**Atmospheric
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Discussions**

Interactive comment on "Studies of aerosol at a coastal site using two aerosol mass spectrometry instruments and identification of biogenic particle types" *by* M. Dall'Osto et al.

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Studies of aerosol at a coastal site using two aerosol mass spectrometry instruments and identification of ocean-dervied Mg particles in biologically active marine environments by M. Dall'Osto et al. [PLEASE NOTE CHANGE IN TITLE] Anonymous Referee #2 Received and published: 7 November 2005

ACPD 5, 10799-10838 Dall'Osto et al. Studies of aerosol at a coastal site using two aerosol mass spectrometry instruments and identification of biogenic particle types. This paper tries to show that a novel type of magnesium-rich biogenic particle was measured with single particle mass spectrometry (ATOFMS) at Mace Head, Ireland.

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AMS data are used to support this claim. I think that the authors have let their excitement run ahead of them. There are more ordinary explanations for the observations than a new type of particle, and the authors have not fulfilled the burden of proof that biogenic particles are the only or even most likely explanation for the mass spectra.

No direct evidence is presented in the mass spectra for biogenic processes, and the indirect evidence for biogenic processes also has other explanations. The paper is not suitable for publication in its current form.

The key observation is a series of mass spectra of individual particles with a large Mg peak along with significant peaks due to Cl, K, and Na. The time series shows that these particles were highly correlated with normal sea salt mass spectra that have Na as the largest peak (Figure 3). Both the Mg-rich and normal sea salt mass spectra were present when the winds were off the ocean.

There are at least three possible explanations of the Mg-rich mass spectra:

- The explanation favoured by the authors: They represent Mg-rich biogenic particles. - They could represent non-biogenic Mg-rich particles, produced either at the ocean surface or afterwards by fragmentation of sea salt particles in the atmosphere. - They could be normal sea salt particles for which ionization biases in the ATOFMS oversampled the natural sea salt Mg. That is, the Mg-rich mass spectra might not represent Mg-rich particles.

I will discuss the last possibility, although there is some literature support for the second. It is important to realize that the ATOFMS does not produce ions from an entire particle, especially above 1 micrometer where most of the Mg-rich spectra were observed (p. 10812). Instead, only a portion of the particle is ionized with some bias toward the surface. Just how representative a mass spectrum is of the particle composition depends on many factors, including laser power, particle size, particle composition, and the internal structure of the particle. The latter depends on relative humidity: a sea salt particle can exist as anything from a solution droplet to an agglomeration of

different salt mineral crystals. If one pictures an electron microscope image of a dried sea salt particle one can easily imagine composition biases from blowing up one side of the particle.

We welcome the possibility of other explanations and we agree that the results are not conclusive. We believe that our hypothesis is the most probable, but will amend the manuscript to include the other possibilities. Perhaps most importantly, we will amend the title to refer to "possible" identification of biogenic particle types.

After sodium, magnesium is the most common cation found in sea water. However, we rarely see it in the spectra of pure sea salt particles. It could be due to a matrix effect, as Na and Mg are often observed together in the spectra of dust particles, but only in low abundance in sea salt particles.

The analogy with electron microscopy is not a good one as the time for which the particles is exposed to high vacuum is far longer than the 1 ms in the ATOFMS, and the drying of particles in the sampling line is likely to be far less efficient than in the electron microscope.

The relative humidity of the inlet line was estimated at roughly 35% for average temperatures inside and outside the sampling trailer (p. 10811). The efflorescence point of sea salt aerosols is roughly 45% RH. Therefore, the mass spectrometer was probably measuring effloresced particles at least some of the time. As a sea salt particle dries, the first precipitates are calcium carbonate, calcium sulfates, and NaCl. A magnesium and potassium rich brine is left behind, possibly surrounding the crystals. This brine crystallizes at lower relative humidity in a complicated sequence. If the ionization in the mass spectrometer occasionally preferentially sampled this Mg-rich brine or its crystals it would explain the observed mass spectra without invoking a new type of biogenic particle.

Laboratory studies by (Cziczo and Abbatt 2000) showed that although NaCl may precipitate from sea salt aerosols upon drying, $MgCl_2$ would still be present in a con-

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centrated liquid state under the same RH conditions. Field measurements appear to support this model, by representing a particle composed of a crystalline solid (NaCl) and a residual brine containing MgCl2 (Murphy et al. 1998). However, in this previous field study, a different mass spectrometer was deployed and a different wavelength was used ( = 193 nm by Murphy). Moreover, different types of sea salt were not presented as different cluster types by Murphy et al. and no temporal variation was shown. The extent of particle drying is speculative as this is a function of relative humidity at the inlet of the ATOFMS (which was not measured) and kinetic constraints on the rate of water loss.

