

Interactive comment on “In-situ physical and chemical characterization of the Eyjafjallajökull aerosol plume in the free troposphere over Italy” by S. Sandrini et al.

Anonymous Referee #1

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REFeree: The paper is an interesting contribution to the substantive body of papers characterising Eyjafjallajökull eruption. There are two reasons why the paper may be of considerable interest to the readers: (1) evidence of the spatial extent and characterisation of the ash plume as far as the Apennines; (2) coupled with the quantitative assessment of the ash contribution to PM₁₀ mass. The paper is generally well written and can be accepted for publication after addressing many but rather minor comments.

Implications for air quality should be considered along with the dilution effect when free tropospheric air mixes into the boundary layer. Dilution ratio of approximately 5 times (depending on the thickness of volcanic ash layer in the free troposphere and the boundary layer height) would result in pretty negligible contribution to air quality at the ground level especially considering typical concentrations of several tens of micrograms m⁻³, e.g. in Po Valley region. The dilution issue is mentioned by the authors, but should be better articulated in the air quality section.

ANSWER: We agree with the referee about the fact that the dilution of volcanic aerosols into the PBL can significantly reduce the concentrations at the low elevations, where air quality impacts are more relevant. However, the actual dilution ratio cannot be easily determined. The Referee suggests a ratio of 5 as realistic, which, for a PBL thickness of 1500 m, is based on the hypothesis of a 300 m thick volcanic plume. On the other hand, as reported in Pappalardo et al., (2013), during the May episode, lidar observations performed on 17 May at Ispra EARLINET station (Lombardy, northern Italy, about 250 km north of CMN), revealed the presence of a volcanic ash over the site with base at about 3 km and top at about 8 km height, with centre of mass at 5 km, for a total thickness of ca. 5000 m. The centre of mass slightly decreased in altitude in the following hours, down to 3.5 km a.s.l. around 20:00 UTC on 18 May (Pappalardo et al., 2013), and the lidar detected the lowest part of the volcanic layer actually in the PBL, but the thickness of the volcanic plume actually entrained is unclear. Therefore, we miss a basic information for estimating the dilution ratio. Certainly, at least for what concerns the April episode, the volcanic contribution of few $\mu\text{g m}^{-3}$ estimated at CMN, furtherly diluted in the PBL, resulted in a negligible contribution on PM₁₀ at ground level, where it was lower than the local background noise. During the May episode ground level PM₁₀ data displayed a relative maximum on 19 May (daily averages) which, compared to the day before the arrival of the plume (17 May), denoted an increase in the coarse fraction of PM₁₀ corresponding to about 10 $\mu\text{g m}^{-3}$ at Bologna and 7 $\mu\text{g m}^{-3}$ at SPC. These amounts are similar to the 9 $\mu\text{g m}^{-3}$ volcanic contribution estimated at CMN from Ti concentration. Considering that the volcanic layer portion entrained was subsequently mixed in the PBL volume, we conclude that the increase in PM₁₀ observed at ground level must be considered as an upper limit for the volcanic contribution, and that probably cannot be entirely attributed to volcanic ash but could partly result from other local sources.

The text has been slightly modified to account for this issue at par. 3.7 and in the Conclusions.

Par. 3.7

“Indeed the weak signal recorded by these low altitude stations during the April episode was probably attributable to the strong dilution of the volcanic plume combined with the masking effect

of anthropogenic pollution. In fact, both sites are characterized by much higher mass concentrations of particles, compared to the background site of CMN; hence a relatively small volcanic contribution superimposed on a much higher background would be hard to distinguish. During the May episode ground level PM10 data displayed a relative maximum on 19 May which, compared to the day before the arrival of the plume (17 May), denoted a PM10 increase in the coarse fraction corresponding to about $10 \mu\text{g m}^{-3}$ at Bologna and $7 \mu\text{g m}^{-3}$ at SPC. These amounts are similar to the $9 \mu\text{g m}^{-3}$ volcanic contribution estimated at CMN from Ti concentration. Considering that the volcanic layer portion entrained was subsequently mixed in the PBL volume, this would result in a dilution of the volcanic contribution at ground level. Unfortunately the actual dilution ratio cannot be easily determined. From lidar observations, in fact, we know that the lowest part of the volcanic layer was actually detected in the PBL on 18 May (Pappalardo et al., 2013), but the thickness of the entrained layer is unclear. Therefore we conclude that the increase in PM10 observed at ground level must be considered as an upper limit for the volcanic contribution, and that probably cannot be entirely attributed to volcanic ash but could partly result from other local sources”.

