< 5%) related to the use of direct calibration in electrothermal atomic absorption spectrometry for rainwater samples having variable salinities (with $\text{Na} < 100 \text{ mg l}^{-1}$).

- possible field or laboratory (bottles, funnels, cups) contaminations, obviously more important at very low concentration levels.

- sampling variability, particularly under strong wind conditions; considering the variability values obtained at the highest concentrations (more precise and less subject to possible contamination), the sampling variability of trace-metal concentrations for the six collectors at this site may be estimated at about 20%. Consequently, the number of collectors necessary to get representative data of this site is also an important parameter and should not be less than three.

From this study, it appears that the variability of trace-metal determinations in rainwater samples (six collectors) for each sampling event may be important at very low

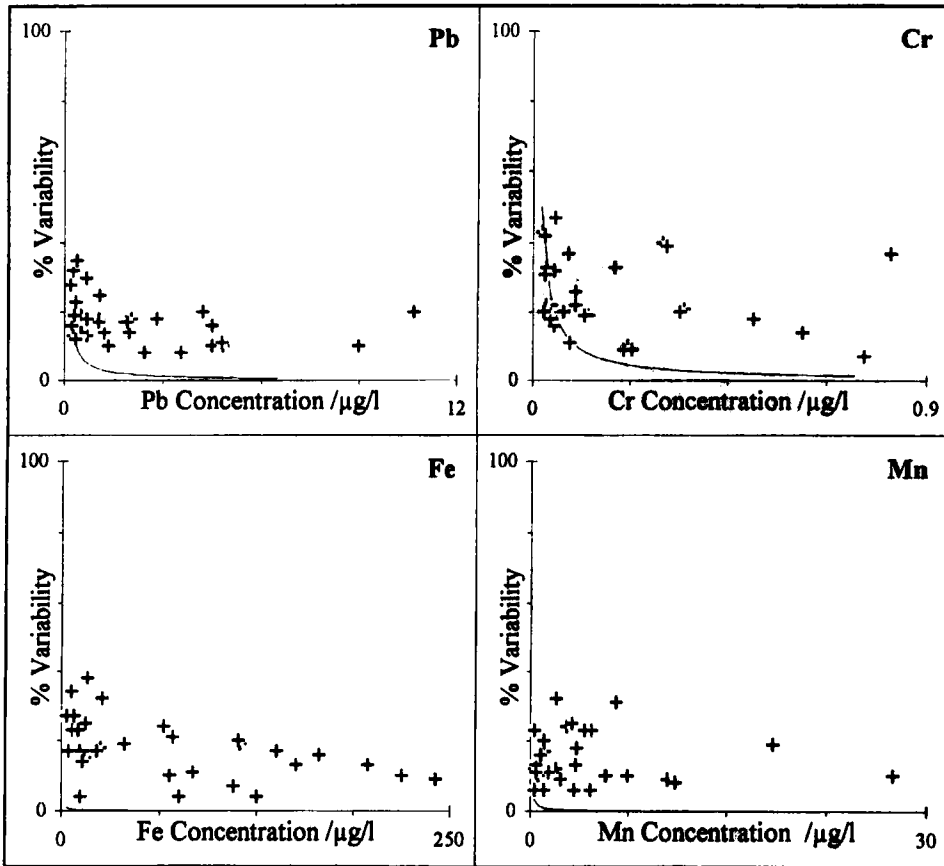


Figure 5 Percent variability of Pb, Cr, Fe and Mn determinations with concentration level in six bulk collectors for each sampling period (+ signs) and limit of precision of the analytical method (full line).

concentration levels but remains rather small as compared to their important temporal concentration variability (Figure 6). Thus, our analytical protocol allows us to follow trace-metal variations in weekly or half-monthly rainwater samples.

