CHAPTER 4

North Sea aerosols

The group of Prof. Van Grieken has been active since several decades in the field of marine aerosol science, especially in applications related to the North Sea. Because of its economical and ecological importance for Europe, the North Sea has always been one of the high-priority research topics in European framework programs. MiTAC has often been a major participant in ecological studies about the North Sea environment, as will be explained later. Therefore, it will be no surprise that TW-EPMA was first tested on marine aerosol particles, sampled above the North Sea. This chapter will present some examples of how TW-EPMA is now able to extend the capabilities of electron microscopy for studying environmental particles, and atmospheric particles in particular.

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1. Introduction

During the last two decades, the research group of Prof. Van Grieken has participated in numerous extensive aerosol sampling campaigns on the North Sea.[1,2,3,4,5,6,7,8,9,10,11] It should therefore not be surprising that the first application of TW-EPMA to a real environmental case is to be found in the study of marine aerosols above the North Sea. First of all, our group has acquired valuable experience in sampling aerosol samples, so it was not so difficult to adapt our procedures for the collection of TW-EPMA samples. Secondly, we already had some projects running which were related to the study of North Sea aerosols at the time of our first experiments with TW-EPMA. Therefore, it was not too difficult to take additional samples for testing this new technique; however, besides carrying out some occasional tests, we also tried to prove the value of TW-EPMA by putting it into real action. We rapidly discovered that the use of TW-EPMA resulted in new insights into the composition and the transformation of atmospheric particles, and this chapter will give a brief overview of some of our experiences. Before we continue to do so, however, it is important to indicate that marine research is not straightforward.

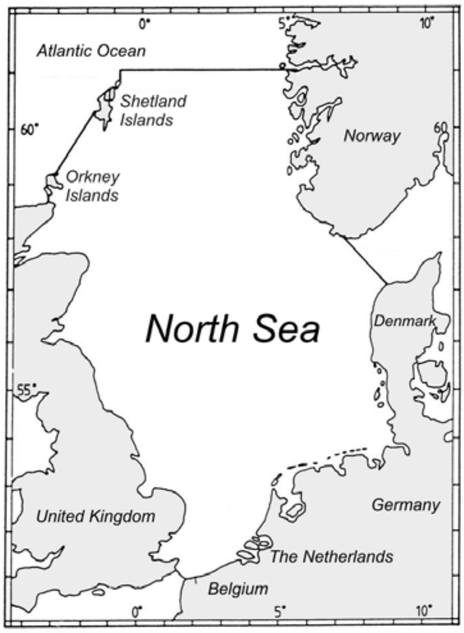


Figure 1: Map of the North Sea

Sampling aerosols above the North Sea is not to be taken lightly, even if the occasional seasickness is left aside. Some of the above-mentioned North Sea projects in which our group has participated, involved sampling with aircrafts at different altitudes, allowing for fast and quite mobile sampling.[3,4,8] On some occasions fixed sampling sites were selected on oil platforms or at coastal sites to get information on seasonal variations at specific locations.[9,11] However, most of the sampling strategies were developed and to get relevant, undisturbed sampling conditions on board of research vessels.[6,7] For example, in several sampling campaigns two ships were positioned on a circle, with a 200-km diameter, continuously downwind from each other in the central area of the North Sea.[6] After sampling first on the upwind ship, a second sampling was carried out on the downwind ship after some delay time, corresponding to the air mass travel time, which was calculated based on the actual wind speed aboard both ships. Many examples of other extensive campaigns for the sampling of marine aerosols can be found in literature, mostly all based on similar sampling strategies.[9,12,13,14,15,16]

Although many sampling strategies have been developed, it still remains very difficult to avoid interpretation problems due to meteorological interferences. Firstly, it is quite difficult to know during the campaign if the sampled air masses are transported along representative wind directions. For example, the North Sea is surrounded by numerous sources of anthropogenic pollution on the Continent and the United Kingdom. So, if during a sampling campaign, the wind is only coming from one direction, the sampled aerosol might not be representative for the conditions over a longer period. Secondly, campaigns on ships and aircrafts can also not be carried out during stormy weather, so often they have to be interrupted, resulting in only a limited amount of data. Thirdly, the sampling location could also be a limitation in view of atmospheric studies. While fixed (coastal) sites are probably cheaper and easier to reach, they only give an idea about the aerosol composition at one location and more sites are required for a thorough investigation of the marine aerosols. Furthermore, the influence of continental sources near the coast could be higher. Although aircrafts can sample at different altitudes and can more easily go from one place to another, they are not able or not allowed to sample very close to the sea surface. On the other hand, sampling on research vessels is limited to the marine boundary layers. However, we are convinced that a cautious, but thorough interpretation of the combined meteorological and chemical data should provide valuable knowledge on the transportation and reaction mechanisms of aerosol particles, even if the weather conditions during sampling are not ideal. The possibilities of TW-EPMA for such experiments on board of a research vessel will be discussed in section 2 of this chapter.

Other limitations in marine aerosol research concern the restrictions of the applied analytical methods. Numerous methods have been applied to analyze and characterize the aerosols that were collected on different types of filters or substrates with a variety of devices, yet not so many of them have been used simultaneously. In the past, researchers have too often focused their analysis on either bulk or else microanalytical techniques only, which could be seen as a shortcoming, or even as a lost opportunity. Although bulk techniques like ion chromatography or X-ray fluorescence are better in providing quantitative data (concentrations per cubic meter of air), they cannot provide data on the level of individual particles, and often longer sampling times are required (e.g. 24h). On the other hand, although single particle analysis allows characterizing the morphology and the composition of each analyzed individual particle (concentrations per particle), quantitative information about the composition of the air is often not produced. Therefore, the combination of bulk and microanalytical techniques is essential for enhancing our knowledge about aerosol chemistry. Our projects related to the North Sea have shown that the combined use of TW-EPMA with ion chromatography opens up new possibilities for the study of marine aerosol particles. Marine nutrients, for example, mostly consist of nitrogen compounds that are very volatile, and the reactions of sea salt with other atmospheric compounds produce nitrates and sulphates, which are also low-Z-type and volatile. From now on, the presence of these compounds can be investigated by Cryo-TW-EPMA, and therefore, electron microscopy is more then ever an efficient complementary technique to ion chromatography. This will be shown in section 3 of this chapter.

2. Sampling campaign on the Belgica

2.1 Introduction

The A962 Belgica is an oceanographic research vessel of the Belgian Navy, especially equipped for scientific campaigns on the North Sea. With four laboratories and special equipment aboard, it has proven to be an ideal host for scientific crews from diverse disciplines at different universities. During the last two decades, the group of Prof. Van Grieken has been involved in several sampling campaigns on board of the Belgica.

Figure 2: A962 Belgica

From 1998 until 2000, the Belgica was put to sea for several sampling campaigns in the project "Air-sea exchange of nutrients, trace metals and organic micropollutants to the North Sea" in the framework of the programme "Sustainable Management of the North Sea", supported by the Belgian State. The Free University of Brussels and the Univerities of Ghent and Antwerp collaborated to map the fluxes of pollutants to the North Sea by analyzing air and water samples with different techniques. The task of our university in this project was to study the extent to which atmospheric nutrient deposition promotes the eutrophication of some areas in the North Sea. Several nitrogen containing compounds are known to be nutrients or nutritive substances for algae in marine environments, and although the phenomenon of algae growth and its mortal effects to the ecosystem have been studied for quite a while, the contribution of atmospheric aerosols had never been subject of a thorough investigation. The results of the three participating universities were used as input for different mathematical models for simulating the mechanisms of air-sea exchange. Most of the results of this project were already reported in the thesis of K. Eyckmans, but one experiment with TW-EPMA will be discussed in this chapter.[17]

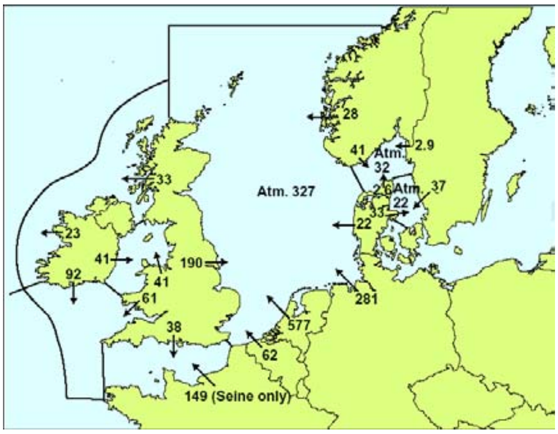


Figure 3: Schematic overview of riverine and atmospheric nitrogen loads to the North Sea (in 1000 t N/year) [18]

2.2 Methodology

Five sets of marine aerosol samples (S1−S5) were collected over the North Sea on the research vessel Belgica, between 28 September and 2 October 1998. A Berner impactor was set up on the highest deck (the so-called 'Monkey bridge') with the inlet nozzle in the direction of the wind and out of the ship's plume, about 10 m above sea level.

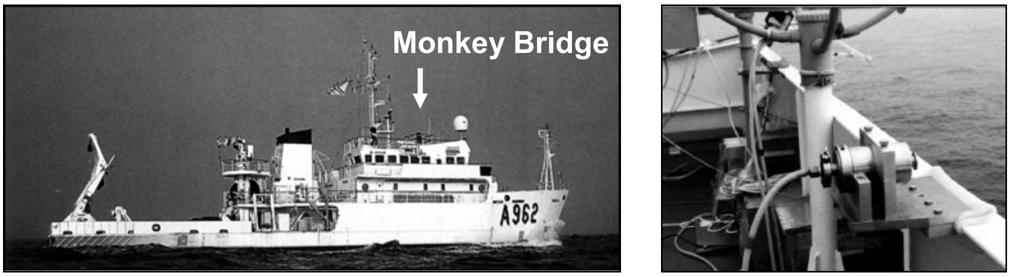


Figure 4: Position of the Berner impactor on the upper deck of the vessel

The particles were sampled on aluminium foil by a Berner-impactor, with cut-off diameters of respectively 0.06, 0.125, 0.25, 0.5, 1, 2, 4, 8 and 16 µm for its nine stages, numbered from 1 to 9. Aluminium was used instead of a more suitable substrate like beryllium, because this experiment was carried out before the systematic comparison of different substrate materials in chapter 2. Considering the cut-off diameters of the different stages, the time available for sampling and the size limit for the detection of particles by the electron probe microanalyzer (0.2 µm), only six stages were selected for this sampling (stages 3 to 8). The sampling time varied between 2 (for stage 3) and 180 (for stage 8) minutes, to obtain the best loading of particles in the impacted spots.

