

Li et al.:

Chemical Characteristics of Marine Fine Aerosols over Sea and at Offshore Islands during Three Cruise Sampling Campaigns in the Taiwan Strait- Sea Salts and Anthropogenic Particles

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Review

General

The paper presents concentrations of major ions, trace elements, organic and elemental carbon in PM_{2.5} samples collected during cruises and on an island in the Taiwan Strait. The results are not particularly surprising but they might potentially be publishable in ACP. However, in the present version of the paper there are serious problems and even some errors and it does not actually bring anything scientifically new information to the field. As it is now, it is mainly a data report and not a very good one even for such a purpose. I would recommend a major revision of the work and resubmission.

Uncertainty analyses are presented in section 2.3 but not detailed enough. The concentrations reported from filter samples involve various sources of uncertainty: uncertainties of flows, weighing, positive and negative artifacts, chemical analysis uncertainties, blank values, blank variability, detection limits, are different for different species. These should be discussed and given numerical values. A table within section 2.3 showing the concentrations (including gravimetric mass) of the analyzed species in the field blanks should be given.

Concentrations and mass balances are not properly presented in the paper. There should at least be a table or tables showing statistics of the concentrations of ions, trace elements and carbonaceous component and the percentages of the gravimetric mass. Now it is not possible to find out whether there was some mass missing compared to the gravimetric mass or whether the sum of species was higher than it. The Al concentration can be used for estimating the crustal mass from $\sim 12 \times \text{Al}(\text{measured})$ since the ratio of Al to other elements in the Earth's crust is relatively constant, see for instance Wedepohl: *Geochimica et cosmochimica Acta*, 59(7), 1217-1232, 1995.

The use of "sea salts" in plural is a bit disturbing, in most cases it would be better to use the singular form "sea salt".

The ion data should be used for calculating something more than only chloride depletion. For instance ion balances by using the ion concentrations you would see whether the samples were acidic, alkaline or neutral. The ion data could be used for calculating enrichment factors compared to seawater composition and the trace element data for calculating enrichment factors compared to average crustal rock composition (for example Duce, et al. 1975, *Science* 10 : 59-61, Artaxo et al. 1992, *Tellus B*, 44: 318–334.; Wedepohl: *Geochimica et cosmochimica Acta*, 59(7), 1217-1232, 1995; Mishra et al, 2004, *Atm.Env.* 38, 4069-4084; etc.).

Source area analysis would definitely be needed for this kind of a work. At least using air mass back trajectories or footprints with some meteorological model. Such are available and easy to use, for instance the HYSPLIT of NOAA can be used openly and it provides both back trajectories and dispersion modeling. They should be used to analyze what kind of concentrations or concentration

ratios or other derived properties – for instance ion balances by using all ions and ammonium to nss-sulfate ratios, or enrichment factors of trace elements, or OC-to-EC ratios or EC contributions – are associated with air masses from the different source areas.

Detailed comments

P3, L12. Write the manufacturer, type and model of the sampler. Also the filter type, filter manufacturer and other details, including diameter. The sampler was a high-volume one. What was the flow rate?

P3,L15: " **... we weighted the mass concentrations of both PM2.5 and PM2.5-10 after appropriate conditioning for each sample ...**". Describe the conditioning and weighing in more detail. At what humidity was the weighing done? Was RH measured? How long were the samples let stabilize at this RH before the actual weighing. The point is that quartz filters are notoriously difficult for gravimetric analyses due to their hygroscopicity.

P3, L16-17: "**PM2.5-10 samples cannot be analyzed for chemical composition since they were contaminated with the oil coated on the surface of the impactors**". If the coarse-particle samples were contaminated, how can you be sure that the fine-particle filters remained clean?

