

CHEMICAL COMPOSITION, SOURCE IDENTIFICATION AND QUANTIFICATION OF
THE ATMOSPHERIC INPUT INTO THE NORTH SEA

by

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ABSTRACT

From December 1984 to June 1988, 71 aerosol samples were collected from the R/V Belgica on the North Sea and the English Channel. Quantitative airborne concentrations for Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, NO_3^- , SO_4^{2-} and NH_4^+ were obtained by X-ray fluorescence and ion chromatography analysis. Background concentrations for anthropogenic and continental elements, measured in the northern part of the North Sea during north-west wind and at the border of the English Channel and the Atlantic Ocean during south-west wind, are a factor of 5 to 50 lower than the concentrations measured in the Southern Bight. Maximum concentrations occur during east wind combined with low temperature inversion height.

Factor analysis on the total data set yields 4 independent factors : sea salt (Cl), soil dust/fly-ash (Al, Si, K, Ca, Fe, S), residual oil (Ni, V) and a factor containing only anthropogenic components (S, K, Ca, Cr, Mn, Fe, Cu, Zn, Pb, NO_3^- , SO_4^{2-} , NH_4^+).

Total deposition of heavy metals is calculated from the airborne concentrations with the use of theoretical values for dry deposition velocities and washout factors. The results are compared with literature data for the North Sea, for other marine environments and with recent aircraft measurements above the North Sea. Furthermore, the total atmospheric deposition into the North Sea is evaluated relative to other input sources.

Electron probe X-ray micro analysis (EPXMA) is also performed on the aerosol samples. With this single particle technique, 500 particles in each sample are characterized both morphologically and chemically. Hierarchical and/or non-hierarchical cluster analysis of the final data set results in the definition of different particle types : sea salt, transformed sea salt, CaSO_4 , soil dust, fly-ash, Si-rich particles, Ca-rich particles, Fe-rich particles, Pb-Cl particles, Pb-Zn particles and other types.

A Few samples of the sea surface micro-layer were analyzed with EPXMA. The results are compared with the bulk sea water composition.

Laser microprobe mass analysis is used for speciation of nitrogen and sulphur compounds and analysis of trace elements in individual aerosol particles.

1 INTRODUCTION

The Southern Bight of the North Sea is surrounded by some of the world's largest industrial areas. Important emissions of sulphur and nitrogen compounds and heavy metals (V, Cr, Mn, Fe, Ni, Cu, Zn and Pb) lead to deposition into the North Sea after chemical transformation and physical dispersion processes. The North Sea atmosphere can therefore be considered as a combination of a marine environment and an industrial one. Aerosol samples are analyzed in order to answer three main questions :

- What is the chemical composition of atmospheric particles over the North Sea as a function of meteorological parameters?
- What sources (natural and anthropogenic) are responsible for the North Sea aerosol?
- How important is the atmospheric input for the North Sea, compared with other inputs, for different pollutants?

2 SAMPLING AND ANALYTICAL TECHNIQUES

2.1 Sampling methodology

Between December 1984 and June 1988, 71 aerosol samples were collected from the R/V Belgica on the North Sea and the English Channel. Some 20 m³ of air was drawn through a 47 mm diameter Nuclepore membrane filter with 0.45 µm pore-size in a period of approximately 8 hours. A single-orifice Battelle-type cascade impactor with cut-off diameters of 4, 2, 1, 0.5 and 0.25 µm was operated for 10 min per sample at a flow rate of 1 l.min⁻¹. The impaction surfaces were covered with Formvar coated electron microscope grids.

Filter holders were placed in the front mast at approximately 10 m above the sea level. In order to protect the filters from contamination by sea water resulting from sea spray, the filter holder inlet was protected by a hat-type cover. Sampling was discontinued whenever the relative wind direction to the ship was not within + or - 45 degrees.

Sea surface micro-layer samples were collected with a Garrett screen (Dedeurwaerder, 1988).

2.2 Analytical techniques

(i) X-Ray fluorescence. XRF was performed with a Spectrace 5000 (Tracor Northern, USA) apparatus. The sample (Nuclepore filter) is irradiated by directly generated X-rays from a Rh tube. The characteristic X-rays from the sample are detected by an energy-dispersive Si(Li) detector and stored in a multi-channel analyzer. The resulting X-ray spectrum is treated with the quantitative deconvolution program AXIL (Van Espen et al., 1977) to yield airborne concentrations for Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn and Pb.