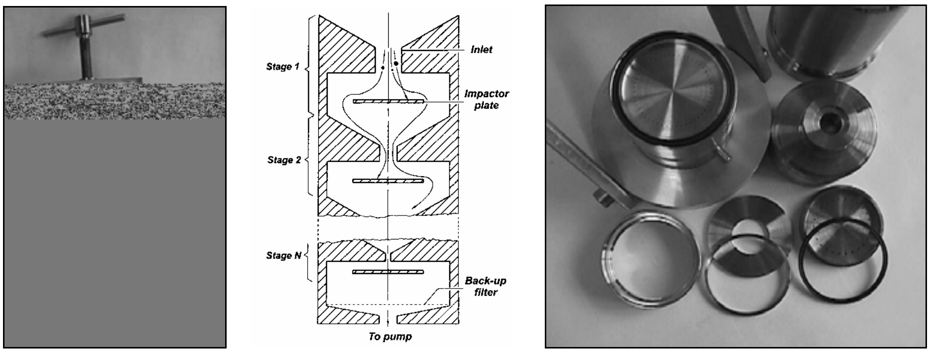
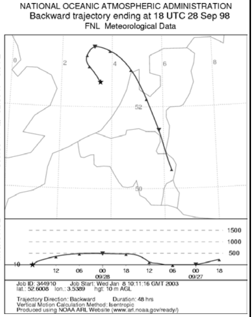
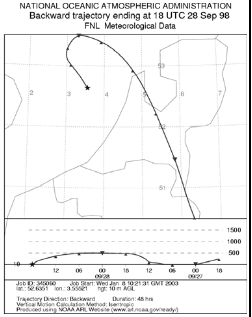
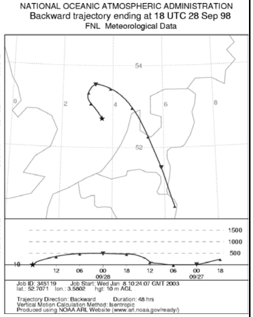
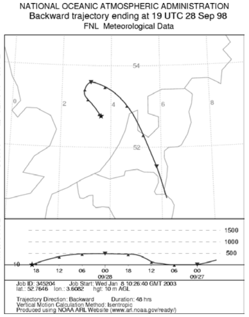
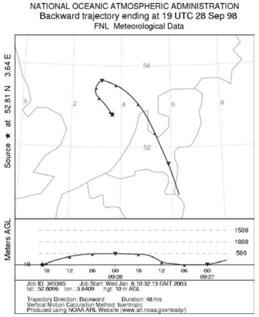
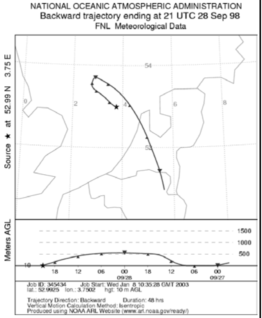
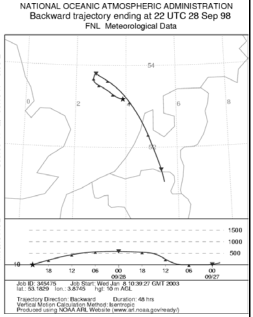


Figure 5: Berner impactor (schematic principle and real model)

Figure 6 shows the air mass backward trajectories at the different sampling points for each of the sampled stages, obtained from HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model which is available on the internet.[19] Since the ship was moving during the sampling, it was decided to calculate the back-trajectories at each step and location, i.e. at the beginning and at the end of each stage. Much care should be taken while interpreting air mass backward trajectories, since many uncertainties exist in their calculation.[20][21,22] When many local parameters are involved, certainly for trajectories below the so-called mixing height, often only indicative information can be provided on air mass movement. However, since local disturbances (e.g. topography) are expected to be less abundant in the marine environment of the North Sea, the (cautious) use of back-trajectories for the study of marine aerosols seems to be more justified than for urban or mountain-rich areas, and many marine applications can be found in literature.

a) SAMPLE S1

START	STAGE 3	STAGE 4	STAGE 5	STAGE 6	STAGE 7	STAGE 8 - STOP
1998-09-28 17u43	1998-09-28 17h45	1998-09-28 18h20	1998-09-28 18h55	1998-09-28 19h25	1998-09-28 20h40	1998-09-28 21h50
N52 36 02.95 E 3 32 19.88	N52 38 06.19 E 3 33 07.43	N52 42 25.50 E 3 34 48.58	N52 45 52.71 E 3 36 29.42	N52 48 34.61 E 3 38 27.17	N52 59 32.88 E 3 45 00.71	N53 10 22.43 E 3 52 28.21
						

b) SAMPLE S2

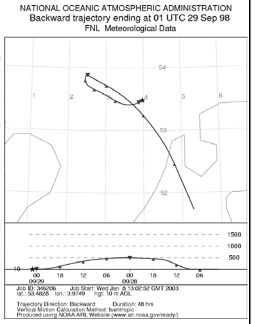
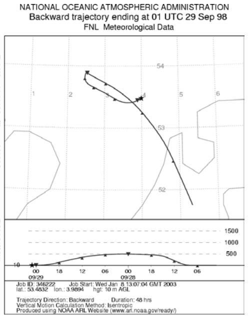
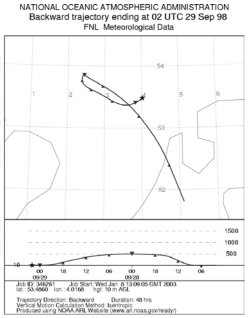
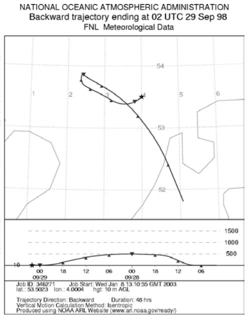
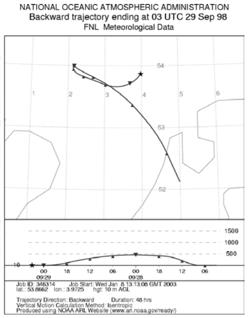
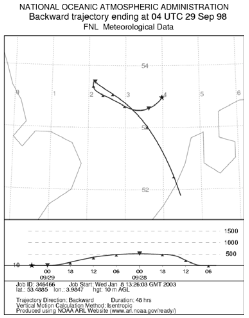
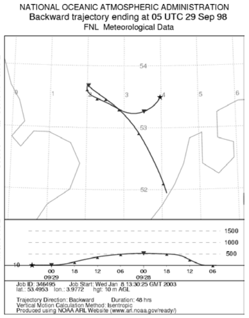
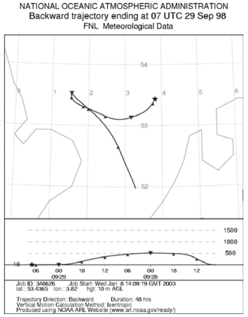
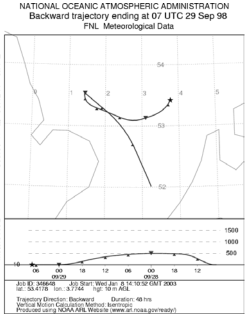
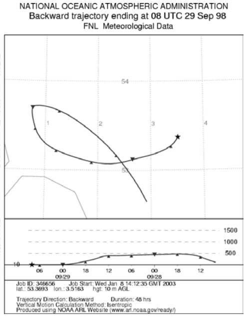
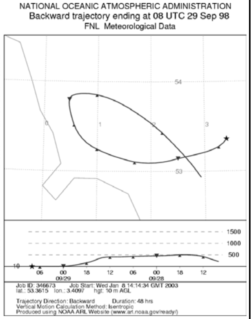
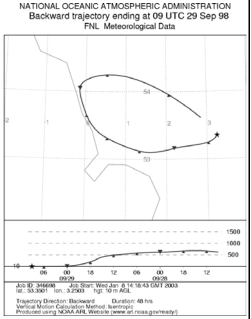
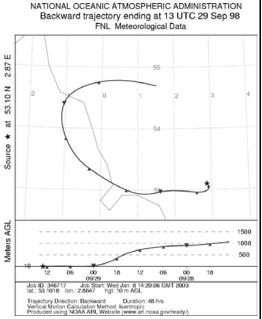
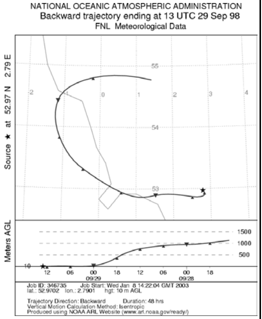
START	STAGE 3	STAGE 4	STAGE 5	STAGE 6	STAGE 7	STAGE 8 - STOP
1998-09-29 01u00	1998-09-29 01h02	1998-09-29 01h34	1998-09-29 02h08	1998-09-29 02h41	1998-09-29 04h00	1998-09-29 05h16 *
N53 28 58.12 E 3 58 29.76	N53 28 59.46 E 3 59 21.95	N53 29 04.55 E 4 01 00.46	N53 30 08.23 E 4 00 01.48	N53 29 11.83 E 3 58 21.07	N53 29 18.70 E 3 59 04.99	N53 29 43.01 E 3 58 37.81
						 Rain

Figure 6a-b: Air mass backward trajectories – (*) indicates rain during sampling, (**) indicates rain just before sampling

c) SAMPLE S3

START	STAGE 3	STAGE 4 (*)	STAGE 5 (*)	STAGE 6	STAGE 7 (*)	STAGE 8 - STOP
1998-09-29 06u40	1998-09-29 06h42	1998-09-29 07h36	1998-09-29 08h01	1998-09-29 08h25	1998-09-29 12h40	1998-09-29 13h20
N53 26 11.42 E 3 49 12.00	N53 25 03.91 E 3 46 28.00	N53 22 09.56 E 3 30 58.54	N53 21 41.24 E 3 24 34.93	N53 21 00.50 E 3 15 01.17	N53 06 06.47 E 2 51 52.81	N52 58 12.59 E 2 47 24.39
		 Rain	 Rain			

d) SAMPLE S4

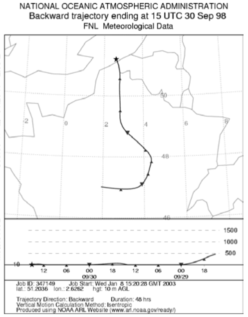
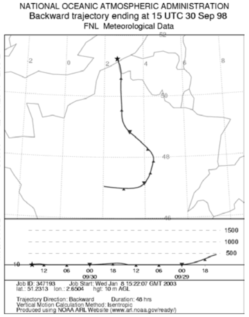
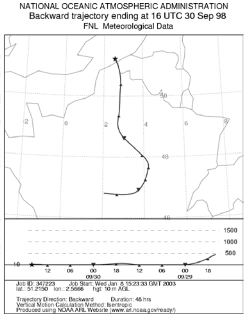
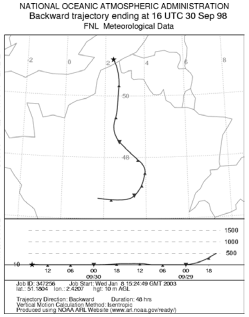
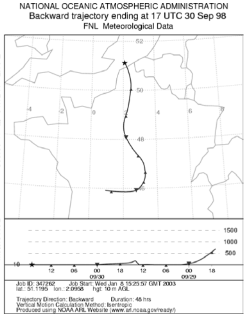
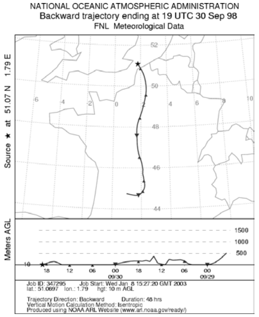
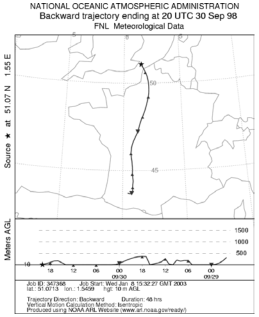
START (**)	STAGE 3	STAGE 4	STAGE 5	STAGE 6 (*)	STAGE 7	STAGE 8 - STOP
1998-09-30 15u10	1998-09-30 15h12	1998-09-30 15h40	1998-09-30 16h05	1998-09-30 17h22	1998-09-30 18h30	1998-09-30 19h40
N51 12 13.05 E 2 37 34.15	N51 13 52.63 E 2 39 01.40	N51 12 54.13 E 2 33 59.68	N51 10 49.43 E 2 25 14.62	N51 07 10.32 E 2 05 44.95	N51 04 10.87 E 1 47 23.87	N51 04 16.63 E 1 32 45.34
 Dry (Rain 08h-10h!)				 Rain		