Conclusions

“The impact of the volcanic plume at CMN did not strongly affect the air quality at ground level. In fact, PM2.5 and PM10 data of the Regional Agency for Environmental Protection in the urban area of Bologna and at the lowland site of San Pietro Capofiume did not evidence any significant increase in aerosol mass during the April episode while displaying an enhancement of about $10 \mu\text{g m}^{-3}$ during the May episode, though this latter cannot be completely attributed to a volcanic origin.”

REFEREE: The other weak point of the study is an ambiguity when authors discuss volatility of species and their condensation onto existing particles. There are many instances of this ambiguity in the comments below, e.g. volatility of metals, condensation of sulphate (an oxymoron) or condensation of particles just to name a few.

ANSWER: We really thank the referee for noting instances of ambiguity in the text about condensation of sulphate or condensation of particles, which have been written erroneously and now corrected in the text.

A more extensive discussion about the volatility of metals is added in the following as response to the specific comments about the presence of metals in volcanic aerosols.

Minor comments:

REFEREE. P20200, line 21. Mass attenuation cross section should be provided.

ANSWER: The following sentence has been added at pag.5 line 17:

Mass absorption efficiency set by default on MAAP and recommended by Petzold et al. (2002) is $6.5 \text{ m}^2 \text{ g}^{-1}$.

The reference Petzold et al. (2002) has been added in the References.

REFEREE. P20201, line 1. CPC range typo, should be 10^4 , not 104 particles.

ANSWER: OK

REFEREE. P20202, line 8. Change to “: : especially around noon time during summer days: : :”.

ANSWER: OK

REFEREE. P20204, line 10. Replace “transfer” with “spread”.

ANSWER: OK

REFEREE. P20205, line 15-20. It is more appropriate to refer to HYSPLIT spatial uncertainty of 15-30% available on NOAA website, but authors are more or less correct in referring to 20% uncertainty.

ANSWER: The more recent reference provided by Draxler and Rolph, (2013) on the NOAA website has been substituted to the old reference of Stohl, (1998) and the uncertainty in the calculation of back trajectories has been replaced by 15-30%.

REFEREE. Line 23. "typical regional background aerosol" otherwise the term background is misleading.

ANSWER: OK

REFEREE. Line 25. Replace "normal" to "typical".

ANSWER: OK

REFEREE. P20206, line 10. ":(ash particles) were able to stay airborne while being transported: :":

ANSWER: OK

REFEREE. Line 25. Specify typical concentrations in numbers when claiming significantly higher concentrations.

ANSWER: The average value has been added in the text as follows:

Such values are significantly higher than the typical concentrations usually observed at CMN, where the average concentration calculated for the period 2008-2010 is 2486 ± 165 (Marinoni et al., 2008; Asmi et al., 2011).

REFEREE. Line 27. Specify detection limit.

ANSWER: The detection limits for absorption and scattering, hence respectively for MAAP (0.07 Mm^{-1}) and nephelometer (0.3 Mm^{-1}), have been specified in the text.

REFEREE. P20207, line 23. Be more specific about applied correction.

ANSWER: The sentence was changed in the following:

In order to obtain a comprehensive view of the aerosol size distribution OPC ($D_{p, \text{opt}} > 300 \text{ nm}$) and DMPS data ($10 < D_{p, \text{mob}} < 500 \text{ nm}$) were combined. Assuming particle sphericity, aerosol number distributions were converted to volume distribution ($dV/d\log(D_p)$), applying a correction on diameters in order to transform OPC diameter in mobility diameter, as in Khlystov et al. (2004).

REFEREE. Line 27. There was marked increase in accumulation mode particle diameter (volume increased only slightly), which implies that the number probably even decreased.

ANSWER: The size distribution out of volcanic plume on 17 April (grey line) shows low concentrations both in accumulation and in coarse mode, while during both volcanic episodes an increase of coarse and accumulation particle volume is observed. The coarse mode peak diameter remains the same during the two events, while in the accumulation fraction the peak diameter on 20 April is slightly higher than on 18 May; this can be due to formation processes or ageing during transport.

The legend of Fig.5 has been modified and the specification of “I volcanic event”, “II volcanic event” and “out of plume” for the three reported days has been added in order to make it clearer.

Fig.5_rev

REFEREE. P20208, end of section 3.2. Make a summary statement that the event was a mixture of volcanic ash advection and anthropogenic pollution.

ANSWER: OK

REFEREE. P20209-P20210. Why the percentiles are different as the values become hardly comparable?