Temporal trace metal variations

In Figure 6, half-monthly precipitation amounts and trace metals weighted mean concentrations are plotted. They have been normalized by dividing them by the volume-weighted station average. For all the metallic elements, we can note important temporal variations of their concentrations. Except for Na, temporal variations of all trace metals are relatively similar and the higher concentrations values are obtained during the driest periods. From the 15th period (September) to the 24th period (December), trace-metal concentration levels are relatively constant and very low; this corresponded with a period of much rain with relatively clean air masses of Atlantic origin. In Figure 7, the trace-metal concentration variations with the amount of precipitation for three metals used as

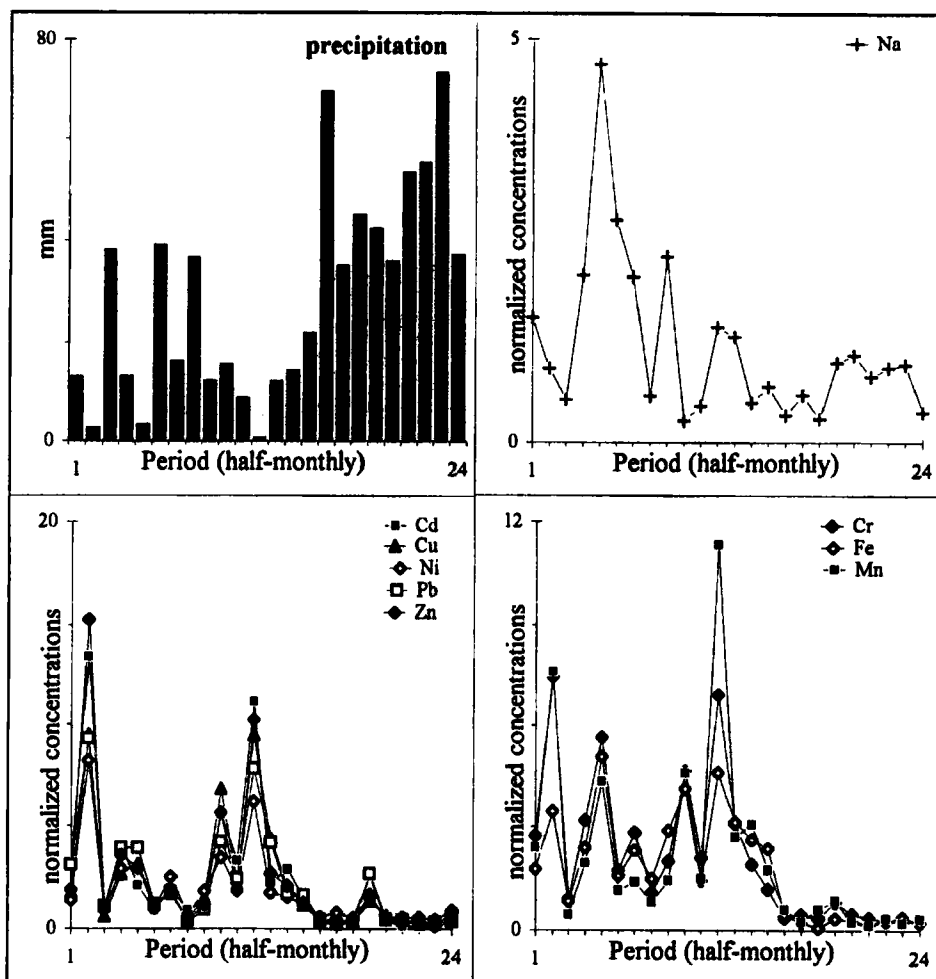


Figure 6 Temporal variations in precipitation amounts and in normalized metal concentrations at F1 in 1992. The values obtained during the 12th sampling period (0.5 mm rainfall) are divided by 10.

tracers are shown. Zn for the anthropogenic source, Fe for the crustal source and Na for the seawater source. The curves fitted by the least-squares method with a power function $C = a \cdot P^b$ indicate an inverse relationship between the precipitation amount, P , and the metal concentrations, C , as previously observed for Na, K, Ca and Mg in bulk deposition samples at a rural site ($C_{Na} < 11 \text{ mg l}^{-1}$)¹⁶. The best fit is observed in the case of Zn; the more important scattering for Fe and Na and the power exponent more different from -1 are probably due to local dry crustal and sea salt inputs, respectively, occurring probably under strong wind conditions.