Both the effloresence point and crystallization sequence of seawater are sensitive to the degree of chemical aging (e.g. replacement of NaCl by NaSO4), so in a partially crystallized particle the composition of the crystals and brine will be different in clean marine versus mixed marine-aged pollution air. This could make it very difficult to distinguish real effects from ionization biases. If the Mg-rich spectra come and go it could be a real effect or it could be that Mg is changing its chemical form in partially dried particles with subsequent changes in ionization biases. Even in a single air mass, some sea salt particles will have been produced right off the coast and others will have had a few days to pick up non-sea-salt sulfate. Then they will effloresce differently in the sample inlet line.

The ATOFMS is very good at identifying aged sea salt particles in which nitrate tends to be the main ion displacing chloride. Mg-type particles were not detected when partially reacted sea salt was detected. Moreover, pure Mg-type particles were not always detected when pure sea salt particles were detected. This strongly suggests that they are a distinct type of particle and not an instrumental artefact.

The first piece of supporting evidence offered for biogenic Mg-rich particles is that the AMS data showed somewhat different sulfate and organic size distributions when Mg-rich spectra were or were not present (Figures 11 and 12). The AMS doesn't measure Mg, so it provides no proof that either the organics or the sulfates were in the same

particles as the Mg. Aged pollution can be present even in a "clean" wind sector, so the organics and sulfate would not have had to come from the ocean.

The EC measurements during the clean air periods (Coe et al., 2005) were not indicative of long-range transported anthropogenic pollution. This is the same sector reported as clean by O'Dowd et al. (2004). No other type of carbonaceous particle indicative of anthropogenic influence was detected by the ATOFMS during this period.

The second piece of supporting evidence offered is that the Mg-rich spectra time series was correlated with rainfall (Figure 13). Since the Mg-rich mass spectra were correlated with winds from the ocean, does this simply mean that it rained more when the wind was off the ocean? Or perhaps the outside and trailer temperatures were systematically different when it rained, leading to different relative humidities in the sampling line causing different amounts of efflorescence and hence different ionization biases?

The temporal variation and abundance of Mg-rich particles was not simply dependent on winds off the ocean. The temperature/RH records are not sufficient to come to a clear view on the second point.

Figure notes: In Figure 4, the mass 77 peak that is provisionally identified as C_6H_5+ from aromatic compounds (p. 10812) could also be a cluster ion: $H_2O.MgCl+$.

This is possible, but we would expect a peak at m/z 59 (MgCl) also to be present and this was not observed.

Anonymous Referee #1 Received and published: 22 December 2005

This paper reports on a dataset of the NAMBLEX campaign which has already been described in an earlier paper. A new analysis using a neural network algorithm has been applied, and the results are reported to be consistent with the old study. This by itself does not qualify yet for a new paper as this algorithm has been shown to work in a number of papers already. The major new finding relates to the claim that a new type of biogenic Mg rich particles has been detected. This is based on the findings of K.A.

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Prather, which however are not published yet. There are a number of questions related to this point, which should be answered before this paper can be published:

TSI ATOFMS data has been analysed for the first time with YAADA. It is important to disseminate this information to other users. Moreover, a full comparison between ART2a results and manual classification has never been reported previously.

a) Even though the peak intensities in Figure 2 agree with the abundance of the Mg stable isotopes (8:1:1) it should be shown that this is indeed the case for individual spectra as well and not only an effect of the averaging procedure. Figure 4 does indeed show this, but does this apply also to the other particles of this type?

Yes it does. Mg- particles always presents the Mg-isotope distribution.

b) The presence of organics in Figure 4 is not convincing. The authors mention that only 5% of the particles in this class show this enhanced spectrum, while the other 95% apparently do not show peaks related to carbon (Fig. 2). I suggest to generate an artificial chlorophyll aerosol to be analyzed by the ATOFMS. A good agreement with such an artificial aerosol appears to me to be a prerequisite for the acceptance of this paper.

