

Supporting Information

Iodine Isotopes (^{127}I and ^{129}I) in Aerosols at High Altitude Alp Stations

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This Supporting Information described the detail of extraction method and measurement of iodine by AMS, and some extended discussions including air trajectories. It also content 6 figures and in total 16 pages.

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Materials and Methods

The aerosols from clean air regions in the Eastern Alps were sampled at two weather observatories, Sonnblick and Zugspitze on glass fiber and cellulose nitrate filters respectively. Both observatories have been operated for more than 100 yr as meteorological stations.

Removal and transport of aerosols was checked by determining ^7Be concentrations. ^7Be is a cosmogenic gamma emitting (477.6 keV) radionuclide with a half-life of 53 days. Only 33 % of ^7Be is produced in the upper troposphere while the main portion comes from stratosphere. Soon after formation ^7Be is attached to aerosol particles (0.4-2 μm). The residence time of these aerosols depends on meteorological conditions. As most of the ^7Be resides in the stratosphere it has been used in many studies as a marker of stratosphere-to-troposphere transport.

The anion exchange method was used for iodine extraction from glass fiber filter¹. After extraction of total particulate iodine in alkaline medium (0.5 M NaOH and 0.05 M NaHSO₃), the solution was filtered through 0.45 μm cellulose acetate filters. The sulphite leaching is known for extraction of organic and inorganic iodine from aerosol particles². Subsequently all the iodine in solution was reduced to iodide with NaHSO₃ at pH <2. Stable iodine concentration was measured on an aliquot by ICP-MS before adding potassium iodide carrier (5mg of I⁻). Dowex 1x 8 (100-200 mesh Cl⁻ form) was used for extraction of iodine. The Dowex was preconditioned using 1M HNO₃. The sample was then loaded to a pre-prepared Dowex. The column was washed using 50 mL of 0.1M HNO₃. Iodide adsorbed on the column was eluted with 200 mL of 0.5M HNO₃. Iodine was precipitated as AgI by addition of AgNO₃ solution after taking an aliquot of solution for chemical yield determination by ICPMS (65 \pm 15 %). Finally, the dried precipitates of AgI were mixed with silver powder (AgI:Ag = 1:1 by weight) and pressed into the copper sample holders used for Accelerator Mass Spectrometry (AMS) measurements at the Vienna Environmental Research Accelerator (VERA). I⁻ ions sputtered from the ion source were stripped to the charge state I⁴⁺ chosen with a yield of 10%, where $^{127}\text{I}^{4+}$ was measured as current using a Faraday cup and $^{129}\text{I}^{4+}$ was measured using a gas ionization detector. VERA is especially equipped with large separators for heavy ions, which can suppress interference from neighbouring tellurium ions³ completely. The samples were measured in 5 different beam times, in which typically three cycles through all samples with 5 min on each sample were performed. Very low negative iodine current was observed for the samples derived from cellulose nitrate filters (ZS). We think this was caused by reduced negative ion yields in the Cesium sputter source. It may be caused by the presence of impurities in the AgI precipitates, mostly likely in the form of Ag₂SO₃ or AgCl, (both white and in low amounts not easily distinguishable from light yellow of AgI) that could not be separated completely by BaCl₂ addition³ and washing the AgI precipitate with 3M HNO₃. It has been

mentioned that chloride amount added should not be too high because chloride excesses of more than ten related to iodide are able to influence the precision of $^{129}\text{I}/\text{I}$ ratio measurement⁴. To omit this possibility AgI precipitates were washed extensively with 25% NH_3 solution⁵.