(ii) Ion chromatography. IC was used for the determination of Cl^- , NO_3^- and SO_4^{2-} after ultrasonic extraction of the Nuclepore filter in 10 ml 1.8 mM Na_2CO_3 / 1.7mM NaHCO_3 eluent. A Dionex 4000i unit, equipped with a HPIC-AS4A column and a conductivity detector, was used for analysis.

(iii) Electron Probe X-Ray Micro Analysis. EPXMA was performed with a 733 Superprobe (JEOL, Japan) equipped with a TN-2000 system (Tracor Northern, USA). With this technique individual particles are characterized both morphologically and chemically (Raeymaekers, 1986). A selected area of the Nuclepore filter is scanned by a 25 kV electron beam. Particles are detected by monitoring the back-scattered electron signal which is proportional to the atomic number of the elements in the irradiated area. Once the particle is localized, the diameter, area and shape factor are computed. Next, an X-ray spectrum is accumulated for each individual particle. For each sample, 500 particles are analyzed. The resulting data set is treated with hierarchical and/or non-hierarchical clustering in order to identify different particle types : sea salt, transformed sea salt, fly-ash, soil dust, CaSO_4 , Fe-oxides, Si-rich particles, Ca-rich particles, Pb-Zn particles, and other types.

(iv) Laser Microprobe Mass Analysis. The principle of LAMMA is based on evaporation and ionization of a micro-volume (one individual particle) by a focused laser beam. The analytical information is obtained by mass spectrometry of the generated ions.

LAMMA spectra contain a massive amount of information about the elemental and molecular content of single particles. Speciation information and detection of trace elements down to the ppm level are two important features. By using a low laser intensity, analysis of the outer surface of particles can be achieved in some cases (Verbueken et al., 1985).

3 RESULTS

3.1 Atmospheric concentrations above the North Sea

Table 1 lists the average atmospheric concentration for several elements above the North Sea, as calculated from 71 analyzed samples. The samples that were taken in the northern part of the North Sea during north-west wind and the ones taken at the border of the English Channel and the Atlantic Ocean during south-west wind are considered to be representative for the background aerosol (i.e. no anthropogenic influences) above the North Sea. From Table 1 it is clear that background concentrations for trace elements are a factor of 5 to 50 lower than concentrations measured in the Southern Bight.

Maximum concentrations were measured in March 1986 during east wind and low temperature inversion height. Samples from that period yield concentrations that are 5 times higher than the average concentration measured in the Southern Bight (up to 300 ng.m⁻³ Pb and 15000 ng.m⁻³ S).

TABLE 1

Average airborne concentrations (ng.m⁻³) above the North Sea (for explanation, see text section 3.1).

Compound	North Sea + Eng. Channel	S.Bight (51°-54°N)	Background
Al	110	160	62
Si	380	580	100
P	180	220	100
S	2750	4060	610
Cl	3380	4100	2420
K	250	370	66
Ca	240	340	70
Ti	14	20	4
V	10	15	2
Cr	10	14	6
Mn	13	22	2
Fe	230	350	16
Ni	5	7	1
Cu	11	17	2
Zn	54	86	2
Pb	39	62	2
NO ₃ ⁻	1890	2710	840
SO ₄ ²⁻	5020	6980	2510
NH ₄ ⁺	1210	2090	77

Factor analysis performed on the total data set yields 4 independent factors that explain 90% of the total variance. The first factor, containing only Cl, is identified as sea salt. The second factor (Ni and V) is described as resulting from residual oil. A third factor contains Al, Si, Ca, K, Fe and S. These elements are typical for fly-ash. The fourth factor contains only anthropogenic elements and compounds: K, Ca, S, Cr, Mn, Fe, Cu, Zn, Pb, NO_3^- , SO_4^{2-} and NH_4^+ . Al, Si, S, K and Ca are distributed over two factors : fly-ash and the anthropogenic factor. These elements have therefore several independent sources.

3.2 Comparison with literature data

(i) Experimental measurements. Table 2 compares our values with those found in literature. Peirson et al. (1974), Cambray et al. (1975) and Cawse (1976) reported average monthly concentrations of several elements in airborne particulate matter. They sampled at six different locations : Leiston (Suffolk), Lerwick (Shetland), Gresham (Norfolk), Collafirth (Shetland) and Petten (North-Holland). One additional sampling location was an unmanned gas platform on the North Sea (position $53^{\circ}5'N$, $2^{\circ}11'E$). In calculating the average concentrations for the whole North Sea area, they did not take into account the values obtained at the gas platform, since these were possibly biased due to contamination by sea spray. The concentrations at the two northern locations (Lerwick and Collafirth, Shetland) are 4 to 5 times lower than the ones measured in the Southern Bight area. Pb-values range between 18 to 24 ng.m^{-3} in the north and 74 to 100 ng.m^{-3} in the south. Although the measured values differ over a large range for the total North Sea, the concentrations for the northern and southern area are quite consistent for V, Cr, Mn, Fe, Zn and Pb. For Cd, Cu and Ni, the differences between northern North Sea and Southern Bight concentrations are smaller (factor 2), which could be explained by analytical problems in detection of low concentrations.