Figure 6c-d: Air mass backward trajectories (continued) – (*) indicates rain during sampling, (**) indicates rain just before sampling

e) SAMPLE S5

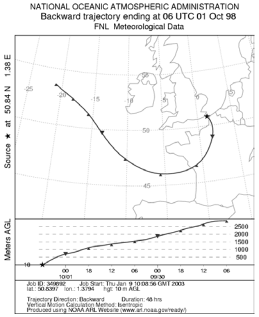
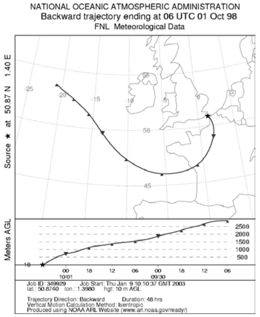
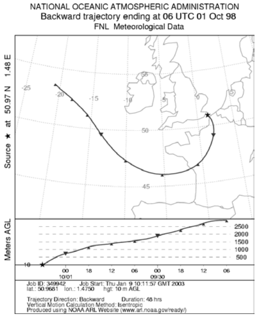
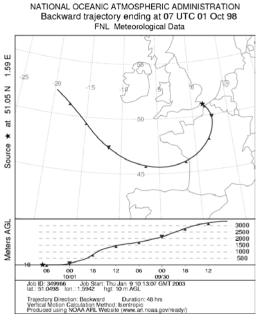
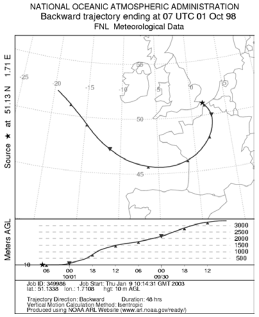
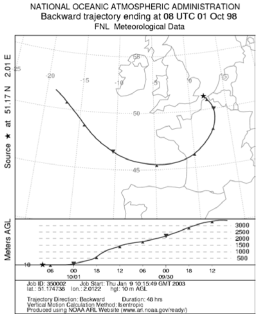
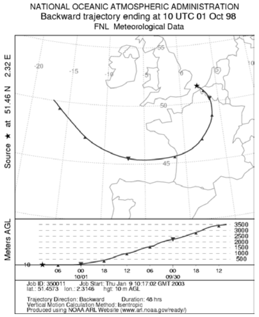
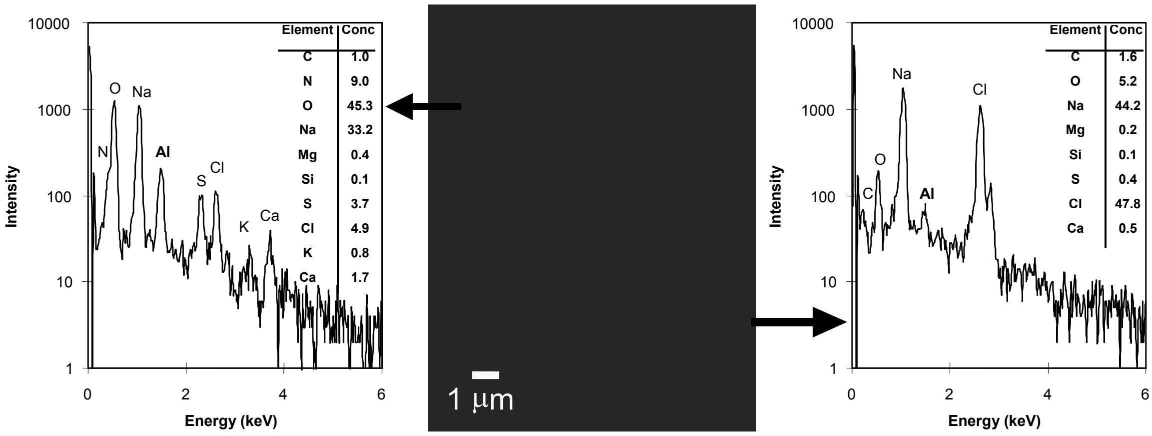
START	STAGE 3	STAGE 4	STAGE 5	STAGE 6	STAGE 7	STAGE 8 - STOP
1998-10-01 05u35	1998-10-01 05h38	1998-10-01 06h10	1998-10-01 06h40	1998-10-01 07h10	1998-10-01 08h20	1998-10-01 09h30
N50 50 23.04 E 1 22 46.01	N50 52 26.43 E 1 23 52.69	N50 58 05.04 E 1 28 30.05	N51 02 59.17 E 1 35 39.13	N51 08 01.57 E 1 42 38.71	N51 17 47.38 E 2 00 44.04	N51 27 26.44 E 2 18 52.69
						

Figure 6e-f: Air mass backward trajectories (continued) – (*) indicates rain during sampling, (**) indicates rain just before sampling

Electron microscope measurements were carried out on our JEOL JXA-733 electron probe X-ray microanalyser equipped with the OXFORD SATW Link energy-dispersive X-ray detector. The accelerating voltage and the beam current were set to 10 kV and 0.5 nA respectively for all measurements. In order to obtain statistically enough counts in the X-ray spectra and to minimise the beam damage effect on the sensitive particles, a typical measuring time of 20 s was used. The cooling stage of the electron microprobe cooled down all particulate samples to –193 °C. The size and shape of each individual particle was measured and estimated from a high-magnification secondary electron image ($M > 10000$). The required net X-ray intensities for the elements were obtained by non-linear least-square fitting of the collected spectra using the AXIL program.[23] Afterwards, our quantification method was applied to calculate the elemental concentrations for each individual particle. As an example, Figure 7 shows an image and two spectra concentration values (%w) for two typical North Sea particles.



Element	Conc
C	1.0
N	9.0
O	45.3
Na	33.2
Mg	0.4
Si	0.1
S	3.7
Cl	4.9
K	0.8
Ca	1.7

Element	Conc
C	1.6
O	5.2
Na	44.2
Mg	0.2
Si	0.1
S	0.4
Cl	47.8
Ca	0.5

Figure 7: Spectra and images for an aged sea salt (left) and a sea salt (right) particle

For obtaining information on the possible sources of the aerosol and the possible chemical interactions between gaseous and particulate pollutants, the particles were classified into representative groups using the chemical and morphological data obtained by TW-EPMA. For the comparison of the sample sets collected at a different location and time, all particles for each impactor stage (size fraction) were classified into typically ten groups using the non-hierarchical Forgy algorithm.[24] For simplifying the graphical representation, some similar clusters were taken together afterwards (e.g. several, slightly different groups of aluminosilicates were considered as one group).

Table 2 below will provide an overview of the overall average elemental concentrations for each cluster type that was found in the data set. The only real identification problem was encountered in case of particles that could contain aluminium, since the quantification of this substrate element was not possible (for the same reason, it is not included in the table). For example, when the silicon and oxygen concentrations for a cluster were found to be relatively high compared to those of other elements, the cluster was identified as “Aluminosilicates”. We cannot prove that all of these particles really were indeed aluminosilicates or that these particles did or did not contain aluminium, but we think it is fair to use this identification based on our experience in conventional SEM. Since the exact identification of (alumino)silicates or other aluminium particles was not our highest priority in these experiments about atmospheric nutrient deposition, we saw no need to go deeper into this matter. It might be interesting to know for the reader, that, from a chronological point of view, this identification problem was in fact the reason for us to carry out the comparative study of different substrates (see chapter 2).

2.3 Results and discussion

The sampling campaign started on September 28, 1998 in the harbor of Zeebrugge, a town at the Belgian coast, where the research vessel Belgica began its journey to location NS1. Shortly after arriving at this point, the first sample (S1) was taken while traveling between locations NS1 and NS4, and sample S2 was taken during a night stop at the latter location. The third sample (S3) was collected while travelling between locations NS4 and NS3. Since it rained at the end of the sampling of stages 4 and 5, and during the sampling of stages 6-8, the results for this sample should be interpreted with much care. Three more samples were taken with the Berner impactor in the southern part of the North Sea and near the English Channel, as can be seen in the table below.

Table 1: Location, date and start time of the sampling

Sample	Location	Start date	Start time
S1	NS1 – NS4	29/09/1998	19:43
S2	NS4	30/09/1998	03:00
S3	NS4 – NS3	30/09/1998	08:40
S4	120 – CH2	30/09/1998	17:10
S5	CH1 – 421	01/10/1998	07:35

The name of the locations were not randomly chosen; fixed codes were assigned to the sampling stations by the Management Unit of the North Sea Mathematical Models and the Scheldt estuary (BMM), and they are applied by all of the visiting scientific crews on the Belgica for reasons of uniformity. Each station also has well-known coordinates, which makes it easier for the scientific crews to plan their sampling campaigns. The figure below shows the exact route that was traveled by the Belgica.

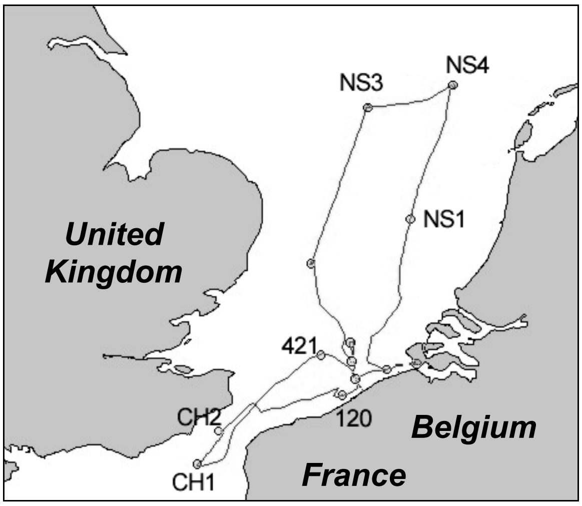


Figure 8: Route traveled by the Belgica

The table below gives the average cluster composition for all stages and for the most important or relevant elements. This table should be considered as an indication of the criteria that were used for the cluster identification (relevant concentrations are printed in bold). As mentioned before, aluminium is not included, since it was the substrate element. The results for all the samples after clustering can be found in Figure 9, which contains graphs showing the abundance of the different particle types present on the stages of the Berner samples.