P3, L26-28, "**The air quality sampling boat sailed to windward during the entire sampling voyage. Consequently, the winds were blown from the prow of the boat in order to avoid the intrusion of oil-burning particles emitted from the air quality sampling boat itself.**"

Hard to believe. I have also sampled on a ship and it is hard to avoid wind blowing from the wrong direction during such a long time. According to Figure 1 the ship sailed partially along direct tracks and turned sharply to the right at the locations marked by the stars. Did wind direction really turn so sharply? For example, I estimated the location of the ship during the cruise leg S14C1. According to the map in Fig.1 the ship started from south of Kaohsiung City and sailed westwards on 2014-04-10. I took a random point estimatedly on the cruise route by using Google Earth, wind data from NOAA-ARL web page and draw a wind rose (ready.arl.noaa.gov/READYamet.php) for the date 2014-04-10. According to that wind blew from the eastern sectors between NE and SE which means from behind the ship. On the other hand, if the ship was sailing at a high enough cruise speed, the relative wind direction may have been from the clean sector. For some other locations and times the model actually does show the ship was sailing against the wind. This kind of an analysis should be shown in time series plots of true and relative wind speed and direrction during the cruises. Was there any sector control?

P3, L29, "**Each sampling course was arranged to collect PM2.5 for continuous 8-12 hours...**". It is not quite clear whether there was only one sample taken during each course or were there more? For example during S14C4 was there only one or were there more samples taken? Explain this so that there is no ambiguity about it. And if there was more than one sample in each course then the values in the tables are averages or what?

P4, L8 " **Xiaomen site (23°38'47.1"N; 11930'31.6"E)**". There is obviously the degree sign (°) missing so that the coordinates should read (23°38'47.1"N; 119°30'31.6"E). But when I type in these coordinates in Google Earth the location seems to be not on any island but in the ocean to the southwest of the Xiaomen island and to the west of the northern part of Xi island. Check the coordinates and give them accurately.

Another small disturbing point is that there was only this one island measurement site but throughout the text it is written "at the islands". That is not justified, especially because the Xiaomen site was really close, only 60 m from the sea shore (sounds like a good location, by the way), so it is definitely less polluted by local sources and much more marine than some other locations on the Penghu islands. It is misleading to write that "on the islands" the concentrations were this or that. Change the text and tables all over so that you write Xiaomen or "on the island" instead of "the islands".

Further, a grammar issue related to the islands. Use the preposition "on" not "at". Check for instance <http://ell.stackexchange.com/questions/8835/in-at-or-on-an-island>

P4, L19-20: "**All quartz fiber filters were divided into four identical parts prior to the chemical analysis.**" What was the uncertainty associated with this division? Were each of these four pieces weighed also separately to find the accurate fraction of the filter that was used for each of the chemical analyses? Or was the division into four parts done only visually? Were the concentrations of the chemical species then scaled accordingly? If not, how do you know actually how big a part of the filter was used for each of the chemical analyses.

P4, L22 and L27. Some species were analyzed both by IC and by ICP-AES. How do these concentrations agree? For instance, at all the sites discussed in this paper Na is definitely only from the sea and the concentrations should be within the uncertainties the same. Ca, Mg, and K have also other sources. Discussion of the Na comparison would fit into the uncertainty section and the other comparisons to the trace element section. Make a figure with scatter plots of the concentrations of the species analyzed with these two methods.

P5,L29 – P6,L8. There is discussion that includes the coarse particles. Earlier, on P3, L16-17 it was written: "**PM_{2.5-10} samples cannot be analyzed for chemical composition since they were contaminated with the oil coated on the surface of the impactors**". How is it then possible you discuss here also the PM_{2.5-10}?

P7,L31-33. There are 3 equations for calculating the concentration of sea salt. Only (1) makes sense. The major ions in sea salt are Na⁺, Cl⁻, K⁺, Mg²⁺, Ca²⁺, SO₄²⁻ and HCO₃⁻, of which Cl⁻ may get replaced. But the other major ions are there and it does not make any sense to calculate sea salt concentration by summing only sodium and chloride (Eq.(2)). Eq. (3) on the other hand does not make sense because in sea water nitrate is far from being a conservative compound, its concentrations vary a lot, and yet its contribution is very low. For instance Seinfeld and Pandis (2006) present in their Table 8: that the nitrate concentrations vary in a range of 3×10^{-6} - 2×10^{-3} % by weight. Measurements have shown that especially in the surface water nitrate concentrations are very low and one of the reasons is that nitrate is a nutrient used by marine biological organisms. Nitrate is a non-conservative tracer that is almost completely depleted in surface waters. So, it is very safe to claim that all nitrate in the filter samples analyzed in this work have come from other sources than sea water. So the only sensible equation for calculating seas salt concentration is (1). Consequently, the comparisons of the sea salt concentrations with the different equations are irrelevant and should be removed from the text, tables and figures.