ANSWER: The two sentences about the percentiles have been slightly modified in order to make them more comprehensible. The two reported percentiles refer to the observed concentration of sulfate and ammonium respectively, and indicate that for sulfate the concentration measured on 18 May is higher than the 92% of the spring sulfate concentrations measured in the years 2009-2011, while for ammonium the measured concentration is higher than 97% of the spring ammonium concentrations for the same period.

The text has been modified as follows:

“In this occurrence, fine aerosol SO_4^{2-} reached a maximum of $3.5 \mu\text{g m}^{-3}$. This concentration corresponds to the 92th percentile of the spring data for the years 2009-2011, and is more than eight times higher than the spring average ($0.41 \pm 0.90 \mu\text{g m}^{-3}$) for the whole 3-year dataset.

On May 18 an NH_4^+ concentration of $1.10 \mu\text{g m}^{-3}$ was also measured. This concentration, corresponding to the 97th percentile for the years 2009 – 2011, was significantly higher than the spring average ($0.15 \pm 0.37 \mu\text{g m}^{-3}$) of the whole 3-year dataset and indicates an enrichment in ammonium against background conditions, which are normally very low at CMN due to the absence of significant sources (Carbone et al., 2010)”.

REFEREE. P20210, line 4. What do you mean by “natural sources”? if volcanic, say it.

ANSWER: The sentence has been integrated by the following specification:

“This ratio can be useful for distinguishing natural sources of sulphates, such as volcanic plumes or Saharan dust transports, from anthropogenic sources”

REFEREE. Line 14. Ammonium is a passive compound arising from ammonia emissions and pick-up by acidic particles. Degree of neutralisation does not allow distinguishing between volcanic and anthropogenic/agricultural ammonia. Nitrate origin is different and nitric acid is neutralised only after most of the sulphuric acid has been neutralised to ammonium (bi)/sulphate.

ANSWER: The sentence has been slightly modified as follows:

“This ammonium could have resulted from the volcanic emission of NH_3 (Rose et al., 1986; Allen et al., 2000) or, more probably (given the long distance travelled by the air mass) from the neutralisation of acidic sulphate particles during the transport downwind”.

REFEREE. Line 19. Sulphate does not condense on the particles, sulphuric acid does.

ANSWER: True, we thank the referee for detecting this error. The text has been corrected accordingly:

“In contrast to the April volcanic plume, on May 18 66% of the total water soluble sulphate was found in the fine fraction, and the remaining 34% in the coarse one (Fig. 1b), probably resulting from the condensation of H_2SO_4 on the surface of mineral particles”

REFEREE. Line 23. Ca-sulphates are most likely gypsum, either volcanic or formed en-route.
ANSWER: OK

REFEREE. Line 24. Particles do not condense on pre-existing particles, they coagulate.

ANSWER: Again, we thank the referee for detecting this mistake which has been corrected in the text.

REFEREE. P20211, line 4. Not absorption, but adsorption/condensation. Line 14. “: : :and superimposed on regional anthropogenic pollution: : : “

ANSWER: The correction has been made in the text.

REFEREE. P20213, line 22. Almost all metals are oxides (with very few exceptions like gaseous mercury (Hg₂) and are not volatile like gaseous compounds at lower temperatures. Some metalloids like As, Sb can form relatively volatile hydrates or thallium which resembles alkali metals and be considered relatively volatile opposite to generally nonvolatile metal oxides. Zr, however, is not in either above category, so what was his source? Metals can be volatile at magma temperatures only at best and, therefore, in the rising plume only, not in the spread-out ash cloud. The reference to Andersson et al. is rather weak as authors are very speculative and ambiguous in that study. The most likely explanation is not volatility of those metals in question, but rather them forming nanoparticles in hot ash plumes which can then coagulate with similar size or larger particles in cooled ash cloud especially that many metal oxides particles can be wetted increasing their coagulation chances. Indeed, ash chemical composition determined in ash fallout may not be identical to the ash plume further away from the volcano and certain differences should be expected.