Table 2: Overall average particle composition for each cluster type (in %wt)

	C	N	O	Na	Mg	Si	S	Cl	K	Ca	Ti	Fe
$(NH_4)_2SO_4$	9.1	**13.5**	**55.5**	2.4	2.2	0.3	**15.2**	0.2	0.6	0.4	0.1	0.1
$(NH_4)_2SO_4 + NH_4NO_3$	7.7	**18.1**	**52.2**	2.8	2.2	2.0	**11.9**	0.6	0.4	0.6	0.0	1.5
$(NH_4/Na)(NO_3/SO_4)$	9.9	**11.2**	**52.9**	**10.7**	1.8	0.9	**10.1**	0.2	1.8	1.0	0.0	0.3
NaCl	9.1	0.6	11.1	**35.0**	1.0	0.1	0.0	**42.0**	0.0	0.2	0.0	0.0
NaCl + Organic	**13.0**	0.6	**16.6**	**32.8**	1.5	0.2	0.4	**32.9**	0.3	0.6	0.0	0.1
$NaCl + NaNO_3$	7.8	**10**	**40**	**25.1**	3.2	0.2	1.8	**10.8**	0.1	0.8	0.0	0.1
NaCl + Aluminosilicates	3.2	0.0	6.1	**19.8**	0.6	**45.7**	0.0	**23.4**	0.0	0.0	0.3	0.0
NaCl + Oxides	7.0	1.4	**27.0**	**31.1**	5.1	0.2	1.2	**19.4**	3.4	0.0	**1.0**	**3.2**
$NaNO_3$	3.9	**14.2**	**51.3**	**25.6**	1.7	0.2	0.0	0.4	1.7	0.2	0.6	0.1
Organic	**46.0**	5.1	**41.6**	0.9	0.4	1.4	2.3	0.4	0.6	0.6	0.1	0.2
Organic + S	**35.1**	4.9	**45.0**	0.6	2.5	0.5	**10.7**	0.1	0.1	0.3	0.0	0.2
Aluminosilicates	8.1	4.4	**51.3**	1.9	2.6	**19.7**	0.2	0.4	1.8	1.2	0.2	**3.2**
Fe_2O_3	6.9	2.4	**38.2**	1.6	2.1	3.8	0.5	1.8	0.3	0.2	0.2	**40.9**
Oxides	9.6	2.7	**72.5**	1.0	**5.2**	**3.3**	0.0	1.0	0.4	0.1	**3.1**	0.0
$(Ca/Mg)(CO_3/SO_4)$	**9.3**	**5.9**	**54.2**	2.6	**3.6**	0.9	6.6	2.1	1.2	**12.2**	0.5	0.2
Biogenic	**40.4**	**7.5**	**39.0**	1.2	1.9	0.7	**3.1**	0.4	**4.5**	0.1	0.0	0.2

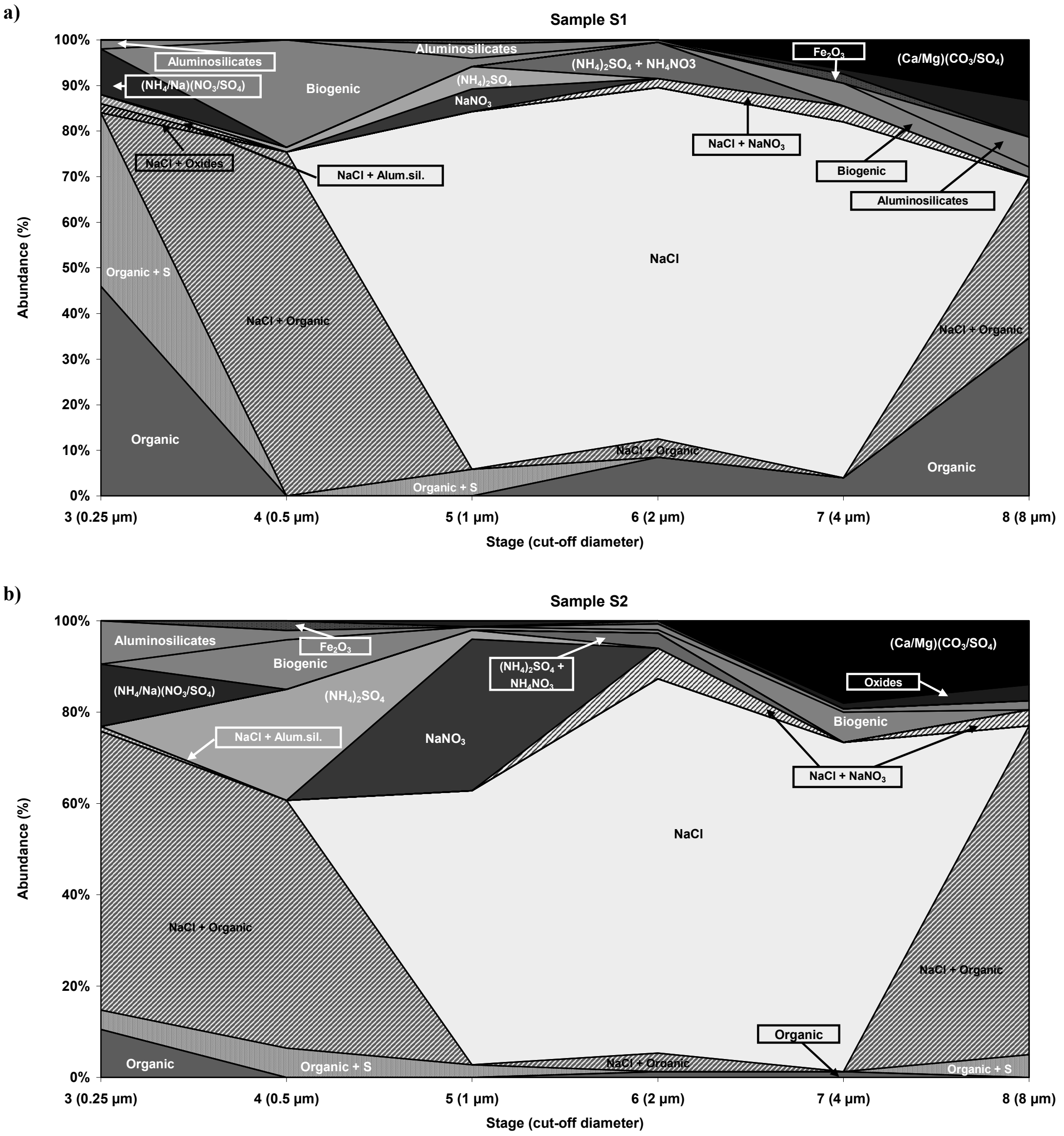


Figure 9a-b: Results of the clustering analysis of the different samples

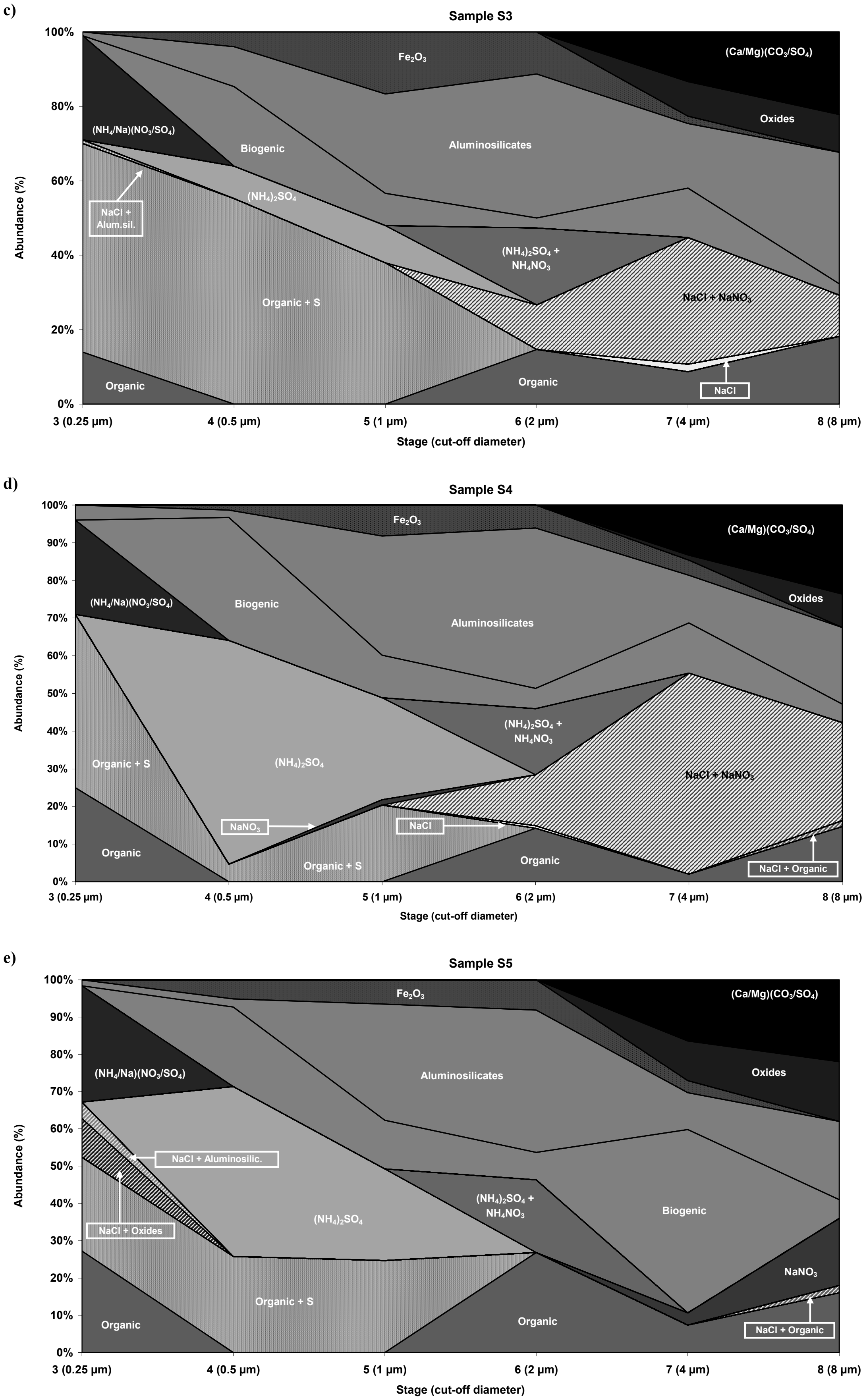


Figure 9c-e: Results of the clustering analysis of the different samples (continued)

Since the aim of our experiment was to find out more about the atmospheric deposition of certain compounds to the North Sea, our starting point was to distinguish the impact of either marine or continental influences on the different samples. A look at the 48h air mass backward trajectories gives us a first indication for this study. Figure 6a shows that the air mass sampled at the beginning of sample S1 had only traveled about 18h over land, followed by 30h over the sea before reaching location NS1. In the final sampling of stages 7 and 8, the air mass traveled even less over land (only 12h). The back-trajectory in Figure 6b shows that in the beginning of the second sampling (S2) at position NS4, the air had traveled 12h over land. However, the air sampled at the end had traveled only over the sea in the previous 48h. Starting from these data, one could expect that the marine influence on the aerosol composition of these samples should be high, which is further endorsed by the fact that these sampling positions are the most distant locations from the continent in our campaign. The back-trajectory of sample S3 in Figure 6c shows an interesting curl above a location known for the enormous amount of ships crossing the English Channel. During the sampling, this curl enrolls, ending up over the United Kingdom. Although the sampled air traveled most of its time above the sea, the composition of this sample could be most interesting, since it is expected to show the influence of sea traffic. A look at the backward trajectories of sample S4 in Figure 6d, shows us that the air sampled at this locations traveled over Central France for almost 48h, before it finally reached the North Sea coast near Belgium. The air mass sampled at the beginning of sample S5 originated from the Bay of Biscay, but it spent most of its time above France before ending up at the sampling location (see Figure 6e). Therefore, samples S4-S5 are expected to have more continental influences, which will be further investigated looking at the results of the individual particle analysis of the samples by TW-EPMA.

Figure 9a-b show that **sodium chloride** (sea salt) particles are highly abundant on stages 5-7 of samples S1-S2, which is indeed a fingerprint for the important marine influence on the sampled aerosol. The so-called *bubble bursting* or *sea spray* process transports water drops from bursting sea waves (white caps) into the air, after which crystallization takes place and some salts remain airborne. Therefore, sea salt should be the main constituent among the coarse particle fractions in marine aerosols, except during episodes of continental dust transport.[12]

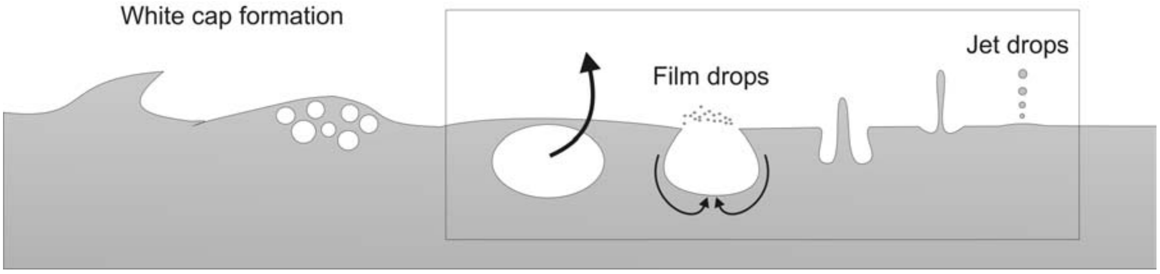


Figure 10: Bubble bursting process

The contrast with samples S3-S5 can be clearly seen in Figure 9c-e, since sea salt particles were almost never found as a ‘pure’ particle type, i.e. without any other compounds. Indeed sodium chloride was often, though not highly abundant, agglomerated with silicates, organics and metal oxides. On the stages with larger particle diameters, however, the influence of continental sources is visible through the presence of so-called *aged sea salt*. Sodium and magnesium chloride are known to react with other compounds in the atmosphere like nitric and sulphuric acid, which results in chloride loss, since hydrochloric acid evaporates while the formed nitrates and sulphates stay behind as “aged” sea salt (together with some remaining chloride if the particle did not react completely).