Extended Discussions

The exchange of air between stratosphere and troposphere was discussed in terms of deposition of cosmogenic ^7Be as a function of time. It is believed that there are four factors controlling the ^7Be variation a) wet scavenging, b) stratosphere-to-troposphere exchange, c) downward transfer in the troposphere and d) transport between lower and higher latitude⁶. But at high altitude Alpine stations, the highest ^7Be concentration observed might be attributed mainly to vertical air mixing and to dry conditions as evident by weather data. Gerasopoulos et al., analysed ^7Be concentration during 1996-1998 at the Alp stations (Jungfraujoch, Zugspitze, Sonnblick and Mt. Cimone) and concluded that in warm periods wet scavenging dominates over transport, and while in cold periods transport becomes important, rather no practical discrimination between wet scavenging and transport is feasible⁷. The statistical analysis between weekly deposition of ^{129}I and ^7Be does not give any significant correlation (Figs. S-1 and S-2).

Large scale wind air flow can be studied with backward trajectory calculations. A trajectory is the path of an infinitesimal air parcel in a given time period indicating origin and direction of air masses but it gives no information where along its path pollution uptake has taken place⁸. We have calculated 96 h back trajectories for both stations. The trajectories are 3D and they are based on the analysed ECMWF wind fields (resolution: 1°). Arrival time is every 3 h. The arrival height of the trajectories is the height of the model topography +100 m. The model topography is different from the real topography (the highest parts of the Alps have a height of only 1800m in the model). We are mainly interested in the transport from pollutant sources close to the earth's surface. More details about method is given in^{8,9}. Statistics of air trajectories also support our assumption that high concentration of ^{129}I measured corresponds to wind from Northwest or North. The investigation period is 22nd Feb. to 1st Mar. (highest concentration of ^{129}I) and 8th to 15th Mar. (lowest reported concentration of ^{129}I) at Sonnblick (see Figs. S-3a and S-3b). In case of Zugspitze lowest and highest concentration of ^{129}I was reported during 16th to 23rd Mar. and 1st to 7th May respectively (see Figs. S-4a and S-4b). Since the residence time of trajectories gives information about potential emission regions therefore, trajectories residence time using 0.5 degree grid were also calculated for the above mentioned period (see Figs. S-5 to S-6).

References

1. Jabbar, T.; Steier, P.; Wallner, G.; Kandler, N.; Katzlberger, C. AMS analysis of iodine-129 in aerosols from Austria. *Nucl. Instrum. Methods Phys. Res., Sect. B.* **269**, 24, 3183-3187.
2. Gäbler, H. E.; Heumann, K. G. Determination of particulate iodine in aerosols from different regions by size fractionating impactor sampling and IDMS. *Int. J. Environ. Anal. Chem.* **1993**, 50(2), 129-146.
3. Lopez-Guitierrez, J. M.; Garcia-Leon, M.; Schnabel, Ch.; Schmidt, A.; Michel, R.; Synal, H-A.; Suter, M. Determination of ^{129}I in atmospheric samples by accelerator mass spectrometry. *Appl. Rad. Isot.* **1999**, 51, 315-322.
4. Wimschneider, A.; Heumann, K.G. Iodine speciation in size fractionated atmospheric particles by isotope dilution mass spectrometry. *Fresenius' J. Anal. Chem.* 1995, 353, 191-196.
5. Roman, D.; Martin, J.F. Iodine-129 and chloride-36 in Uranium Ores 1. Preparation of Samples for analysis by AMS. *Chem. Geol.* 1988, 72, 1-6.
6. Feely, H. W.; Larsen, R. J.; Sanderson, C. G. Factors that cause seasonal variations in Beryllium-7 concentrations in surface air. *J. Environ. Radioact.* **1989**, 9(3), 223-249.
7. Gerasopoulos, E.; Zanis, P.; Stohl, A.; Zerefos, C.S.; Papastefanou, C.; Ringer, W.; Tobler, L.; Hübener, S.; Gäggeler, H.W.; Kanter, H.J.; Tositti, L.; Sandrini, S. A climotolgh of ^7Be at four high altitude stations at the Alps and the Northern Apennines. *Atmos. Environ.* **2001**, 35, 6347-6360.
8. Kaiser, A. Origin of polluted air masses in the Alps. An overview and first results for MANORPOP. *Enviorn. Pollut.* **2009**, 157, 3232-3237.
9. Kaiser, A.; Scheifinger, H.; Spangl, W.; Weiss, A.; Gilge, S.; Fricke, W.; Ries, L.; Cemas, D.; Jesenovec, B. Transport of nitrogen oxides, carbon monoxide and ozone to the Alpine Global Atmosphere Watch stations Jungfraujoch (Switzerland), Zugspitze and Hohenpeissenberg