ANSWER: Indeed the origin of trace elements in volcanic aerosols is complex; trace elements are considerably enriched in volcanic plumes as they form stable volatile compounds with strong ligands such as Cl, F and S which are gaseous at magmatic temperatures (e.g., Symonds et al., 1987 and Symonds et al., 1994). As volcanic gases cool, the condensation of volatile species (including trace metals) released directly from the magma occurs (Mather et al., 2003). We agree with the referee that metals volatility is limited to the time during which the plume temperature is above the metal species T_{boiling} , but at least during the first phase some differences in volatility exist among different elements. Volatility is sometimes estimated through the use of Enrichment Factors (EF) of the element between gas phase and lava phase, compared to a reference element chosen for normalization. According to Moune et al., (2006) four classes of trace element volatility could be distinguished in their study on the basis of EFs: refractory elements (very low EFs), poorly volatile elements (slightly increased EFs), moderately volatile elements (including Zr and Sb) up to highly volatile elements (Pb, Cu, Bi, Tl, Te, and Cd). Anyway it is true that the high boiling points of many trace metal species, suggests that the atmospheric transport of many of them is predominantly in the solid phase, with some exceptions for appreciable quantities of Hg, Se and As which can be transported as gases.

As the referee suggests, volcanic aerosols evolve chemically but also physically during cooling (e.g., aerosol collision/aggregation processes, condensation of acid gases and magmatic water, and adsorption onto volcanic ash; see, for instance, Witham et al., 2005). The Referee's suggestions are well kept and the text of the new manuscript will be revised accordingly. However, we believe that the chemical processes such as the conversion of halides to oxides can affect trace metals EFs during the first stages of plume evolution.

REFEREE. P20215, line 23. You indicate “very low”, but specify as being only twice lower – 73 versus 30ng/m³. Correct it.

ANSWER: The 30 ng/m³ average reported in Marenco et al., (2006) doesn't represent a real background concentration for CMN, in fact the mentioned campaign refers to a short period of time in the summer, moreover under the influence of Saharan dust transports, which contribute to Ti

and other mineral elements concentration. Though, this was the only concentration available in bibliography for comparison and anyway it still remains more than twice lower than the concentration observed during the volcanic plume. During our sampling period the Ti concentrations out of plume were always below detection limit, while Ti was measurable during the two volcanic episodes.

The “very low” has been changed into “low” and the following paragraph has been modified like this in order to better clarify this aspect:

“In fact, during the observation period, Ti concentrations measured by PIXE were above detection limits only in the samples corresponding to the two volcanic plume transits, with a maximum of 73 ng m⁻³ on May 18. This concentration was more than 2 times higher than the mean of 30 ng m⁻³ reported in Marengo et al., (2006) as measured by ED-XRF during a summer campaign at CMN (90th percentile equal to 58 ng m⁻³). Anyway, according to the authors, that concentration cannot be assumed representative of the annual average at CMN, as their measurements refer to a relatively short period of time and to the summer season only; moreover the campaign was under the influence of Saharan dust transports, which are known to contribute to the concentration of mineral elements, including Ti; hence the 30 ng m⁻³ average doesn't represent a real background concentration but a somehow higher concentration”.

REFEREE. P20216, line 25. “The Table exhibits high variability in such estimates arising from variability in the input parameters”.

ANSWER: OK

REFEREE. P20217, line 10. “: :with concurrent contributions of other than the volcanic source in April a different sites which are difficult to quantify”.

ANSWER: OK

REFEREE. Line 12-17. Use past tense consistently as in the first sentence.

ANSWER: OK

REFEREE. Line 23. Replace relative maximum” with “marked increase”.

ANSWER: OK

REFEREE. P20219, line 5. “: :degassed by the volcano and sulphuric acid subsequently condensed.”.

ANSWER: OK

REFEREE. Line 14. “reconstructed PM10 mass”.

ANSWER: OK

REFEREE. Line 16. “: :were reported over Spain: : :

ANSWER: OK

REFEREE. Table 1. “particle number concentrations”

ANSWER: OK

REFEREE. Figure 1. Change Y axis to accumulation mode particle number. Same for “coarse”.

ANSWER: The Y axis has been modified (Fig.1_rev)

REFEREE. Figure 3. Change to accumulation mode N, #/cm³ and so on.

ANSWER: The axis have been modified

Fig.3_rev

Fig.4_rev

REFeree. Figure 6. Y axis notation should be fixed – decimal points increased.

ANSWER: The Y axis notations have been made the same as X axis.

In the caption it has been specified that data refer to PIXE-PIGE measurements.