Linear regression analysis

Linear regression analysis was used to study relationships in trace-metal concentrations. Table 2 presents the correlation coefficients (r) matrix; the scatter plots of metals versus

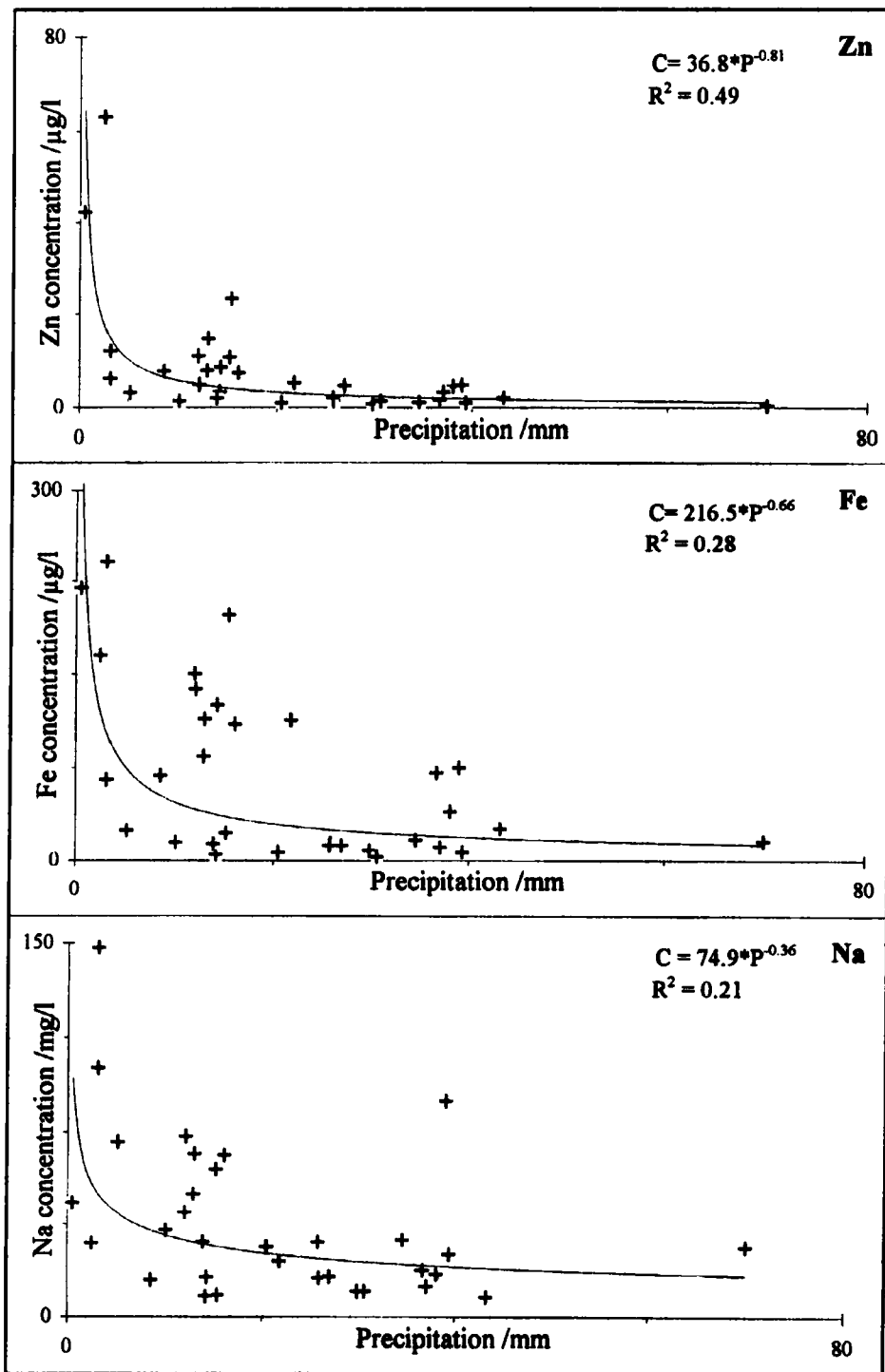


Figure 7 Variations of Zn, Fe and Na concentrations with precipitation amount (+ signs) and regression function $C = a \cdot P^b$ (full line).