P8, L6-7 "**Previous studies reported that the mass of sea salts can be adopted by the sum of Cl⁻ and Na⁺ (equation (2)) (Chow et al., 1996; Kim et al., 2000; Tsai et al., 2011; Han et al., 2003; Virkkula et al., 2006). ...**"

Let us check what these papers write about calculating sea salt.

-- Chow et al. (1996), p. 2106: "... sum of the soluble sodium and chloride to account for sea salt ..."

- Kim et al. (2000) don't tell at all how to calculate sea salt mass. On p. 2037 they write: "The Cl^- to Na^+ ratio of sea water is 1.8; however, due to the loss of Cl^- during transport, it is normally assumed to be 1.0." But nowhere in that paper they present how to calculate sea salt mass.

- Tsai et al.(2011) don't give any formula on how to calculate sea salt mass.

- Han et al. (2003) is a conference abstract not available in the open literature. I could not check it and it would be better not to refer to it at all.

- Virkkula et al. (2006) write on p.2: " Sea salt mass concentration was calculated from $\text{Cl}^- + 1.47\text{Na}^+$ where 1.47 is the seawater ratio of $(\text{Na}^+ + \text{K}^+ + \text{Mg}^{2+} + \text{Ca}^{2+} + \text{SO}_4^{2-} + \text{HCO}_3^-)/\text{Na}^+$ [Bates et al., 2001; Quinn et al., 2001]..." .

So, only Chow et al. (1996) write that sea salt mass could be calculated by summing up only sodium and chloride. But even if that is so in that paper it is definitely wrong, the other major sea-salt ions are present, as I wrote above.

P9,L2. Eq (8) is definitely wrong. As I wrote above, nitrate is not a seasalt compound. In the aerosol it is safe to claim that all nitrate is nss.

P9,L6 – 9. All sodium and chloride in aerosol are definitely sea salt on an island 60 m from the ocean shore and on the ship sailing on the ocean. So the texts ss-Cl and ss-Na should be removed. The concentrations of seasalt sulfate, seasalt magnesium, seasalt kalium and seasalt calcium are all calculated simply by multiplying observed sodium concentrations with the wellknown ratios of the ion X to sodium in seawater. The raw data for this calculation is only sodium concentration. So the ordering of ss ion concentrations in line 9 makes no sense at all. And there is an error even in that: ss Ca concentration should be higher than ss K.

P9,L29 "**Chloride deficit is a process**". No. Chloride deficit is a number calculated in Eq. (9). Chloride replacement is a process.

P10, L19-21 "**Previous study indicated that the aged nature of sea salt particles were about 150 km from the open sea, giving these particles enough time to react with atmospheric acidic gases (Virkkula et al., 2006).**" The referenced paper presented chloride depletion at a very clean Antarctic site so it is not comparable with the Taiwan Strait. The chloride replacement process can take place in a short period and distance if the concentrations of acidic gases are high.

P11, L11. "**... crustal elements (Al, Fe, Mg, K, and Ca), ...**" of these Mg, K, and Ca are also from sea salt. If you want to show the crustal elements only, do the seasalt correction.

P12, L17, Eq.(11) is strange. If you set in eq (10) it reduces to $\text{POC} = \text{EC} \times (\text{OC}/\text{EC})_{\text{pri}}$ so why don't you show it so? The method is very, very uncertain. The ratio $(\text{OC}/\text{EC})_{\text{pri}}$ definitely varies according to burning material, burning temperature and other conditions. Then during transport organics condense on the particles. Your sampling sites are so far away from any sources that even the lowest OC/EC ratio at in the samples cannot represent the primary ratio at any conditions. Remove all text and results where you discuss SOC and POC. Just discuss OC, EC and particulate organic matter (POM). POM you would calculate by multipling OC with a factor that takes into account thpe amount of oxygen in organic aerosol. There are several references for this, look for them.