Fig.6_rev

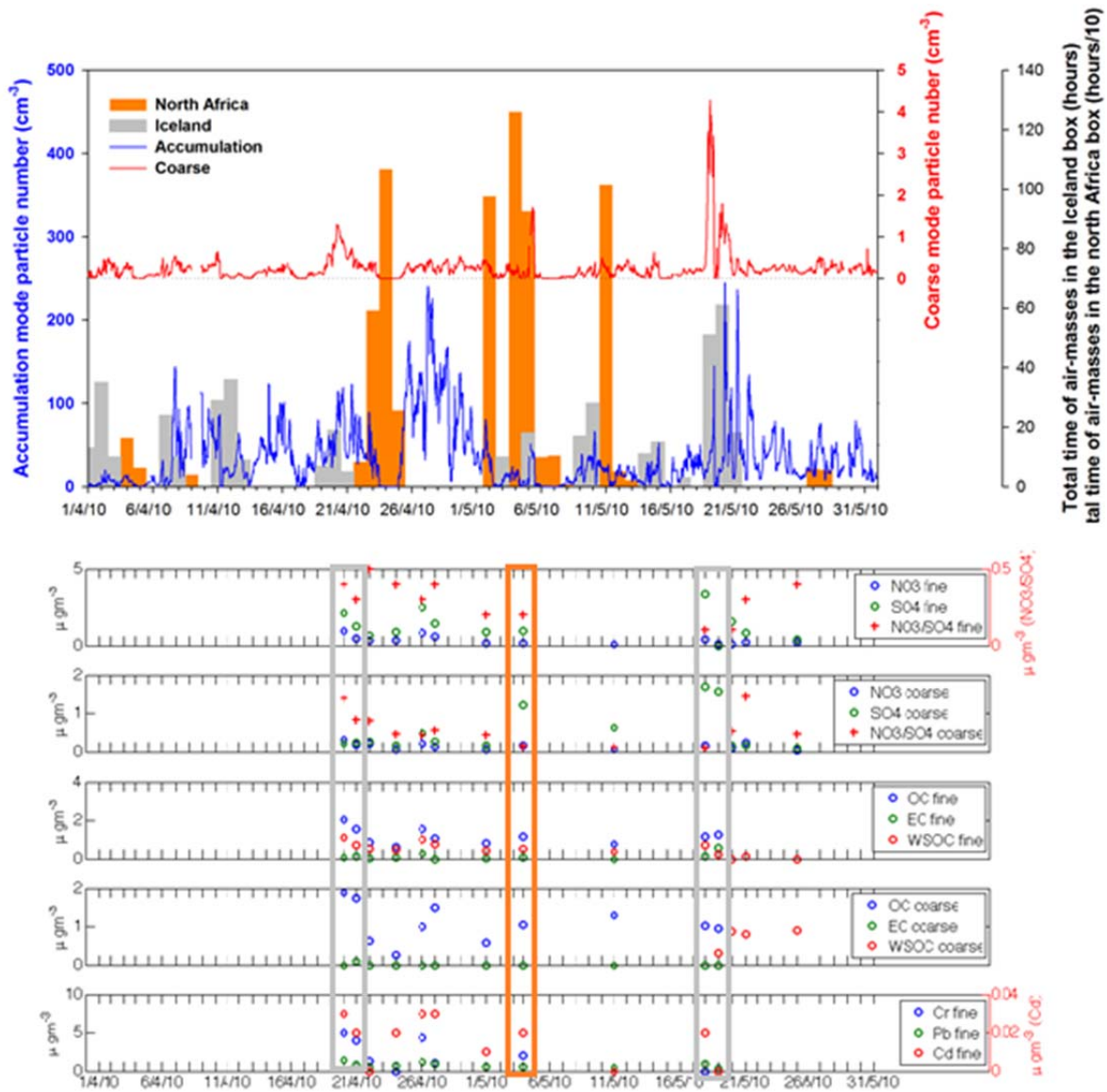


Figure 1. a) Particle number concentration recorded at CMN from 1/4 to 31/5/2010 measured by OPC (0.3–20 μm), separately for the accumulation mode ($< 1 \mu\text{m}$) and coarse mode ($> 1 \mu\text{m}$). The vertical bars denote the daily total number of back-trajectory points falling within the “Iceland” (grey) and the north Africa (orange) geographical boxes. b) Temporal evolution of sulphate, nitrate, NO₃/SO₄ ratio, OC, EC and WSOC, separately for the fine and coarse mode, and Cr, Pb and Cd in the fine fraction.