TW-EPMA is able to detect nitrogen and oxygen, so we were able to clearly identify **sodium nitrate**.[25,26] Conventional EPMA could only identify these particles as "sodium-rich", not excluding the presence of organic sodium-containing particles among them. Most of the sodium nitrate type particles were found to be hemispherical, which might indicate that they had been in liquid form during sample collection, since these sampled droplets splash apart during impaction on the substrate surface (see Figure 11). A solution of this so-called particle bounce-off effect is often avoided by using coated collecting substrates with a sticky surface. This was not possible for our analysis by TW-EPMA, so that size misclassification could have occurred.

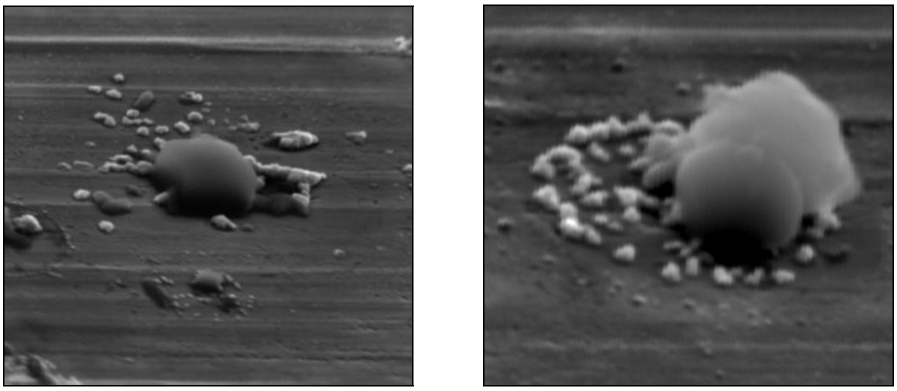


Figure 11: Images of two tilted 'particle droplets' (M=5000, tilt=60°)

Although we only used "$NaNO_3$" as the name for the particle type identification, small sodium sulphate crystals were often observed to be connected to the surface of larger sodium nitrate particles. A possible reason for this effect is the inhomogeneous crystallization at the impacting surface, since sodium sulphate crystallizes at higher relative humidity.[27] Nitric and sulphuric acid in the air find their origin in transformations and reactions of nitrogen and sulphuric oxides. In urban environments, these compounds are mostly found as exhaust gases from combustion processes (domestic heating, industrial processes, traffic). Marine organisms in oceans and seas are also known as sources for organic sulphur-containing compounds, but considerable uncertainty still exists with regard to the nature and sources of nitrogen-containing precursor gases and their conversion mechanisms to particulate nitrate.[12,28] Since the sea is a continuous source of fresh sodium chloride, and since the sea salt in air masses traveling over land has more chance to react with anthropogenic nitrogen and sulphur oxides, we could say that relatively high abundances of (progressive) sea salt aging is an indication for continental influences. The abundance of aged or completely transformed sea salt, like sodium nitrate, was also much higher in the more continentally influenced samples (S4-S5) than in the first two, more marine samples (S1-S2). The sampled air of sample S3 travelled most of its time over sea, but not much pure sodium chloride could be found (only some small fraction on stages 3 and 7). Like in S4 and S5, sample S3 contains a big amount of aged sea salt on stages 6-8, and two explanations can be found for this continental behaviour. First of all, it rained at the end of the sampling of stages 4 and 5, which explains the missing amount of pure sea salt on these stages, and also on stages 6-8 (which were also being sampled, but were not finished yet). Secondly, S3 was sampled in one of the busiest areas for sea traffic, and ship plumes could also contain sulphur and nitrogen oxides. Furthermore, it might be that the meteorological conditions after the rain showers (humidity), could have improved the reaction conditions for sea salt aging. However, these conclusions should be considered with reservation, because it is difficult to judge the impact of the rain showers.

Organic particles and biogenic particles (recognized by their relatively higher potassium or phosphorus content) were detected with TW-EPMA on the different stages of all Berner samples, and this is of course a strong improvement compared to conventional EPMA. However, we must mention that these particles are difficult to characterize more specifically, since only elemental concentrations can be determined with TW-EPMA for elements with $Z > 5$, so excluding hydrogen. For the samples influenced by marine sources, we see a higher abundance of organic particles on stage 6-8 of sample S1, while in sample S2 they are more abundant on stages 3-4. The amount of organic and biogenic particles is considerably higher in samples S3-S5, which seems logical taking into account the possible continental sources of these particle types (traffic, industrial processes, domestic heating; vegetation, other bioactivity). In urban aerosols, most carbon-containing particles (soot and carbon) originate from combustion processes, so these sources must certainly be involved. The marine bubble bursting process might contribute to the organic fraction, since it also causes (bio)organic materials from the sea water to be transported into the atmosphere. The fact that numerous sea salt particles also appeared to contain certain amounts of carbon and oxygen (maybe as an organic layer on top of the sodium chloride crystals) is probably a result of this process. Even a mixed particle type of sea salt and organic compounds was found in these samples ("NaCl + Organic"). The presence of organic particle layers or coatings was demonstrated earlier for particles suspended in seawater by using an indirect method (staining with ruthenium for organic carbon),[29] but with TW-EPMA we could now directly show the presence of carbon in the X-ray spectra. Various organic compounds are emitted by anthropogenic or natural sources, and through many different mechanisms they could react with and adsorb to the surface of atmospheric particles. For example, the bubble bursting is also able take organic matter from the sea into the air. [12]

Ammonium sulphate and nitrate particles originate from transformations and reactions of nitrogen and sulphur oxides in the air and, like for sea salt aging, the presence of ammonium particles can be related to continental influences. Again, TW-EPMA has extended the capabilities of conventional EPMA, since it was able to specify the origin of sulphur-rich particles (now split up in "Organic + S" and "$(NH_4)_2SO_4$"). Moreover, it is now able to clearly identify ammonium nitrate, which only consists of low-Z elements and, therefore, could have been confused with organic compounds before. However, we never found any pure ammonium nitrate in our samples, but ammonium sulphate particles on the higher stages showed to contain higher nitrogen concentrations, suggesting the presence of ammonium nitrate. Compared to samples S1-S2, a considerable increase in ammonium sulphate and nitrate particles can be found for the continentally influenced samples, especially for S4-S5. Ammonium sulphate appears to be more dominant on stages 3-4, while the particles with mixed ammonium sulphate and nitrate are most abundant on stage 6. We also found a group of particles, which was very difficult to identify (especially in sample S5), since it contained a mixture of different elements (Na, N, O, S). This irresolvable mixture was called "$(NH_4/Na)(NO_3/SO_4)$", which indicates that it could not be appointed to one or two compounds only, since it could exist of ammonium, sodium, nitrate and sulphate in different possible combinations. The presence of this more complex particle composition indicates again the progressive continental influence.

The **(alumino)silicates** in the fine particle range of samples S1-S2 are expected to have their origin in soil dust, which is transported overseas by the wind (comparable with the more extreme effect of e.g. the transportation of mineral dust from Central-Asian deserts over China to Korea, Japan and even America). [12,25,30] Large soil dust particles are not often transported over large distances because of their fast deposition rates, and, therefore, their abundance is expected to be only very high on stages 6-8 if the analyzed samples would have been strongly influenced by continental sources.

This is indeed not the case for the marine samples (below 7% for silicate particles on all stages), although the highest stages (7-8) contain other soil dust particles like metal oxides, but to a lesser extent. Another source for silicates and metal oxides are incomplete combustion processes, producing fly ash particles, but since the sampled air was found to have mostly traveled over sea, this source is expected to have a lower impact on the aerosol composition. In both more marine samples (S1-S2), we also found small quantities of internally mixed sea salt and mineral dust particles, which could result from cloud processes like coagulation of cloud condensation nuclei of both particle types and/or the scavenging of the mineral particles by cloud droplets.[1] The contribution of mineral particles, like aluminosilicates or oxides, to the aerosol composition was much higher for samples S4-S5 (as expected), which again proves the evident fact that soil dust is more abundant above the continent. Iron oxide and other metal oxides showed to be more abundant than in the more marine samples, which could also partly be explained by the presence of the intense metallurgic industry in Northern France.[3]

On the stages with the larger particles, we found **calcium or magnesium carbonate** and sulphate particles originating from both continental and marine sources. The order of the crystallization of several salts after the evaporation of seawater is known to be: calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), gypsum ($CaSO_4(aq)$), halite (NaCl) and Mg-K salts.[31] The crystallized calcium carbonate particles could further react with sulphuric acid to form calcium sulphate. On the other hand, numerous land-based sources were also suggested in literature, like the weathering of limestone buildings; the erosion, blasting and transport of building materials; combustion processes.[7] The abundance of calcium and magnesium carbonate or sulphate was not considerably higher for samples S4-S5 than for the more marine samples S1-S2, so maybe this shows that the marine and continental sources have similar strength.

To confirm the conclusions of our small-scale experiment above, we did an objective, additional test. In order to investigate the fingerprints of the possible sources of the particles, a data matrix containing the abundance values of the particle types on stage 5 (cut-off diameter 1.0 µm) of the five Berner samples was subjected to **principal component analysis**, without *z*-transform prior to the analysis. The first two components of this purely mathematical evaluation were sufficient to describe more than 95 % of the variance of the data set, therefore the loadings and the scores of these components are plotted in the figure below (loadings on the left, scores on the right).

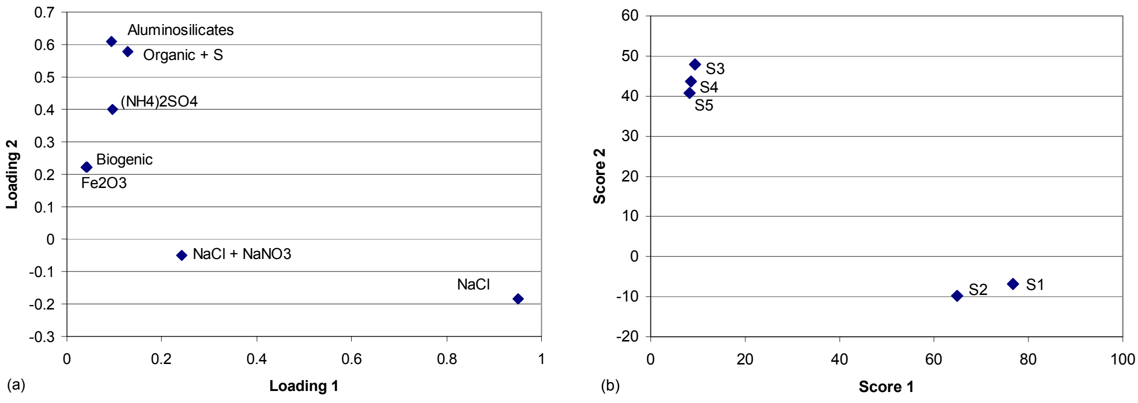


Figure 12: Loadings and scores of PCA applied to the Berner stage 5 samples (> 10 µm) a) loading plot, b) score plot

By looking at the loadings of the different particle types, the first component can be connected to marine origins, since ‘pure’ sea salt has the highest values of this component, followed by ‘aged’ sea salt (containing sodium nitrate). The second component can be connected to more continental origins. From the scores plot, it is clear that the samples also form two distinct groups. The first two samples (S1-2) are again grouped, due to their marine origin, while S3-S5 show continental origin. Again good correlation could be found between these PCA results and the backtrajectories.