Table 2 Correlation matrix for trace-metals in precipitation.

	<i>Zn</i>	<i>Na</i>	<i>Fe</i>	<i>Mn</i>	<i>Cr</i>	<i>Pb</i>	<i>Cu</i>	<i>Ni</i>
<i>Cd</i>	0.96	0.002	0.44	0.82	0.77	0.91	0.89	0.9
<i>Ni</i>	0.94	0.058	0.54	0.81	0.85	0.88	0.87	—
<i>Cu</i>	0.9	0.018	0.61	0.88	0.86	0.9	—	—
<i>Pb</i>	0.89	0.052	0.56	0.81	0.85	—	—	—
<i>Cr</i>	0.79	0.128	0.81	0.84	—	—	—	—
<i>Mn</i>	0.79	0.045	0.65	—	—	—	—	—
<i>Fe</i>	0.44	0.206	—	—	—	—	—	—
<i>Na</i>	0.01	—	—	—	—	—	—	—

Zn are presented in Figures 8 and 9. Anthropogenic trace metals (Cd, Cu, Ni, Pb and Zn) have high correlations, generally higher than observed in Sweden¹⁷, particularly for Cu; Cd and Zn have the highest correlation ($r = 0.96$). In the table, trace metals are classified in the first column according to their decreasing correlation to Zn, which may be taken as a tracer of anthropogenic pollution. These results indicate that the processes governing Cd, Ni, Cu, Pb and Zn deposition are probably similar and that their major sources are continental anthropogenic emissions. Cr and Mn, which have mainly crustal origin, also present relatively high correlations with anthropogenic trace metals, also indicative of an anthropogenic source. Fe has the lowest correlation with anthropogenic trace metals, indicating its more important crustal source. All trace elements have a poor correlation with Na indicating that seawater is not a significant source of trace metals in rainwater for long periods of sampling. From these results, it appears that trace metals like Zn and Cd which have a high correlation may be useful tracers to follow long-range transport of anthropogenic emissions—Zn being analytically easier to determine in rainwater by direct electrothermal atomic absorption spectrometry than Cd, due to its higher concentration levels (about 200 times the Cd concentration) and similar detection limits.

Comparison with literature values

Due to the variability of sampling and analytical protocols presented in the literature, comparison of trace-metal concentrations obtained in other regions are difficult. In Table 3, the values obtained at ATMOS stations for 1992 are presented¹⁸. These values were generally obtained for different periods of sampling (rain events, daily, weekly, half-monthly or monthly), using various types of collectors of different designs (bulk or wet-only), and different analytical protocols (preconcentration, various sample treatments). They are therefore rather difficult to compare. However, we can note important values for the mean concentrations of anthropogenic trace metals in precipitation for the ATMOS stations in 1992 around the North Sea, indicating an important level of pollution. The mean trace-metal concentration values determined at station F1 for 1992 are generally significantly lower than the values obtained at the other ATMOS stations; they are related to the important number of samples collected under a cleaner Atlantic air mass influence. The mean concentration values determined at F1 in 1992 are of the same order as the values obtained for Cu, Ni, Pb and Zn in Bermuda rainwater^{19,20}. The Cd mean concentration is significantly lower at F1. The higher Fe and Mn concentrations may be attributed to a more important crustal