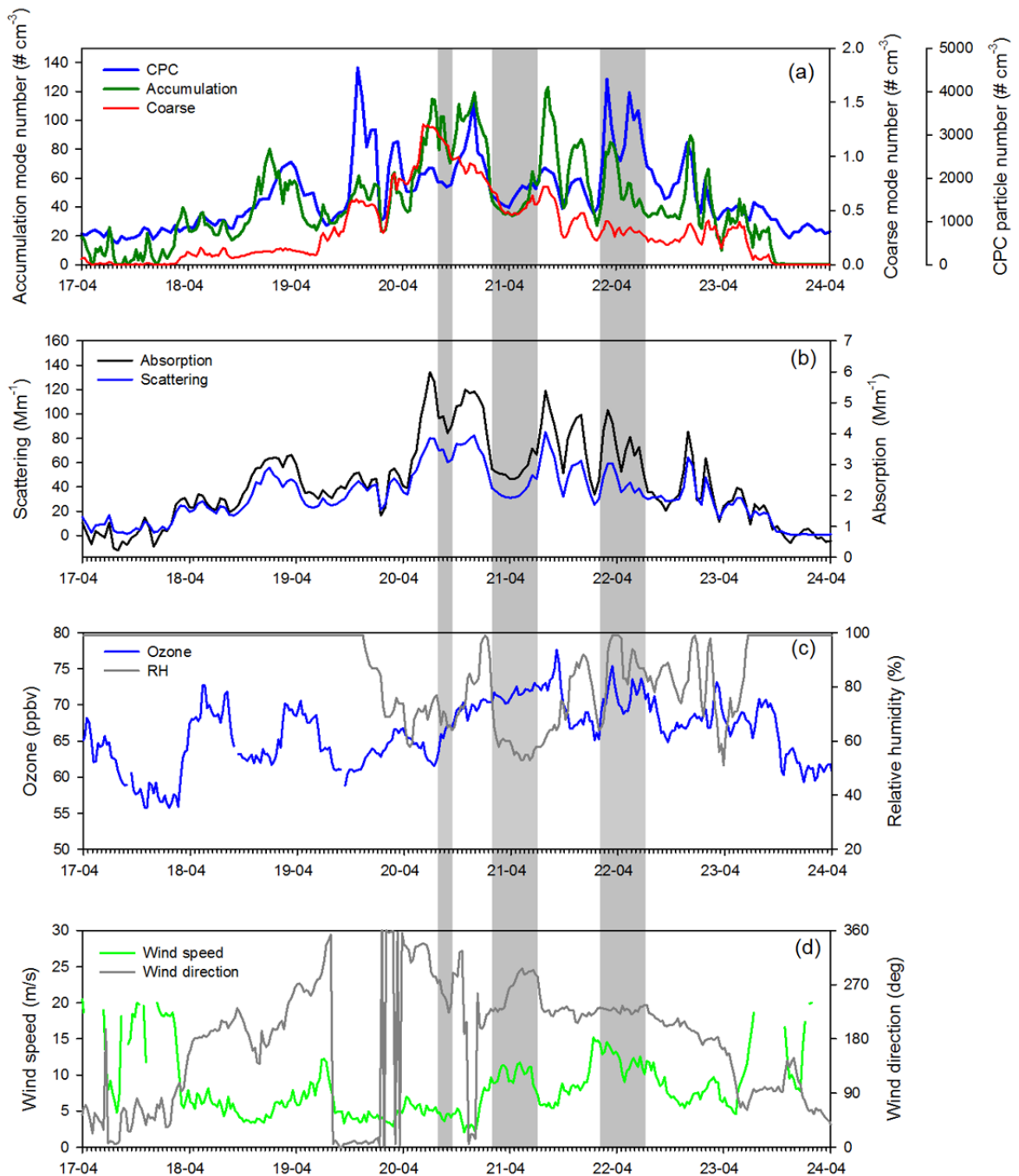


Figure 3. April 2010: Time series of (a) particle concentration (cm⁻³) in the CPC, accumulation and coarse mode, (b) absorption and scattering coefficient, (c) surface ozone and relative humidity and (d) wind speed and wind direction. The time periods covered by samples for chemical analyses are shaded.