Between May 1972 and April 1977, Kretzschmar et al. (1979) measured daily concentrations of heavy metals at a coastal location in Ostend. They reported rather high values for all elements. If we split the results in different wind sectors (320° - 20° = north, 30° - 90° = east, 100° - 250° = south and 260° - 310° = west), it is clear that continental values (east and south sector) are 2 to 4 times higher than for the west and north sector.

Table 2 includes also the results of DCMR (1981) and Diederer

TABLE 2

Airborne concentrations ($\text{ng}\cdot\text{m}^{-3}$) for the North Sea area (literature values).

Reference	Location	V	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb
Peirson et al. (1974)	Leiston	8.5	5.8	16	260	3.2		124		85
	Lerwick	1.8	0.9	2.4	52	1.6		30		22
Cambray et al. (1975)	North Sea	6.1	2.5	11	190	4.0	5.8	62		75
	Leiston	8.5	4.2	15	240	3.7		93		100
	Gresham	7.8	2.6	16	250	4.2		81		100
	Collafirth	1.4	0.8	2.5	54	2.2		19		24
	Petten	7.0	2.4	11	220	5.7		58		74
	Lerwick	1.4	0.5	1.9	40	2.1		19		18
	Gas platform	7.5	2.9	14	210	6.4		97		93
Cawse (1976)	Leiston		2.5			5.6	13	106	6.4	120
	Collafirth		0.8			3.7	15	15	4.0	20
Kretzschmar and Cosemans (1979)	Oostende (average)	28	13	81	1430	13	19	300	8	278
	wind: 320°-20°	29	6.5	22	400	6.7	10	110	2.7	100
	30°-90°	50	15	77	1320	13	25	310	6	290
	100°-250°	51	15	89	1660	14	22	360	7.1	350
DCMR (1981)	260°-310°	27	6.4	13	300	6.9	5.7	61	1.9	63
	Rijnmond					14	11		2.5	180
Diederer and Guicherit (1981)	Haamstede		7.5			22	350	130	2.5	180
Flament (1985)	Schiermonnikoog		0.8			5	12	20	0.4	30
Schneider (1987)	East Channel			130	500		20	100	3	56
Dedeurwaerder (1988)	Kiel Bight	9.7	2.9	15	370	4.0	7.7	57		53
	Westhinder (filters)			28	560			17	150	3.9
	Continental windsector			49	910			22	250	4.6
Otten et al. (this report)	Impactor samples			25	440			21	143	4.2
	North Sea	10	10	13	230	5	11	54		39
	Southern Bight	15	14	22	350	7	17	86		62
	Background	2	6	2	16	1	2	2		2

and Guicherit (1981) as reported by Van Aalst et al. (1983).

Flament (1985) reported airborne concentrations measured at five different locations at the east coast of the English Channel.

Schneider (1987) measured weekly concentrations of several elements from an artificial island in the Kiel Bight.

Besides these coastal station measurements, Dedeurwaerder (1988) and Otten et al. (this report) measured atmospheric concentrations from ships. Dedeurwaerder (1988) collected 96 aerosol samples from the Westhinder light vessel over a period of 5 years. Both results from filter and from impactor samples are listed in Table 2.

In comparing our results with the literature data, we think it is opportune to divide the measurements in Southern Bight values (beneath 54° N) and northern North Sea values (above 54° N). In doing so and leaving out some of the extremely deviating measurements from Table 2, we estimate the concentration range for the Southern Bight of the North Sea to be 5 to 15 ng.m⁻³ for V, 2 to 8 ng.m⁻³ for Cr, 10 to 30 ng.m⁻³ for Mn, 200 to 600 ng.m⁻³ for Fe, 3 to 10 ng.m⁻³ for Ni, 3 to 20 ng.m⁻³ for Cu, 50 to 150 ng.m⁻³ for Zn, 0.4 to 8 ng.m⁻³ for Cd and 50 to 150 ng.m⁻³ for Pb. For the northern part of the North Sea, a much lower concentration (factor 5 to 50) should be taken into account if one would try to calculate an average value for the total North Sea