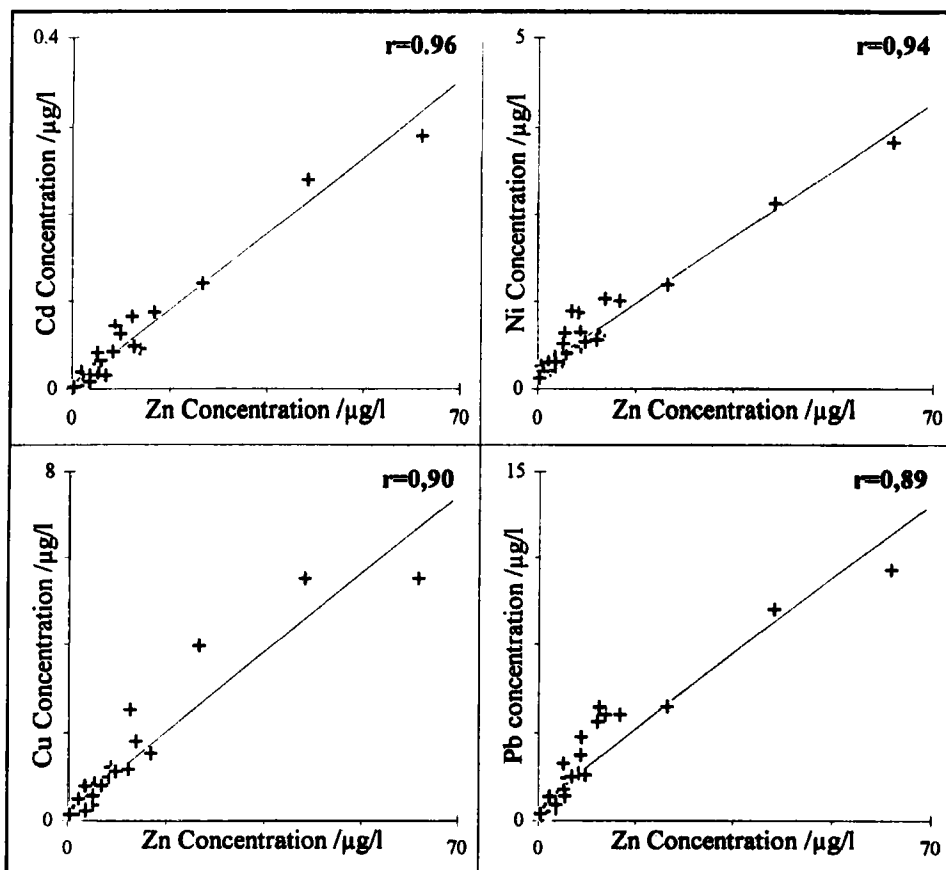


Figure 8 Scatter plots of Cd, Ni, Cu and Pb to Zn. Regression lines and correlation coefficients are indicated.

influence under strong wind conditions. During 1992, the lowest minimum concentration values were observed at F1 station, except for Pb at the S2 location in Sweden the lower minimum concentration values determined at station F1 corresponded to rainy periods with air masses advected from the Atlantic (September to December). Minimum trace-metal concentrations at F1 in 1992 are not very different from minimum concentrations determined in Bermuda rainwater in 1982^{19,20}, except for Cd (10 times lower at F1) and Ni (10 times lower in Bermuda rainwater 1982–83; Table 3). The trace-metal concentration values obtained for single rain events at the three locations 2, 6P and 7P (Figure 1) during two North-Atlantic expeditions in 1988 are also presented in Table 3^{21,22}. The trace-metal concentration values obtained at location 2²¹ are seen to be significantly higher for all the elements than our minimum values and were attributed to a North American pollution. For the location 6P rain sampling²², trace-metal concentrations are of the same order as the minimum concentrations at F1 in 1992 for Cu, Fe, Mn and Zn; the minimum concentrations obtained at F1 being 10-fold lower for Cd but 3-fold higher for lead. For the location 7P fog-sampling period²², higher values are obtained for all the metals studied, except Pb. From these results it appears