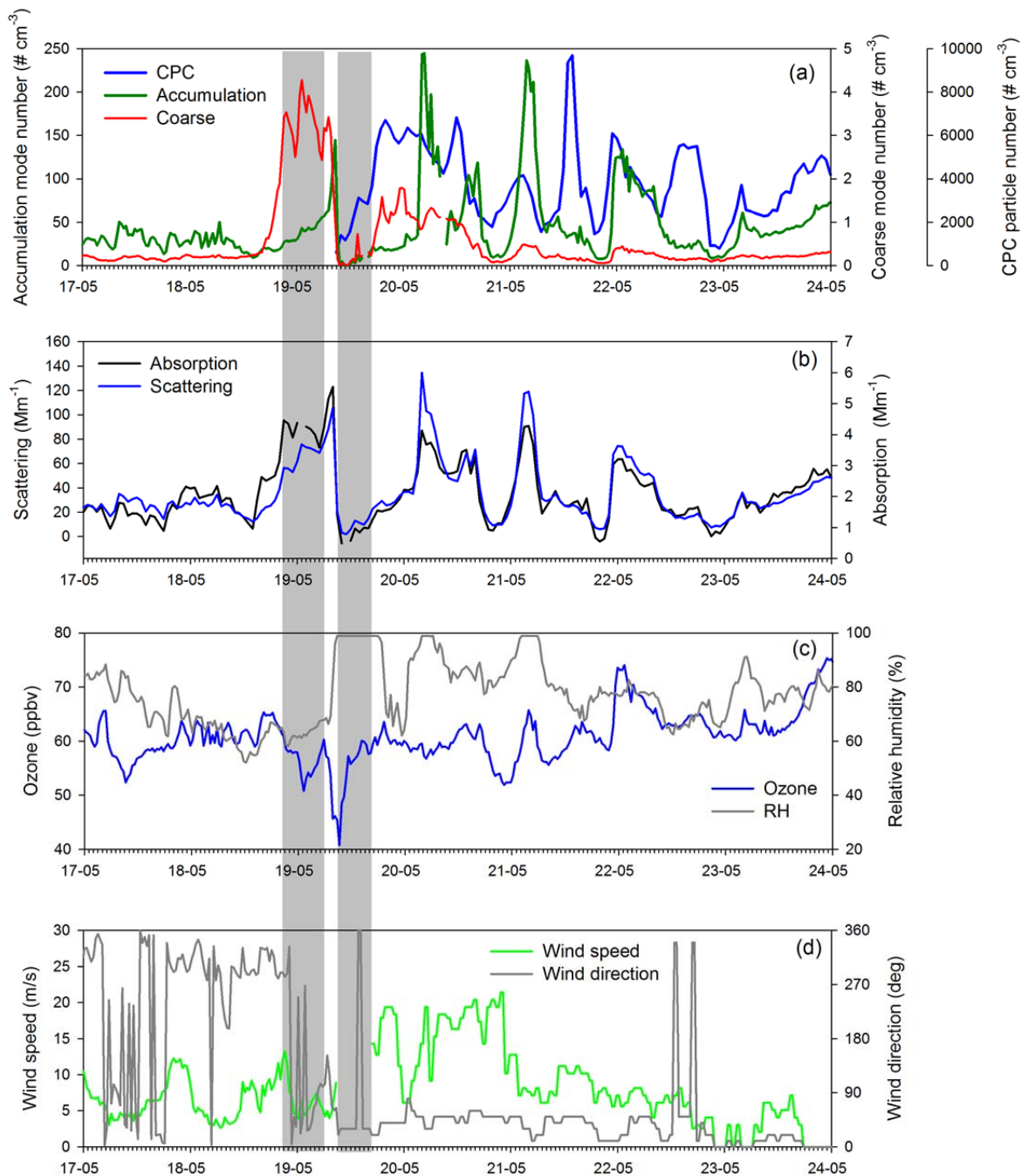


Figure 4. May 2010: Time series of (a) particle concentration (cm^{-3}) in the CPC, accumulation and coarse mode, (b) absorption and scattering coefficient, (c) surface ozone and relative humidity and (d) wind speed and wind direction. The time periods covered by samples for chemical analyses are shaded.