(ii) Comparison with model calculations. Deposition processes can be divided into two categories : dry deposition (gravitational settling, diffusional settling and impaction under dry weather conditions) and wet deposition (rainout and washout). Total deposition of heavy metals to the North Sea has been calculated by different authors (Van Jaarsveld et al., 1986, Krell and Roekner, 1988 and GKSS, 1987). These model calculations are based on the emission inventory of Pacyna (1985), a three dimensional dispersion model, and on theoretical dry deposition velocities and washout factors.

TABLE 3

Total deposition to the North Sea (ton.year⁻¹)
Comparison with model calculations

Reference\Element	Cd	Cr	Cu	Ni	Pb	Zn
Van Jaarsveld et al., 1986	14	74	130	150	2600	1200
Krell and Roekner, 1988	14				1530	
GKSS, 1987					1440	
Otten et al. (this report)		740	840	370	2940	4100

For our values, dry deposition is calculated from the average airborne concentration and a dry deposition velocity of 0.2 cm.s⁻¹. Wet deposition is estimated from the average airborne concentration, a washout factor of 150000 and a precipitation intensity of 500 mm (Van Jaarsveld et al., 1986). It must be stated however that the average airborne concentration we use, is based on relatively more measurements in the Southern Bight of the North Sea. Therefore, these numbers should be interpreted as maximum values for total deposition into North Sea.

(iii) Comparison with other marine environments. Table 4 compares our deposition values with those found in the literature for other marine environments. The deposition of heavy metals into the Southern Bight of the North Sea is a factor of 100 higher than for the most remote areas (tropical North Pacific Ocean), except for Al and Fe, where minimum and maximum values do not differ more than a factor of 5. The values we found for the Southern Bight of the North Sea are comparable with those of the Mediterranean Sea (GESAMP, 1985).

(iv) Comparison with other input sources. Pollutants reach the North sea through different channels. Both organic and inorganic contaminants are transported by rivers. Direct input of industrial waste and dumping of toxic materials by ships are two other causes of North Sea pollution. Based on the data of Van Aalst et al. (1983) for these input routes, the relative importance of the atmosphere as an input source of pollutants for the North Sea is evaluated in Table 5 (All values listed are total deposition estimates). For Cr and Ni the relative contribution of the atmosphere is estimated to be 16%, for Cu 17%, for Zn 15% and for Pb 38%. As mentioned in 3.2 (ii), these estimates should be interpreted as maximum values. For most elements, the atmosphere

TABLE 4

Atmospheric deposition (dry + wet) to the North Sea ($\text{kg.km}^{-2}.\text{y}^{-1}$)
Comparison with other marine environments. (GESAMP, 1985)

Location/Element	Al	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
North Sea	16	1.4	1.4	1.9	33	0.7	1.6	7.8	5.6
Southern Bight	23	2.2	2.0	3.2	50	1.0	2.4	12	8.9
New York Bight	60				57			14	39
W. Meditteranean Sea	50		0.5		51		1.0	11	11
South Atlantic Bight	29			0.6	59	3.9	2.2	7.5	6.6
Bermuda	39	0.05	0.09	0.45	30	0.03	0.3	0.75	1.0
Tropical North-Atlantic	50	0.017	0.14	0.7	32	0.2	0.25	1.3	3.1
Tropical North-Pacific	19	0.028	0.06	0.18	13		0.02	0.13	0.07

TABLE 5

Total atmospheric input into the North Sea (ton.year^{-1})
Comparison with other input sources. (Van Aalst et al., 1983)

Input source/Element	Cr	Ni	Cu	Zn	Cd	Pb
Riverine input	1900	1430	1600	16500	230	2400
Direct discharges	1800	560	2300	5700	85	2200
Dumping	60	10	100	900	25	300
Atmosphere	min. 70	360	1400	7200	110	3600
(Van Aalst et al., 1983) max.	1400	3600	10000	58000	430	13000
Atmosphere (this report)	740	370	840	4100		2940
Atmosphere (as % of total)	16	16	17	15		38

can be considered as a minor input source, except for Pb. Future reduction of emission of automotive lead by use of lead free gasoline will reduce also the resulting deposition into the North Sea.