The **conclusion** of our experiment is that we have obtained quite a lot of knowledge about the transformation and transportation mechanisms of atmospheric particles with just a few small-scale test measurements. The combination of meteorological data (backtrajectories, weather conditions) with information about the morphology and composition of single particles has provided us several insights in the relations between the natural marine environment and the influence of anthropogenic pollution sources.

As indicated in the introduction, it was clear to us that TW-EPMA on its own would not be able to produce useful quantitative data about the fluxes of atmospheric pollutants from the air to the sea. For this, we would need another method, which we found in ion chromatography. Unfortunately, we did not take exactly parallel samples for analysis by IC during the sampling of the previously discussed Berner sets, since these were only taken for testing TW-EPMA only. However, the next section of this chapter will discuss another experiment for a similar project in which we did combine IC and TW-EPMA.

3. Sampling campaign in Adinkerke

3.1 Introduction

Transboundary pollution is currently a hot topic for the member states of the European Union. In order to improve the air quality, different European directives oblige the different national environmental administrations to take actions against the emission of certain pollutants. For some pollutants, however, actions are very difficult to take on the national level, since large fractions of the pollution loads originate from sources in neighboring countries. Especially for Belgium, it is sometimes hard to take effective measures against air pollution, since it is surrounded by highly industrialized regions in France and Germany. Studies have shown that about 47% of the acidifying pollutants and 79% of the non-diffuse anthropogenic particulates in Flanders originate from abroad.[32,33] Of course, this is not a one-way effect, since Belgian sources affect the air quality in other countries as well. Therefore, it is important for Europe to study these transboundary effects, in order to address the problem of air pollution in an efficient and effective way.

French and Flemish environmental agencies have started up the INTERREG projects AEROSOL and EXPER/PF to study the air quality in the region of Nord-Pas-de-Calais at both sides of the border.[34,35,36] Joint sampling and measurement campaigns were organized in combination with the setup of a combined monitoring network to build up a database that can be used for this purpose. In 2001, we joined in on a campaign in Adinkerke, a borough of De Panne which is a town near the Belgian coast at the border with France (see Figure 13).

This was again an opportunity for us to test the possibilities of TW-EPMA for applications in environmental research. Therefore, a short experiment was organized to carry out parallel collection of samples for analysis by IC and TW-EPMA. We realized it would be interesting to compare the results of a bulk analysis technique, such as ion chromatography (IC) with the statistically evaluated data for a large number of analyzed single particles derived from a microanalytical technique like TW-EPMA. Some of the results were already discussed in the thesis of K. Eyckmans, but we will now go into more detail to show the mutual advantages of both complementary techniques.

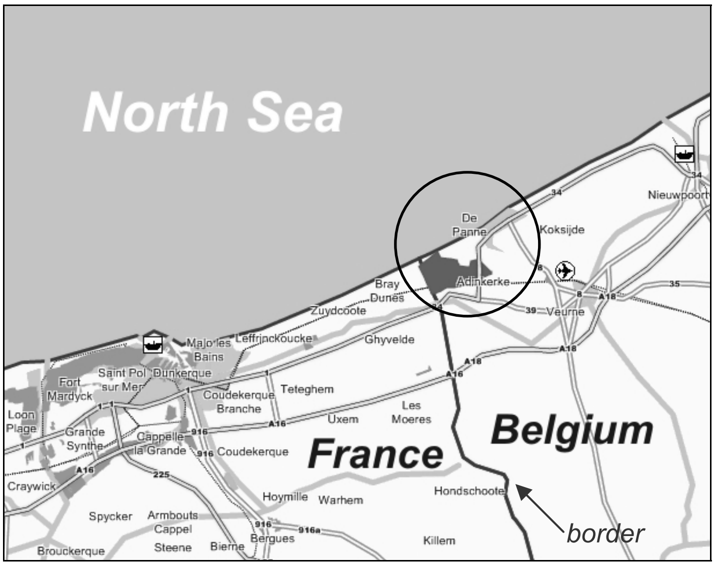


Figure 13: Location of Adinkerke, Belgium

3.2 Methodology

The sampling campaign was organized at Adinkerke, De Panne, Belgium, at 3 km from the French border and 2 km from the coast. The station is located in a rural environment, east of the nearby Belgian nature reserve Westhoek and of the French industrial area of Dunkerque. The air quality in the region is frequently affected by the industrial area due to the dominant western-southwestern wind.

For atmospheric aerosol analysis, most often filter samples are collected for subsequent bulk analysis.[37] However, no information is then obtained about the size distribution of the particles. Size-segregating impactor sampling may offer a broader insight concerning the sources, the transformation and the transportation of the aerosol particles. For this study, the airborne particulate phase was sampled with different impactors (May and Berner types).[38,39] For *bulk analysis* by IC, the air was sampled with a May impactor (cut-off for the different stages: 0.25, 0.5, 1, 2, 4, 8, and 16 µm). On each stage, a glass support covered with a Nuclepore filter was used as impactor plate or collection substrate. After the sampling, the Nuclepore filter was removed from the glass plate, subsequently immersed into three ml of Milli-Q water and treated ultrasonically for ten minutes.[10] The solution was, after filtering by a Millex 0.22 µm filter, ready for IC analysis (Dionex, DX 120, equipped with an AS 14 anionic and a CS 12 cationic column). Sampling for the *single particle analysis* by TW-EPMA was done with a Berner impactor using stages 3-8, having cut-offs of 0.25, 0.5, 1, 2, 4 and 8 µm respectively. The used impaction substrates were silicon for stages 3 and 4 and a polished silver foil for stages 5 to 8. Different sets were sampled per day, with a sampling duration of 2 minutes for stage 3, 10 minutes for stage 4, 45 minutes for stage 5, 90 minutes for stage 6, and 150 minutes for stages 7 and 8. Afterwards, the samples were analyzed with our JEOL 733-JXA electron microprobe, equipped with the Oxford Link Pentafet EDS thin-window detector and a liquid-nitrogen cooling stage to prevent evaporation of volatile particles. For stages 3 and 4, typically 100 particles were analyzed manually, while for the large-size stages, 150 particles were analyzed automatically. After analysis, the different spectra for the particles on each stage of both samples were statistically interpreted using AXIL software, followed by our Monte Carlo quantification and clustering procedures.[23,24,40]

Samples were taken on two different days (06/06/2001 and 12/06/2001), with almost identical meteorological conditions. The temperatures were comparable, between 9 °C and 19°C. During these days, there was a westerly wind with an average wind speed of about 18 km/h and there was no precipitation during the sampling period. The air mass backward trajectory plots are presented in Figure 1a and 1b. The air masses had marine origins with possible continental influences, since they crossed France (June 6) or the U.K. and Ireland (June 12). The sampling was started every day in the morning at 9.00 h and was terminated around 16.00 h.

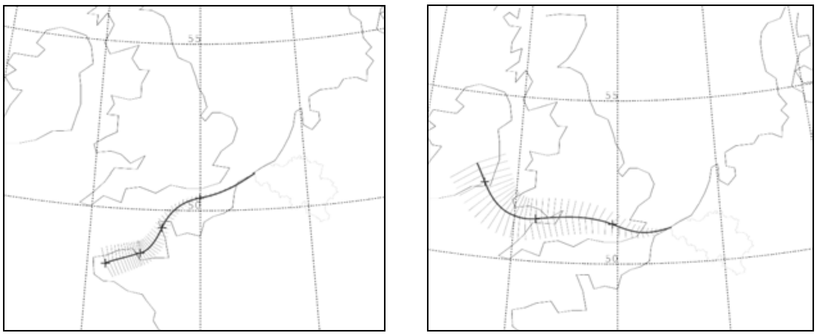


Figure 14: Backtrajectories for Adinkerke on June 6 (left) and June 12 (right)

3.3 Results and discussion

Figure 15 gives a compact overview of the obtained results from IC and TW-EPMA analysis, which will be discussed here.

From the **IC results**, one could conclude that the concentration profiles are quite comparable for both samples. The highest concentrations were collected in the smallest size fraction, with much lower and comparable concentrations for the rest of the size fractions. Sulphate appeared to be the dominant compound for the smallest aerosol fractions. For particles larger than 1 µm, the nitrate and sodium compounds were most abundant. Except for the smallest size fraction, chloride concentrations increased with the particle size, especially on June 12.

A limitation of IC as a bulk technique is of course the fact that the bulk concentrations cannot be traced back to individual particle concentrations. However, it would already be interesting to know how the dissolved ions were present in solid particles; in other words: which anions are linked to which cations and vice versa. For the smallest particle fraction of the June 6 sample, the presence of a large amount of sodium or ammonium sulphate particles is highly probable, but it is impossible to know the exact absolute or even relative amounts, in pure and/or mixed particles. The ammonium fraction could also be linked to ammonium sulphate, ammonium nitrate or mixtures of both. The nitrate fraction might originate from sodium nitrate, ammonium nitrate, etc. In the larger size fractions, a mixture with high nitrate and sodium concentrations suggests the presence of sodium nitrate. The higher sodium and chloride concentrations for the largest size fractions indicate the growing influence of coarse sea salt particles. Similar conclusions can be drawn from the June 12 sample. The high sulphate concentrations for the smallest size fraction probably originate from sodium sulphate, while the high chloride fraction is again connected to primary sea salt. For the larger particles, higher nitrate and sodium concentrations were found. Chloride again suggests the presence of sea salt, but it is unclear whether it is present as pure particles or as aged sea salt agglomerations.

On the stages with the smallest particles in the 6 June sample, typical **TW-EPMA** clusters for fine particles can be found (organic compounds, ammonium nitrate and sulphate, sodium nitrate and sulphate). In stages 3 and 4, clusters of ammonium nitrate and sulphate could be clearly identified. On the stages with larger particles, aluminosilicates and calcium-containing particles are more abundant. Important was the fact that on stages 5-8, mostly irresolvable clusters ("Mix") were found, i.e. they could not be split up into different, smaller clusters. These clusters consisted of a mixture of elements (N, O, Na, S and Cl), quite similar to the clusters that were identified as "(Na/NH_4)(SO_4/NO_3)" in the Belgica experiment. Some stages could only be associated to this cluster type, which makes the clustering look quite odd. Aluminosilicate mixtures of the same elements elements were also found on the stages with larger particles. For the sample from June 12, the same conclusions could be drawn. We could again distinguish clusters of ammonium nitrate and sulphate particles, although the presence of these compounds was less pronounced in the smallest size fraction. On the other hand, a higher concentration of nitrate and sodium compounds was found for the larger particles. A large fraction could again only be defined as "Mix", with limited compositional information about the concerned particle fractions as a result. At first sight, the only additional information could be found in the fact that the concentration of chlorine in the mixtures increased with increasing particle size. This confirms that the mixtures indeed originate from reacted sea salt particles, since the increasing chlorine content could be explained by the fact that larger particles have less been affected by the so-called 'aging' process (i.e. a smaller amount of their sodium chloride content has reacted to form other compounds).