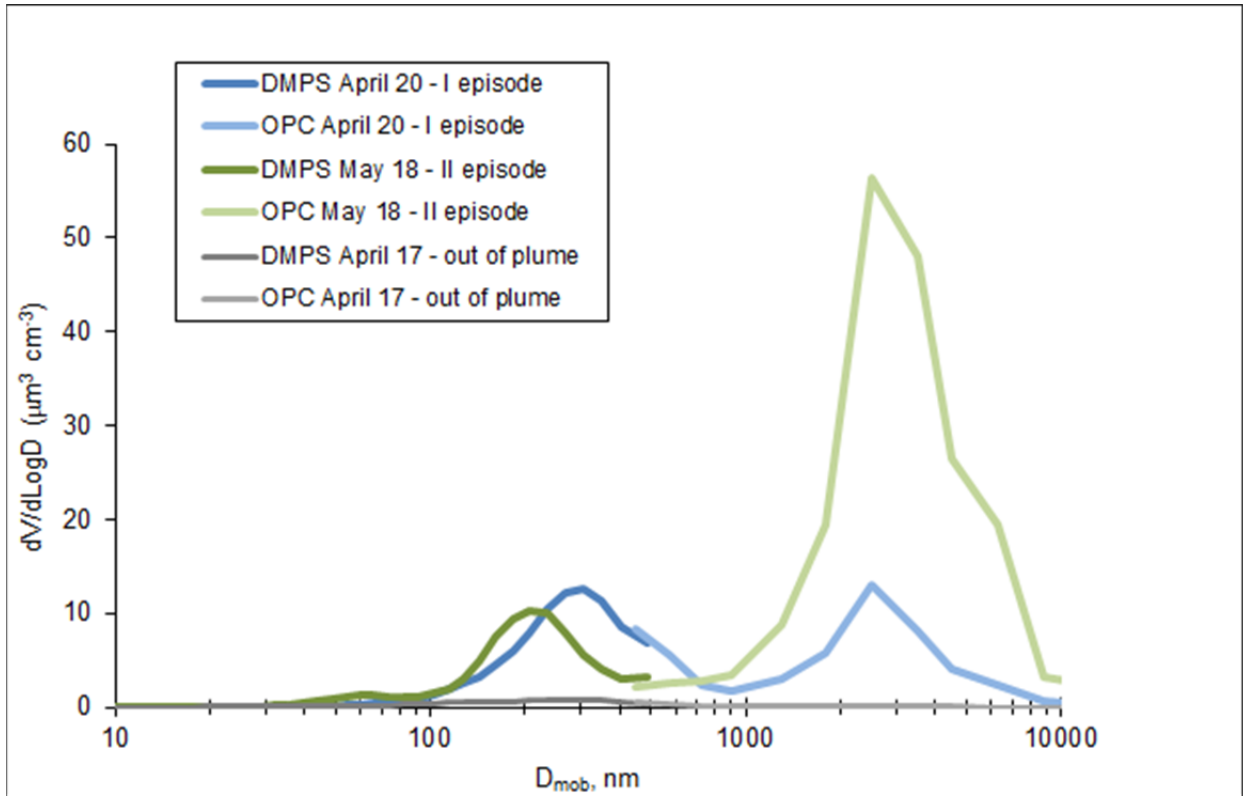


Figure 5. Comparison between the aerosol size distribution before the arrival of the volcanic plume, April 17 (black/grey – out of plume) and during its most intense impact on April 20 (blue/light blue – I episode) and May 18 (green/light green – II episode), derived from DMPS (10-500 nm) and OPC (300 nm - 20 μm) measurements.

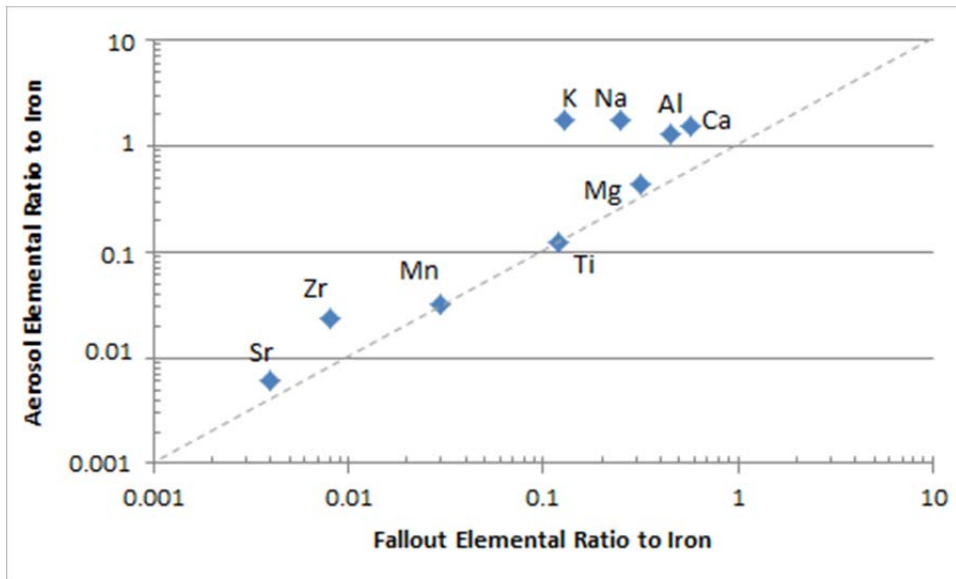


Figure 6. Elemental ratio to iron in the aerosol sample collected at CMN on May 18, 2010 vs. direct fallout collected on May 16 (GSV165-3) near the Eyjafjallajokull crater (http://earthice.hi.is/eyjafjallajokull_2010_chemical_composition). The dashed line indicates equal ratio. Data refer to PIXE-PIGE analyses.

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