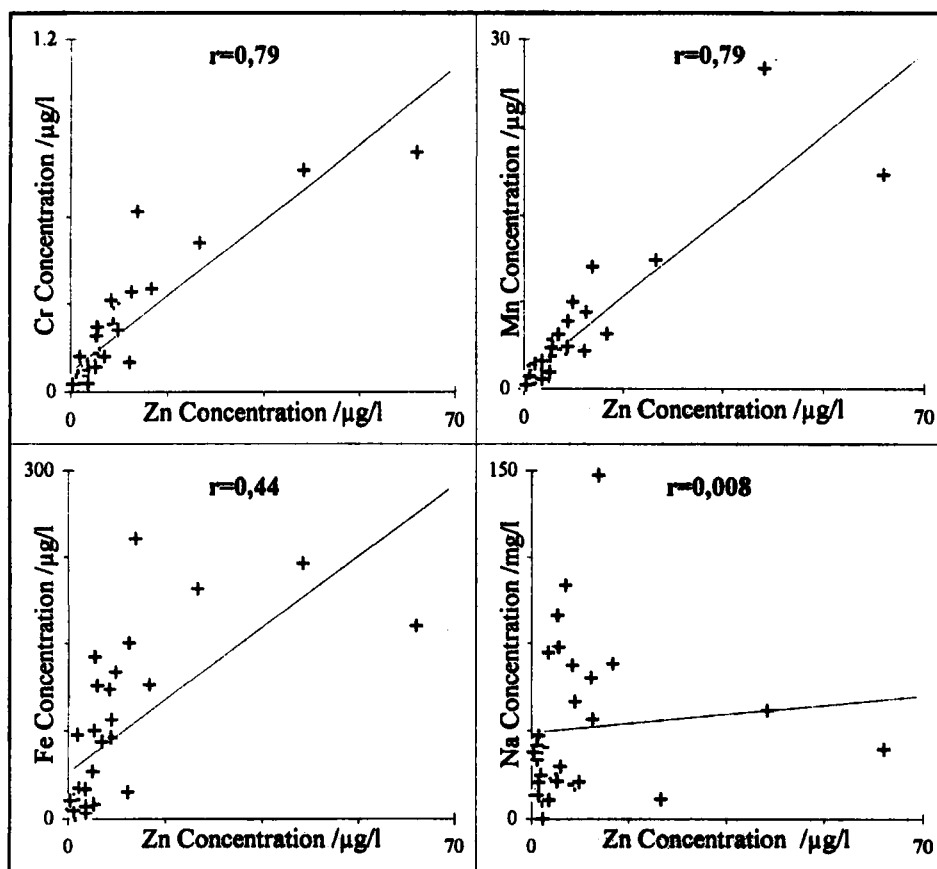


Figure 9 Scatter plots of Cr, Mn, Fe and Na to Zn. Regression lines and correlation coefficients are indicated.

that trace-metal concentrations and their respective ratios in precipitation are highly variable, depending essentially upon air-mass origins.

From the annual wet deposition densities values (Table 4), it appears that the level of pollution measured at the stations around the North Sea in 1992 is very important. F1 is not directly exposed to European anthropogenic activities under Atlantic (west-south west) meteorological conditions during a large part of the year. Consequently, the level of pollution at F1 is up to 10 lower than¹¹ at all the other ATMOS stations which are more exposed to polluted air masses under practically all meteorological conditions.

CONCLUSIONS

Direct determination of trace metals in precipitation by electrothermal atomic absorption spectrometry may be routinely used to follow their temporal variations at coastal stations. However, sea salt at the concentration levels encountered at such sites may induce severe interference effects leading to erroneous concentration values even in the presence of 0.08 M nitric acid. This is particularly true for Cd, Mn, Pb and Zn if peak

Table 3 Comparison of trace-metal concentrations at ATMOS stations and in Atlantic precipitations.

			Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
<i>ATMOS mean concentrations ($\mu\text{g l}^{-1}$) in 1992</i>										
France	F1	B, w or hm	0.022	0.11	0.58	48.1	2.4	0.43	1.15	4.1
Netherlands	NL2	WO, hm	0.102	0.402	2.27	—	—	0.72	5.33	7.73
Netherlands	NL3	WO, hm	0.12	—	1.79	—	—	0.67	2.76	10.32
Norway	N3	B, w	0.07	2.97	1.8	—	—	1	3.35	7.94
Sweden	S2	B, hm	0.05	0.43	0.93	—	—	0.37	2.57	6.09
United Kingdom	GB1	B, w	0.22	0.31	1.95	—	—	1.6	5.2	16.63
United Kingdom	GB2	B, m	0.3	0.56	2.56	—	—	2.15	8.98	41.26
United Kingdom	GB3	B, m	0.05	1.32	2.36	—	—	0.58	2.49	5.88
United Kingdom	GB4	B, m	0.11	0.18	1.43	—	—	0.37	1.39	11.29
<i>ATMOS minimum concentrations ($\mu\text{g l}^{-1}$) in 1992</i>										
France	F1	B, hm	0.002	0.02	0.13	3.3	0.32	0.15	0.2	0.4
Netherlands	NL2	WO, hm	0.056	0.52	0.64	—	—	0.59	2.28	6.55
Netherlands	NL3	WO, hm	0.05	—	0.64	—	—	0.59	1.66	6.55
Norway	N3	B	0.05	1.88	0.62	—	—	0.5	1.91	4.09
Sweden	S2	B, hm	0.01	0.23	0.26	—	—	0.14	0.06	1.62
United Kingdom	GB1	B, w	0.06	0.12	0.91	—	—	0.77	2.3	4
United Kingdom	GB2	B, m	0.05	0.41	1.1	—	—	0.92	4	11
United Kingdom	GB3	B, m	0.01	0.09	0.58	—	—	0.16	0.45	3.5
United Kingdom	GB4	B, m	0.01	0.03	0.31	—	—	0.11	0.28	2.5
Bermuda 1982–83			0.034	—	0.27	0.99	0.06	0.023	0.479	0.28
Bermuda 1982		rain events	0.02	—	0.09	1.9	0.10	0.1	0.5	0.2
Atlantic (Lim)	2	rain event	0.16	—	0.18	115	4.4	—	0.59	0.6
Atlantic (Church)	6P	rain event	0.018	—	0.1	1.5	0.4	—	0.06	0.6
Atlantic (Church)	7P	fog event	0.02	—	0.6	18.0	0.9	—	0.02	3.3

WO: wet-only; w: weekly; hm: half-monthly; m: monthly

Table 4 Annual wet deposition densities for 1992 at ATMOS stations ($\mu\text{g/m}^2$).

		mm	Cd	Cr	Cu	Ni	Pb	Zn
F1	France	649	14	73	376	279	750	2681
NL2	Netherlands	938	96	395	2131	679	5000	7250
NL3	Netherlands	672	84	—	1204	450	1855	6941
N3	Norway	1376	97	4081	2843	1375	4615	10920
S2	Sweden	832	44	447	848	668	2097	5160
GB1	United Kingdom	812	176	250	1583	1304	4226	15138
GB2	United Kingdom	342	104	191	879	737	3076	14130
GB3	United Kingdom	781	42	1033	1845	456	1945	4593
GB4	United Kingdom	1454	161	2560	2074	542	2014	16414

height measurements and direct calibration with aqueous standards are used. In the presence of 0.08 M nitric acid, acid-leachable trace-metal concentrations (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) may be routinely determined by direct calibration with an error of less than 5% in oceanic samples having a sea salt concentration less than 1% if integrated absorbance measurements and standards prepared in a 0.2% sea salt—0.08 M

nitric acid solution are used. Under these conditions, it appears important to check sea salt concentrations in rainwater samples (salinity, Na concentration, etc.) before atomic absorption measurements.

Bulk collectors which have been considered adequate to evaluate trace-metal wet deposition in low-dust regions²³ appear adequate to monitor total (wet + dry) trace-metal deposition at a coastal site over long sampling periods and probably to estimate the contribution of the atmospheric inputs to geochemical fluxes. In such a site, collectors have to be carefully protected from bird droppings or insect contaminations; due to the variability of trace-metal collection under strong wind conditions, low trace-metal concentration level and risks of contamination at the site or at the laboratory, we consider that at least three collectors should be used.

At station F1, trace-metal concentrations in precipitation have an important variability according to their Atlantic or continental air-mass origin and the amount of precipitation. The minimum concentrations are obtained in precipitation advected from the Atlantic. The measured trace-metal concentrations and annual wet deposition densities are generally lower than at ATMOS North Sea stations which are more subject to European anthropogenic pollution. Anthropogenic trace metals (Cd, Cu, Ni, Pb and Zn) are generally well correlated; Zn and Cd appear the best tracers of anthropogenic pollution. For Cr, Fe and Mn, a significant correlation with anthropogenic metals is observed indicating both crustal and anthropogenic origins. Trace metals are not significantly correlated to Na concentration and their seawater origin is not detected under these experimental conditions.

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