During November 2004 an ATOFMS field study was conducted in the Californian Pacific Ocean. The California Oceanic Cooperative Fisheries Investigation (CalCOFI) is a unique partnership of the California Department of Fish and Game, the NOAA Fisheries Services and the Scripps institution of Oceanography. The goal of this study was to measure real time aerosol properties and to relate them with oceanographic measurements. It is important to note that by analysing bubbled sea-water with ATOFMS, different percentages of Mg-rich particles were recorded. The higher the chlorophyll concentrations in the sea-water samples, the higher the percentages of Mg-rich particles analysed (Furutani et. al; in preparation). It is beyond the scope of current research to generate artificial chlorophyll aerosols, although this could be done as part of a future study. At this stage, this is one hypothesis that could explain these results,

but it is yet to be tested.

b) The AMS is claimed to support the above findings. The authors report that around 1000 nm diameter there is an enhancement of the organic content compared to the sulphate in the two clean cases (Fig. 11). However, changes by just a factor of 2 in this ratio are not conclusive enough, as this is easily possible for two different polluted cases as well. The authors state that there is very little signal for organics and sulphate above 600 nm in the polluted case, in contrast to the clean case with Mg present. However, the organic contents above 600 nm are virtually identical in these two cases (Fig. 11).

The figure isn't explained as well as it could have been. In previous studies, accumulation-mode organic particulate matter has been observed to be consistently matched to the sulphate distribution at the high end, both in near and far field polluted environments, due to a high degree of internal mixing (Allan et al., J. Geophys. Res.-Atmos., 108, 4091, 2003; Topping et al., Atmos. Environ., 38, 2111-2123, 2004). While the absolute amounts of organics at the larger sizes do not vary by much, there is a significant shift in the shape of the distribution to the larger sizes when compared with the sulphate, which would not be expected if the two components were internally mixed. While it is accepted that this is far from conclusive, it does support the hypothesis.

c) The explanation with the rain is not convincing either. I expect a general decrease of the number concentrations of the large particles with increasing rain intensity, due to below-cloud scavenging. This may have a number of consequences as well.

The highest concentrations of Mg-rich particles (relative to the total number of fresh sea salt particles) were recorded during period of intense rain, regardless of the wind speed. In other words, Mg-rich particles were detected when the wind was blowing at high wind speed from the clean sector. When the wind speed values (speed and direction) were similar but it was also raining, even more Mg-rich particles were detected.

d) The blank negative ion spectrum for cluster 1B was attributed to the negative data acquisition board overheating or another type of sea salt particles. If so, may this

overheating be the reason for cluster 2A (Fig. 7) as well? And how much may this failure affect the whole data analysis?

Cluster 1B did not present negative spectra. This class apportioned 19.3% of the particles analysed and did not present any correlation with any other particles type. Moreover, cluster 1B and 2A did not correlate and it is unlikely cluster 2A is due to the negative data acquisition board overheating

Then there are a number of minor issues. The size of the particles in the AMS time of flight vacuum region is not proportional to their size. The mass collection efficiency is not necessarily 100% even for spherical particles.

Agreed that there are issues regarding the sizing and quantification of larger particles in the AMS, mainly due to the fact that the sampling lens is optimized for submicron aerosol. However, this does not affect any of the analysis presented here; any sampling biases will largely be cancelled out as it is the relative, not absolute, changes in the mass loadings which are of interest and the interpretations drawn are purely qualitative. There may be additional artifacts caused by differences in particle density affecting sizing, however these are likely to be very small, as very wide size averaging bands were chosen.

I suggest to avoid commercial statements comparing AMS and ATOFMS uptake by the scientific community, especially if this number is given by one of the involved companies. There is very little information about vigilance factor and learning rate. I suggest to either give more information or delete these sentences.

Then there are numerous repetitions in the text, e.g., 'the AMS can quantify the size resolved organic carbon, sulphate, ammonium and nitrate mass loading', and 'the results obtained with the ART-2a algorithm are consistent with the manual clustering presented by Dall'Osto et al. (2004).

These points will be addressed in a revised paper.

Coe, H., Allan J., Alfarra M., Bower K., Flynn M., McFiggans G., Topping D., Williams P., Dall'Osto M., Beddows D. and Harrison R.M. (2005) "A physical and chemical characterisation of aerosol particles during the North Atlantic Boundary Layer Experiment", this issue. Cziczo, D. J. and J. P. D. Abbatt (2000) "Infrared observations of the response of NaCl, MgCl2, NH4HSO4, and NH4NO3 aerosols to changes in relative humidity from 298 to 238 K", Journal of Physical Chemistry A, 104, 2038-2047. Murphy, D. M., D. S. Thomson, A. M. Middlebrook and M. E. Schein (1998) "In situ single-particle characterization at Cape Grim", Journal of Geophysical Research-Atmospheres, 103, 16485-16491. O'Dowd, C. D., M. C. Facchini, F. Cavalli, D. Ceburnis, M. Mircea, S. Decesari, S. Fuzzi, Y. J. Yoon and J. P. Putaud (2004) "Biogenically driven organic contribution to marine aerosol", Nature, 431, 676-680.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 10799, 2005.

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