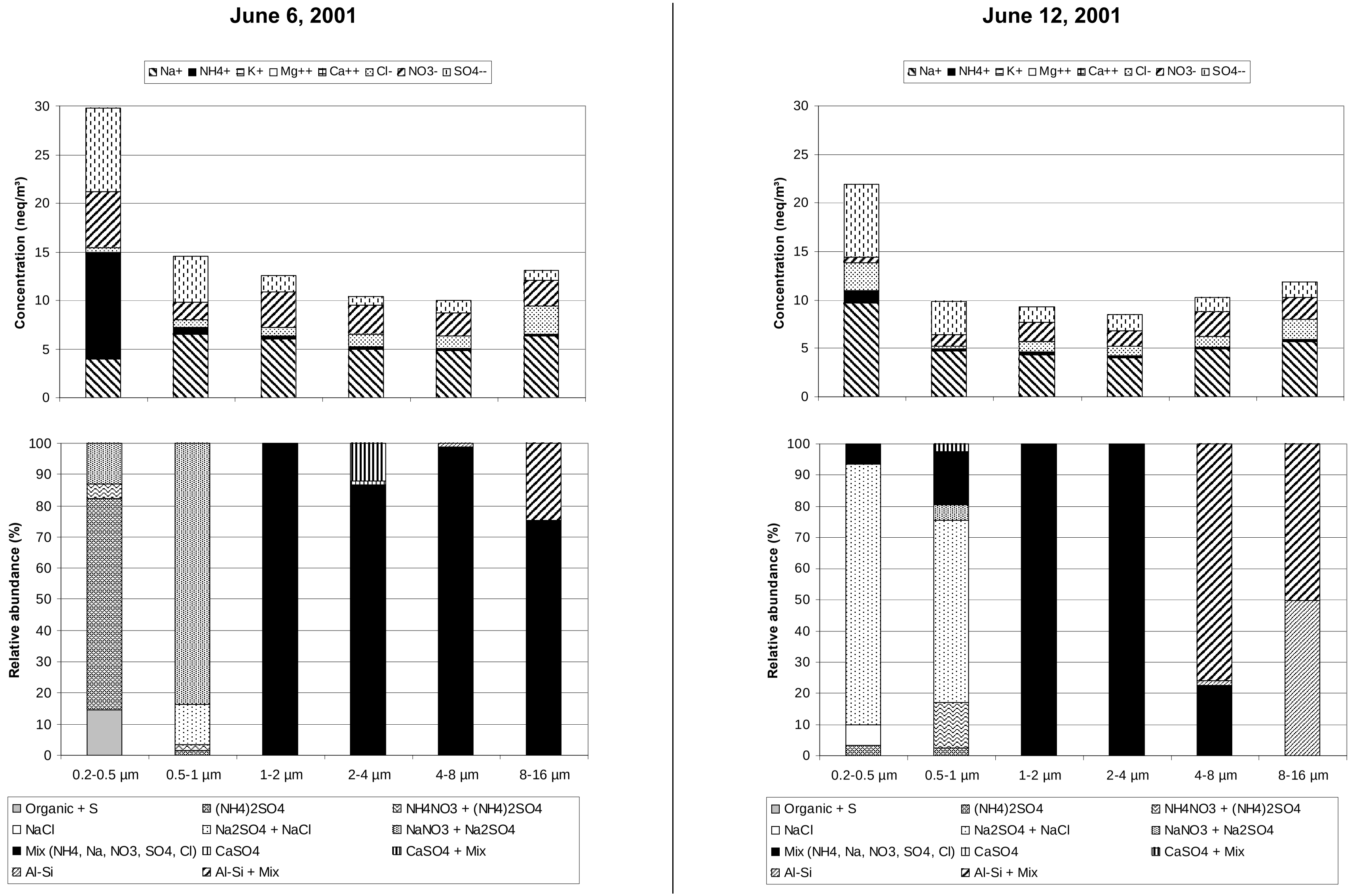


Figure 15: Results of IC (top) and TW-EPMA (bottom) analysis in the Adinkerke experiments

The purely mathematical, statistical classification of the analyzed particles could not resolve these mixtures, which might be an indication that the particles in these statistical clusters are indeed clusters of chemical compounds in the atmosphere. Atmospheric particles react with each other or with gases to form new compounds, resulting in internally mixed particles, e.g. sodium chloride particles might be transformed to mixed particles consisting of sodium chloride, nitrate and sulphate. However, a quantitative comparison at the individual particle level showed more variation. Therefore, our next goal was to exploit all the available results in order to extend our knowledge as far as possible.

Our first tactic existed of **combining the bulk and single particle results** from IC and TW-EPMA respectively, especially to find additional information about the irresolvable 'Mix'-clusters.

For the *June 6* sample, the relative amounts for all the stages are very comparable for the different techniques, with higher ammonium and sulphate concentrations in the smallest stage, higher sodium and sulphate concentrations in stage 4 and significant amounts of sulphate, nitrate, sodium and chloride for the rest of the stages. For stage 3 (0.2-0.5 µm), the large amount of sulphate in the IC results (1.3 µg/m³) seems to originate from ammonium sulphate aerosols and to a lesser extent from sodium sulphate. This also implies that most of the ammonium fraction is linked to ammonium sulphate, and that the nitrate fraction is more connected to the sodium nitrate particles. The sulphate fraction of stage 4 (0.5-1 µm) could almost exclusively be linked to the sodium sulphate fraction (small ammonium sulphate cluster, 1.64%). The rest of the sodium comes from sodium nitrate and sodium chloride. A qualitative interpretation of the IC results for the larger size fractions is not possible, because they are dominated by the 'mixed' clusters for the TW-EPMA analysis. However, it is possible to determine the qualitative and quantitative composition of the indefinable TW-EPMA mixtures based on the IC results. For the comparison and evaluation of the different outputs, the relative abundances of the determined species are shown in the tables below. The abundance of the ions was determined using the concentrations for the whole stage, expressed in nano-equivalents per m³. The particle abundance only relate to that of the 'mixed' clusters.

Table 3: Comparison of relative abundances (%) for elucidating 'Mix'-clusters (June 6)

Size fraction (µm)	Na^+	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	Mix	$CaSO_4$+Mix	Al-Si+Mix
1-2	48	2	7	29	13	100	0	0
2-4	48	2	12	29	8	87	12	0
4-8	48	2	13	24	13	99	0	0
8-16	48	1	22	21	7	75	0	25

The 100% and 99 % mix for stages 5 and 7, respectively, can be directly "quantified" out of the IC output. For stage 6 and 8, we find pure 'Mix'-clusters of 87 % and 75 % respectively, combined with a second cluster that is partly 'Mix'. For stage 6, there is an uncertainty concerning the quantification since the calcium sulphate interferes with the 'Mix' composition (which is assumed to contain sulphate as well). For stage 8, however, the aluminosilicate (crustal dust) fraction does not interfere and again we can quantify this stage for 100%.

When we compare the results of the *June 12* sample, we can deduce very similar relationships between both techniques. Figure 15 shows that the smallest particles (on stages 3 and 4) mainly consist of sodium sulphate.

The rest of the size fractions show a mix of the various compounds, with a clear influence of soil dust in the largest fractions. The smallest particle fraction on stage 3 apparently consists mostly of a mixture of sodium sulphate and sodium chloride. The amount of sea salt becomes less important on stage 4, while the sodium sulphate fraction increases. Stages 5 and 6 contain again mixed particles, while the largest particles contain a large fraction of crustal dust (aluminium silicates). The comparison between both techniques again provides direct quantification of the 'Mix' on stages 5 and 6. For stages 7 and 8, the soil dust fraction is expected not to interfere with the mixture fraction, and thus it is not causing any problems for the quantification of the mix.

Table 4: Comparison of relative abundances (%) for elucidating 'Mix'-clusters (June 12)

Size fraction (µm)	Na^+	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	Mix	Al-Si+Mix
0.25-0.5	44	5	13	3	34	7	0
0.5-1	48	2	3	12	35	17	0
1-2	47	2	12	21	17	100	0
2-4	47	2	12	19	19	100	0
4-8	48	2	10	25	15	23	76
8-16	48	1	17	20	13	0	50

After this initial, combined approach, we concluded that the application of the combination of both techniques is quite rewarding. They offer each their own specific interpretation of the composition, but both methods show the same trends in particle composition. The output of the bulk and individual particle analysis techniques is quite complementary. Both produce different types of analytical results (absolute versus relative concentrations) and this on a different level for both methods (bulk filters versus single particles). This might seem a limitation for both techniques separately, but it turned into an advantage when both methods were combined. Combining the IC results with the TW-EPMA output, we were able to determine which inorganic compounds were present in the most important size fractions, for which IC only provided quantitative ion concentrations. Before the interpretation of TW-EPMA with the IC output, some irresolvable, undefined clusters could only be seen as a mixture of different compounds. In the present case, the TW-EPMA technique was very limited in offering adequate information, but the combination with the IC data made it possible to quantify these mixed clusters.

Around the same time that we encountered the problems above, the idea rose to set-up an expert system for **resolving the chemical composition of the single particles**, like the mixed ones we found in Adinkerke. Once the system was developed (explained in the previous chapter),[41] we were of course anxious to find out which insights it could offer about our data. We applied the expert system to both datasets and specifically to the type of particles that were clustered and assigned as 'Mix'. The following tables contain the results of the resolved particle compositions, and these clearly show much more detail than the classical clustering tools. For each 'mixed' cluster that was obtained above, we grouped the types of particles that were found by the expert system.
It should be noted that the X-ray spectra of the analyzed particles often contained a carbon peak, suggesting that some carbon-containing compounds might be present in relatively small quantities (maybe as adsorbed layers on the outside of the particle). The presence of such (organic) species is not reflected in the results of the expert system due to their low concentrations, and the composition could probably not be easily resolved anyway.