(v) Comparison with aircraft data. Between July 1988 and November 1988 (Otten et al., 1989), 48 aerosol samples were collected with an aircraft above the Southern Bight of the North Sea. In each flight, six samples were taken at different altitudes under the temperature inversion height and one sample was collected at 10 to 30 m above sea level in order to evaluate the contribution of sea spray to the atmospheric concentration of several trace elements. Table 6 lists the average concentrations as calculated from these 48 samples.

Concentrations measured at sea level with the aircraft are about 20% higher than the average concentration over the total mixing layer, except for Si and Ca which are 50% higher. Concentrations above the mixing layer are at least a factor of 100 lower.

Compared with the R/V Belgica data the concentrations measured at sea level with the aircraft are 7 to 66% lower, which suggest that the deposition estimates listed in Table 5 are still too high. This certainly confirms the fact that the atmosphere is a minor source (maximum 15% of the total input for most trace elements except Pb) for input of pollutants into the North Sea.

TABLE 6

Atmospheric concentrations (ng.m^{-3})
Comparison of R/V Belgica data with aircraft data

	R/V Belgica	Aircraft measurements	
	Southern Bight	Mixing layer	Sea level
Si	580	140	200
S	4060	2300	2800
K	370	280	340
Ca	340	180	280
Fe	350	150	170
Cu	17	7.8	7.8
Zn	86	66	80
Cd		0.78	1.3
Pb	62	32	39

3.3 Electron Probe X-Ray Micro Analysis (EPXMA)

In total, 52 aerosol samples were analyzed with EPXMA in order to identify the different particle types that constitute the North Sea aerosol. In general, the samples can be classified into three categories : samples with more than 50% sea salt particles (average composition : 74% sea salt, 13% transformed sea salt, 11% other types of particles), samples with more than 1% and less than 50% sea salt particles (average composition : 12% sea salt, 12% transformed sea salt, 34% fly-ash, 20% sulphur-rich particles, 12% other types of particles) and samples with less than 1% sea salt particles (average composition : 36% sulphur-rich particles, 20% fly-ash, 20% CaSO₄, 8% Fe-rich particles, 9% other types of particles).

Besides sea salt particles (only Na and Cl detected), several other types of particles have been observed. Particles with Na, Cl and S as detectable elements are described as transformed sea salt particles. They are the result of chemical interaction between NaCl and sulfuric acid, which releases HCl into the atmosphere.

Fly-ash particles (Al, Si, K, Fe, S) are detected frequently in the North Sea atmosphere. With west wind (emission from the UK), up to 70% of the inorganic particles are identified as fly-ash.

CaSO₄ is generally detected in almost all samples. It can have both natural (marine and continental) and anthropogenic sources. Fractional crystallization of sea water droplets leads to NaCl and CaSO₄ crystals that can be separated by impaction on filter surfaces. CaSO₄ can also be the result of eolian CaCO₃ that reacted with sulfuric acid. Furthermore, CaSO₄ can be the result of combustion processes (Storms, 1988). High abundance of CaSO₄ particles are found with continental winds (east and south).

Si-rich particles (quartz) and Ti-rich particles are detected at a few occasions.

Spherical Fe-rich particles, that originate from combustion processes, are identified in most samples. Highly polluted samples however, show different types of Fe particles : Fe-oxides, Fe-Zn particles and Fe-S particles.

Sulphur-rich particles are detected both with east and west wind conditions. Some samples contain up to 70% of sulphur-rich particles. Since no or very few other inorganic elements are detected in these particles, they consist for a large part of organic substances.

A few surface microlayer samples from the Southern Bight of the North sea were also analyzed with EPXMA. Both the microlayer and

the simultaneously collected bulk sea water were filtered off on a Nuclepore filter. In the microlayer samples relatively more organic particles are found. It seems that the inorganic content however does not differ dramatically from the bulk sea water content, but we do not have enough samples that were collected in ideal conditions to state any final conclusions.

3.4 Laser Microprobe Mass Analysis (LAMMA)

LAMMA was performed on some selected samples in order to study some specific aspects of North Sea aerosols. It was shown that transformed sea salt particles made up of Na^+ , K^+ , Cl^- , NO_3^- and SO_4^{2-} consisted of a central NaCl cube covered with a NaNO_3 and Na_2SO_4 layer (Otten et al., 1986). This can be the result of both fractional crystallization and of atmospheric interaction between NaCl particles or droplets with nitric and sulfuric acid.

LAMMA was also used to study thermally unstable compounds like ammonium salts in individual aerosol particles. During the March 1986 sampling campaign with east wind and low temperature inversion height, extremely high ammonium concentrations were found in aerosol particles : 30% of the analyzed particles contained up to 90% of ammonium compounds, mainly nitrate and sulfate.

Carbonaceous particles with different trace elements (V, Mn, Fe, Ni and Pb) are detected frequently in smaller particles (0.25 μm) during continental influence.

Generally spoken, LAMMA has shown that North Sea aerosol particles can be quite complex in structure and composition : very often, a single particle is a mixture of different major compounds together with several trace elements (Bruynseels, 1987).

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REFERENCES

- Bruynseels F., 1987. Applications of Laser Microprobe Mass Analysis in aerosol research. Ph. D. Dissertation, University of Antwerp (UIA), Belgium.
- Cambray R.S., Jefferies D.F. and Topping G., 1975. An estimate of the input of atmospheric trace elements into the North Sea and the Clyde Sea. AERE Report 7733.

- Cawse P.A., 1976. A survey of atmospheric trace elements in the United Kingdom. AERE Harwell Report R7669, UKAEA, HMSO, London.
- DCMR, 1981. Quarterly and yearly reports. DCMR, Schiedam, The Netherlands.
- Dedeurwaerder, H.L., 1988. Study of the dynamic transport and of the fall-out of some ecotoxicological heavy metals in the troposphere of the Southern Bight of the North Sea. Ph. D. Dissertation, University of Brussels (VUB), Belgium.
- Diederer H.S.M.A. and Guicherit R., 1981. Bronherkenning door middel van concentratiemetingen van elementen in de buitenlucht. IMG-TNO Report G 799.
- Flament P., 1985. Les métaux traces associés aux aerosols atmosphériques : apports au milieu marin de littoral Nord-Pas-de-Calais. Ph. D. Dissertation, University of Lille, France.
- GESAMP - IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution, 1985. Interchange of pollutants between the atmosphere and the oceans. Reports and Studies GESAMP (23).
- GKSS, Geesthaacht, West Germany, 1987. Methodology for model calculations of the atmospheric input of trace elements into the North Sea and the Baltic Sea. 5th ATMOS meeting, November 1987, Berlin, West Germany.
- Krell U. and Roekner E., 1988. Model simulation of the atmospheric input of lead and cadmium into the North Sea. Atmospheric Environment, 22, 375-381.
- Kretzschmar J.G. and Cosemans G., 1979. A five year study of some heavy metal levels in air at the Belgian North Sea coast. Atmospheric Environment, 13, 267-277.
- Otten Ph., Bruynseels F. and Van Grieken R., 1986. Nitric acid interaction with marine aerosols sampled by impaction. Bull. Soc. Chim. Belg., 95, 447.
- Otten Ph., Rojas C., Wouters L. and Van Grieken R., 1989. Atmospheric deposition of heavy metals (Cd, Cu, Pb and Zn) into the North Sea. Report Rijkswaterstaat #2, University of Antwerp (UIA), Belgium.
- Pacyna J.M., 1985. Spatial distributions of As, Cd, Cu, Pb, V and Zn emissions in Europe within a 1.5° grid net. Nilu Report 60/85.
- Peirson D.H., Cawse P.A. and Cambray R.S., 1974. Chemical uniformity of airborne particulate matter and a maritime effect. Nature, 251, 675.
- Raeymaekers B., 1986. Characterization of particles by automated electron probe micro analysis. Ph. D. Dissertation, University of Antwerp (UIA), Belgium.
- Schneider B., 1987. Source characterization for atmospheric trace metals over Kiel Bight. Atmospheric Environment, 21, 1275-1283.
- Storms H., 1988. Quantification of automated Electron Microprobe X-Ray Analysis and application in aerosol research. Ph. D. Dissertation, University of Antwerp (UIA), Belgium.
- Van Aalst R.M., Van Ardenne R.A.M., De Kreuk J.F. and Lems Th., 1983. Pollution of the North Sea from the atmosphere. TNO Report CL 82/152.
- Van Espen P., Nullens H. and Adams F., 1977. A computer analysis of X-ray fluorescence spectra. Nuclear Instruments and Methods, 142, 243-250.
- Van Jaarsveld J.A., Van Aalst R.M. and Onderlinden D., 1986. Deposition of metals from the atmosphere into the North Sea: model calculations. RIVM Report 84015002.
- Verbueken A.H., Bruynseels F.J. and Van Grieken R.E., 1985. Laser microprobe mass analysis : a review of applications in life sciences. Biomed. Mass Spectrom., 12, 438.