Table 5: Expert classification of 'mixed' clusters in June 6 sample

	ABUNDANCE (%) PER STAGE (µm)			
CLASSIFICATION	*1-2*	*2-4*	*4-8*	*8-16*
Mix	**100.0**	**86.6**	**98.7**	**75.3**
$NaNO_3$-FeOx	3.33		3.23	6.67
$Na(NO_3,Cl)$	3.33	9.38		
$Na(NO_3,Cl)$-SiOx	3.33			
$Na(NO_3,Cl)$-FeOx			3.23	6.67
$Na(NO_3,SO_4)$-SiOx				13.33
$Na(NO_3,SO_4)\text{-}(Ca,Mg)SO_4$		3.13		6.67
$Na(NO_3,SO_4,Cl)\text{-}(Ca,Mg)(NO_3,SO_4)$	10.00			
$(Na,Ca)NO_3$			3.23	
$(Na,Ca)NO_3\text{-}NaCl$		6.25	3.23	6.67
$(Na,Ca)(NO_3,SO_4)$	10.00	15.63	6.45	
$(Na,Ca)(NO_3,SO_4)\text{-}NaCl$	3.33	3.13	3.23	
$(Na,Mg)(NO_3,Cl)$		3.13		
$(Na,Mg)(NO_3,SO_4)$	26.67	28.13	3.23	6.67
$(Na,Mg)(NO_3,SO_4,Cl)$	6.67	3.13	16.13	6.67
$(Na,K)(NO_3,SO_4)$			3.23	
$(Na,Ca,Mg)NO_3$		3.13	3.23	
$(Na,Ca,K)NO_3$				6.67
$(Na,Ca,Mg)(NO_3,SO_4)$	3.33	3.13		
$NH_4(SO_4,Cl)$			6.45	6.67
$NH_4(CO_3,SO_4)$			6.45	6.67
$(NH_4,Ca)(SO_4,CO_3)$			6.45	13.33
$(NH_4,Mg)(SO_4,Cl)$	6.67			
$(NH_4,Mg)(SO_4,CO_3,Cl)$		9.38	6.45	6.67
$(NH_4,Na)SO_4$	3.33		6.45	
$(NH_4,Na)(SO_4,Cl)$			3.23	
$(NH_4,Na)(SO_4,Cl)\text{-}(Ca,Mg)SO_4$	3.33			
$(NH_4,Na,Ca)SO_4$	6.67	3.13	6.45	
$(NH_4,Na,Ca)(SO_4,Cl)$			3.23	
$(NH_4,Na,Ca)(SO_4,CO_3)$			3.23	
$(NH_4,Na,Mg)SO_4$	3.33	6.25		6.67
$(NH_4,Na,Mg)(SO_4,Cl)$	3.33	3.13		
$(NH_4,Na,K)SO_4$			3.23	
$(NH_4,Na,Mg,Ca)SO_4$	3.33			
$CaSO_4$ + Mix		**12.0**		
$(Ca,Mg)(NO_3,SO_4,Cl)$		15.9		
$(Ca,Mg)(NO_3,SO_4)$-SiOx-FeOx		29.4		
$(Ca,Mg,Na)(NO_3,SO_4)$		41.1		
$(Ca,Mg,NH_4)(SO_4,CO_3)\text{-}(Ca,Mg)Cl_2$		1.8		
$(Ca,NH_4,Na,K)SO_4$		11.8		
Al-Si + Mix				**24.7**
$AlSi\text{-}Na(NO_3,SO_4)$				89.5
$AlSi\text{-}(Ca,Mg)(NO_3,CaSO_4)$				10.5

Table 6: Expert classification of 'mixed' clusters in June 12 sample

	ABUNDANCE (%) PER STAGE (µm)					
CLASSIFICATION	*0.25-0.5*	*0.5-1*	*1-2*	*2-4*	*4-8*	*8-16*
Mix	**6.56**	**17.1**	**100.0**	**100.0**	**22.7**	
$Na(SO_4,Cl)$	33.33		11.11	2.78		
$Na(NO_3,Cl)$			5.56	13.89		
$Na(NO_3,Cl)\text{-}Ca(NO_3,SO_4)$			2.78			
$Na(NO_3,SO_4,Cl)$	11.11			11.11	18.18	
$(Na,Ca)(NO_3,SO_4)$			2.78	5.56	9.09	
$(Na,Ca)(NO_3,SO_4,Cl)$			8.33	5.56		
$(Na,Mg)SO_4$	55.56		2.78			
$(Na,Mg)(SO_4,Cl)\text{-}FeOx$			2.78	2.78		
$(Na,Mg)(NO_3,SO_4)$			16.67	27.78	27.27	
$(Na,Mg)(NO_3,SO_4)\text{-}SiOx$			2.78			
$(Na,Mg)(NO_3,SO_4,Cl)$		35.71	2.78	5.56		
$(Na,Mg,Ca)SO_4$			5.56	2.78		
$(Na,Mg,Ca)NO_3$			2.78			
$(Na,Mg,Ca)(NO_3,SO_4)$			11.11	13.89		
$(Na,NH_4,Mg,K)SO_4$				2.78		
$NH_4(SO_4,Cl)$					9.09	
$(NH_4,Na)(SO_4,Cl)$		28.57			18.18	
$(NH_4,Na)(CO_3,SO_4)$		7.14			9.09	
$(NH_4,Ca)SO_4$			2.78			
$(NH_4,K)SO_4$		7.14				
$(NH_4,Ca,Mg)SO_4$			5.56	5.56		
$(NH_4,Na,Ca)SO_4$		21.43	13.89			
$(NH_4,Na,Mg)SO_4$					9.09	
$CaSO_4$ + Mix		**2.44**				
$Ca(CO_3,NO_3)$		14.29				
$Ca(CO_3,SO_4)$		42.86				
$Ca(NO_3,SO_4)$		28.57				
$(Ca,Mg)(NO_3,SO_4)$		14.29				
Al-Si + Mix					**76.0**	**50.1**
$AlSi\text{-}Na(NO_3,SO_4)$					7.14	16.67
$AlSi\text{-}Na(NO_3,SO_4,Cl)$					82.14	41.67
$AlSi\text{-}(Na,Ca)(NO_3,Cl)$						8.33
$AlSi\text{-}(Na,Mg)SO_4$						25.00
$AlSi\text{-}Ca(NO_3,SO_4)$					10.71	8.33

It is clear from the tables above that the composition of the particles in the 'mixed' clusters is quite diverse. The main purpose of the cluster analysis technique is to reduce the dataset, but due to its mathematical nature, the obtained clusters did not reflect the variety of particles that we found with the expert system. It would of course be possible to limit the clustering, so that a higher number of clusters is retained, but it is never guaranteed that the method will split-up or group exactly those particle clusters that we are interested in. The difference with the expert system is clearly demonstrated, since the expert classification works the other way round. It first suggests a possible composition for each of the individual particles, after which it is possible to combine similar particles into classes. In this way the analyst is able to reduce the level of diversity to exactly the level he desires.

The results show that pure particles, i.e. existing of only one compound, are indeed very rare. Most particles consist of many species, and the expert system is able to suggest a possible composition based on the calculated concentration values and the charge balance rule (as explained in the previous chapter). The results should of course be interpreted with some reservation because of the semi-quantitative nature of the concentration calculations. However, the expert system is a powerful instrument that very easily allows us to distil as much insights as possible out of our datasets. Although the identification of organic compounds is not possible, the speciation of inorganic compounds is a significant achievement that will allow enhancing our knowledge about atmospheric chemistry.

Another aspect is of course the heterogeneity of the particle structure, which can be assessed by MV-EPMA. We applied the technique to a number of aged sea-salt particles, and we found that some were clearly heterogeneous (e.g. as agglomerates or as layered particles), while others could as well be homogeneous in composition. For example, the figures below show two particles that were analyzed at three voltages (5, 10 and 20 kV). The first particle (a) appears to consist of a chloride shell surrounded by a nitrate layer (possibly with some sulphate), because the nitrogen and oxygen peaks dramatically increase relative to the other peaks at lower voltages. The chloride influence in the other figure suggests that the second particle (b) might be more homogeneous, or that its layer is quite thick.

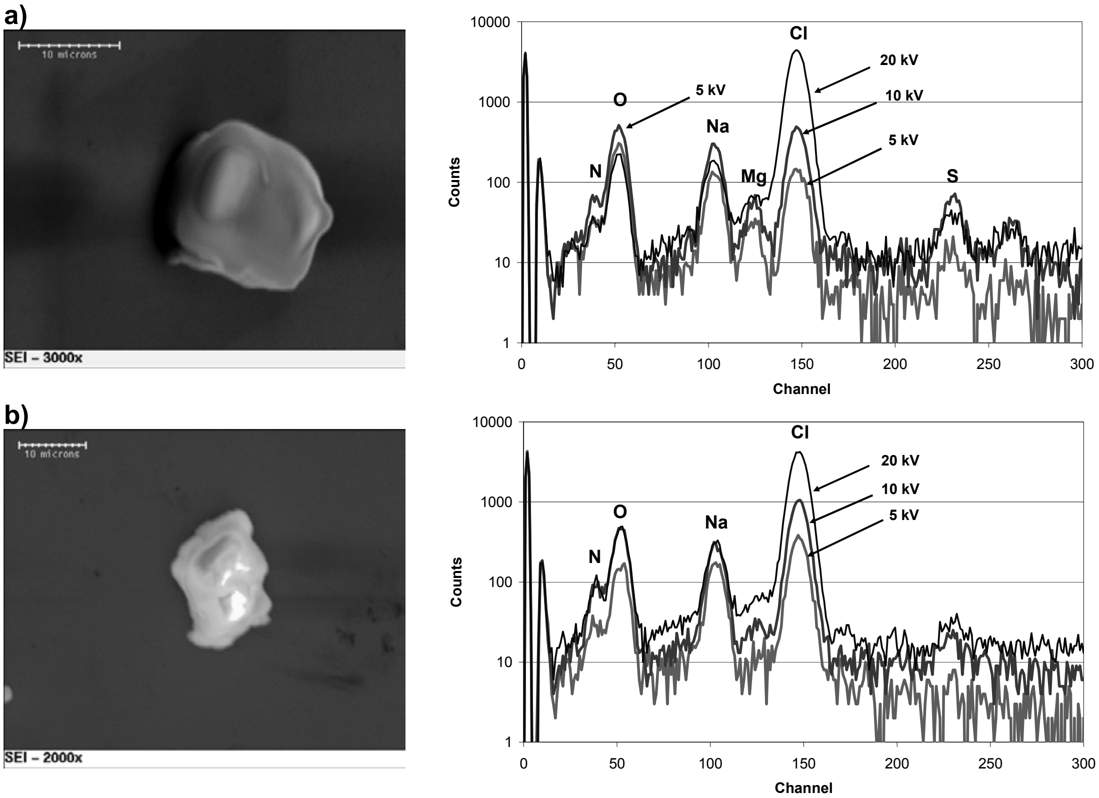


Figure 16: Application of MV-EPMA to aged sea-salt particles

4. Conclusions

The semi-quantitative determination of light elements by TW-EPMA was applied to the analysis of North Sea aerosol particles, and it appears to be an efficient tool for the investigation of a huge number of individual microparticles. The method offers good statistics to study their chemical properties and their behavior in the atmosphere. The results of the collected aerosol samples show that the light-element analysis of single particles gives additional useful chemical information to marine aerosol studies, compared to the conventional EPMA methods. The detection of characteristic X-ray radiation of low-*Z* elements, which was not possible before, now offers the possibility to identify more compounds (e.g. NH_4NO_3, organic particles), or it makes it possible to differentiate between different particle types, like e.g. $(NH_4)_2SO_4$ and sulphur-containing organic particles which previously only showed a sulphur peak in their X-ray spectra. The extended, semi-quantitative knowledge of low-*Z* element concentrations leads to a more relevant particle classification; therefore, the possible sources and interactions occurring in the troposphere can be traced in much more detail by the analysis of large numbers of individual particles. Through the combination of chemical data with meteorological data, the environmental link was found between the chemical composition of the different samples and the environmental conditions during sampling.

Compared to bulk analysis, individual particle analysis also can provide more detailed information concerning the origin, formation, transport, reactivity, transformation reactions and environmental impact of particles and it is therefore valuable as a complement to conventional bulk analysis.[42,43,44] IC analysis of the different samples offers quantitative results of different ionic compounds. But when evaluating and interpreting the results, it is not possible to give any conclusion concerning the total composition with respect to speciation on single particle composition. It offers the possibility to quantify a certain cationic or anionic fraction, but, unfortunately, it is not possible to specifically link the cationic species to the anionic species in the individual particles, and certainly not in a quantitative way. The combined approach of IC and TW-EPMA results offered clearer insights in the contribution of the different aerosol fractions. In addition, the application of an expert system to the TW-EPMA data provided a more detailed study of the particle species, and was able to suggest different compositions for clustered particles that were difficult to identify, because they contained many different elements that could be linked to a variety of ammonium, sulphate and nitrate species. Where clustering analysis could not provide more details about the composition of these ‘mixed’ particles, the expert system offers a confined method of speciation.

The application of the methods that were described in this chapter provides more precise information about the air mass history (marine and continental), a better definition of the pollution sources (speciation) and a better insight in the different atmospheric interactions of the pollutants (e.g. sea-salt aging).

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