(Germany), Sonnblick (Austria) and Mt. Krvavec (Slovenia). *Atmos. Environ.* **2007**, 41, 9273-9287.

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- Fig. S-3 Study period at Sonnblick
a) 20010223 to 20010301 b) 20010308 to 20010315
96 hours back trajectory; colours indicate the height of trajectory, black higher than 3000m
- Fig. S-4 Study period at Zugspitze
a) 20010316 to 20010323 b) 20010501 to 20010507
96 hours back trajectory; colours indicate the height of trajectory, black higher than 3000m
- Fig. S-5 Study period at Sonnblick
a) 20010223 to 20010301 b) 20010308 to 20010315
Potential source regions for ^{129}I , 0-6000m; 0-600m; 0-200m (x-axis Long. deg. Y-axis Lat. deg.)
- Fig. S-6 Study period at Zugspitze
a) 20010316 to 20010323 b) 20010501 to 20010507
Potential source regions for ^{129}I , 0-6000m; 0-600m; 0-200m (x-axis Long. deg. Y-axis Lat. deg.) colours show time in hours.

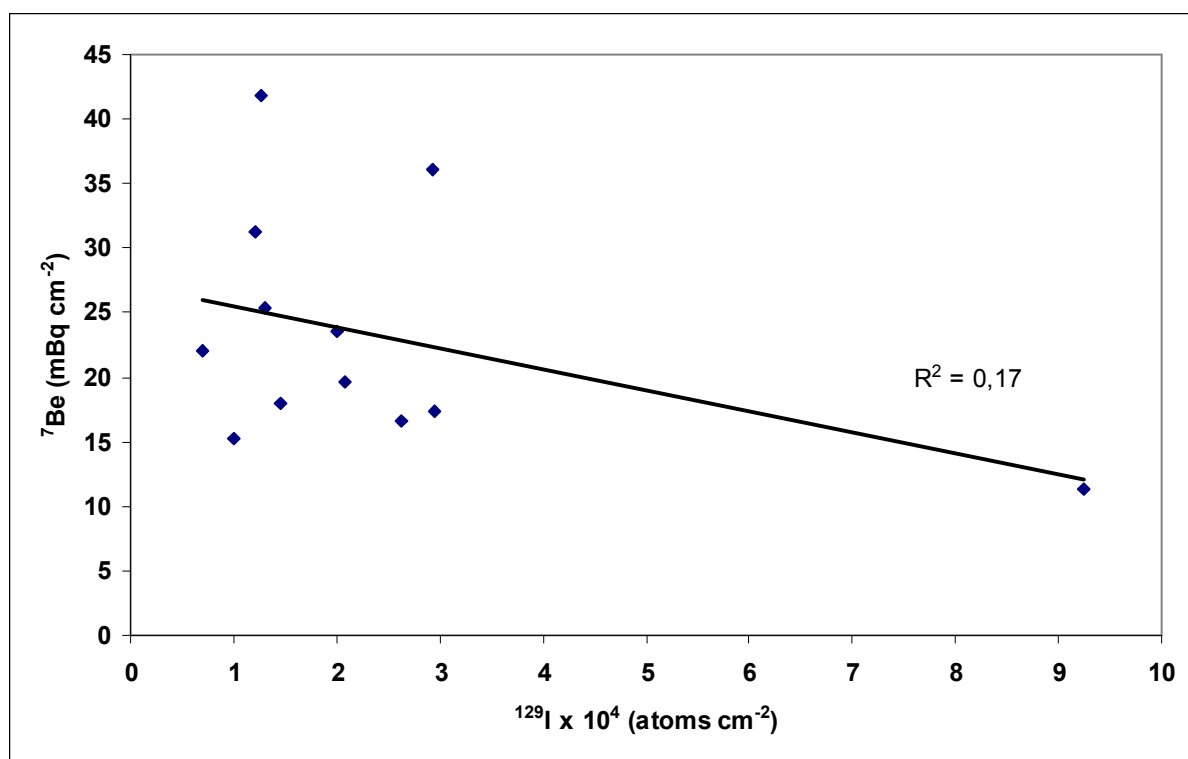


Fig. S-1

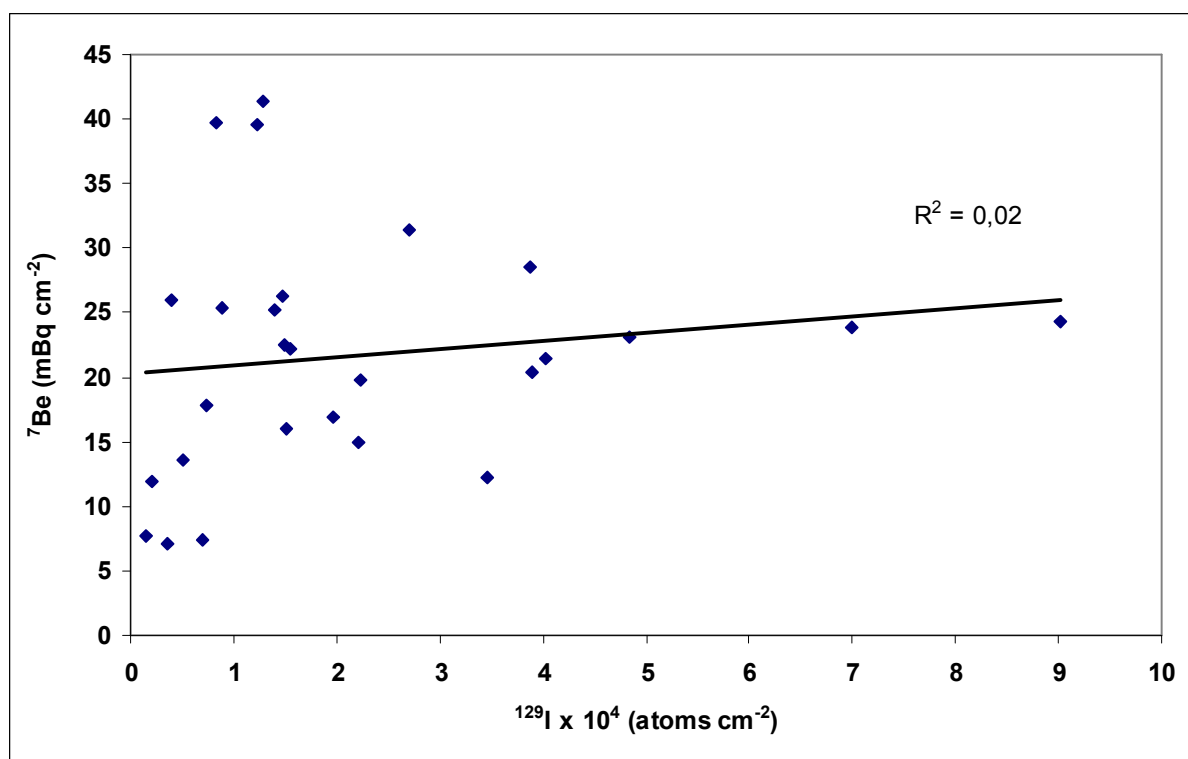


Fig. S-2

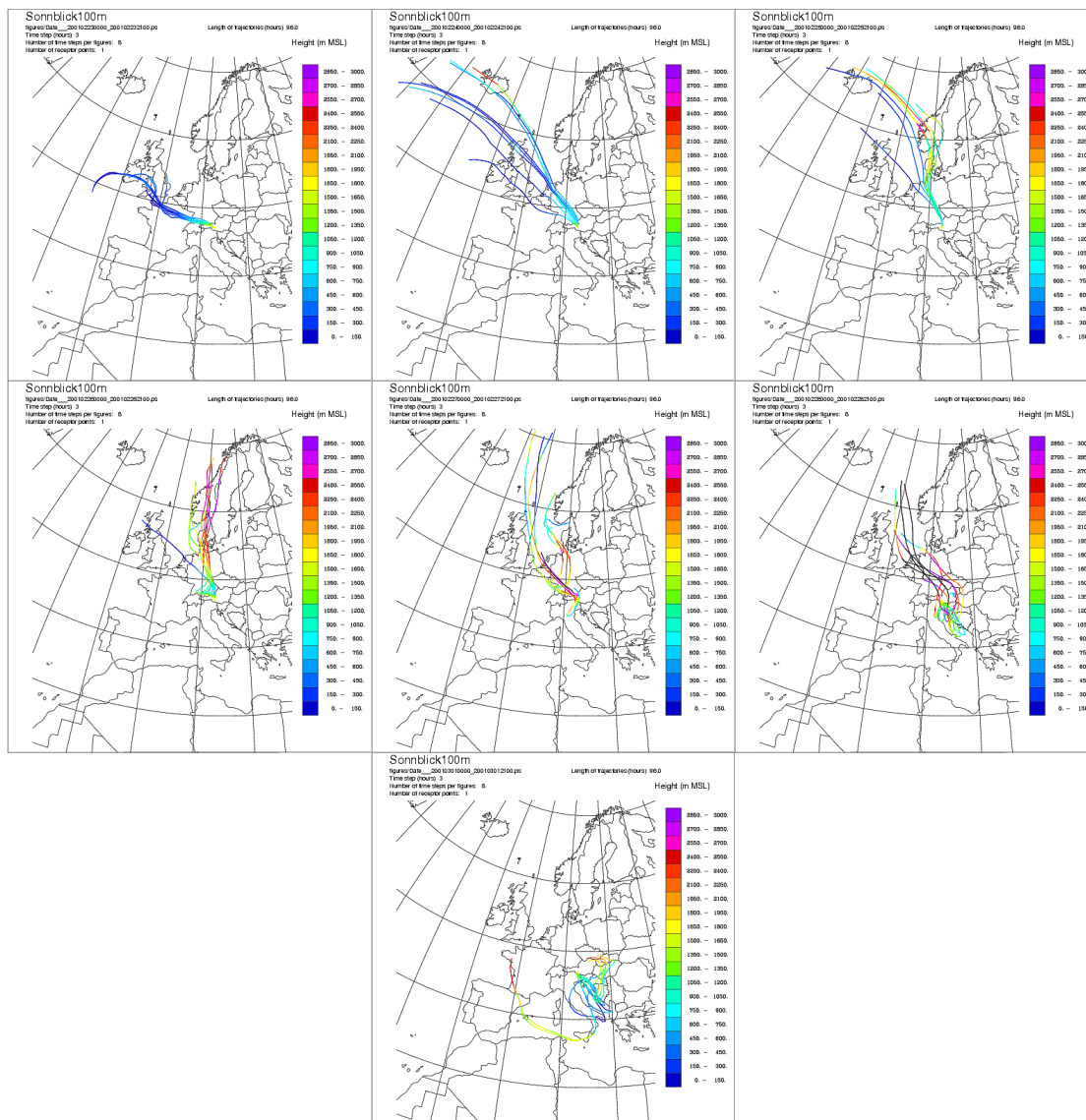


Fig. S-3 a

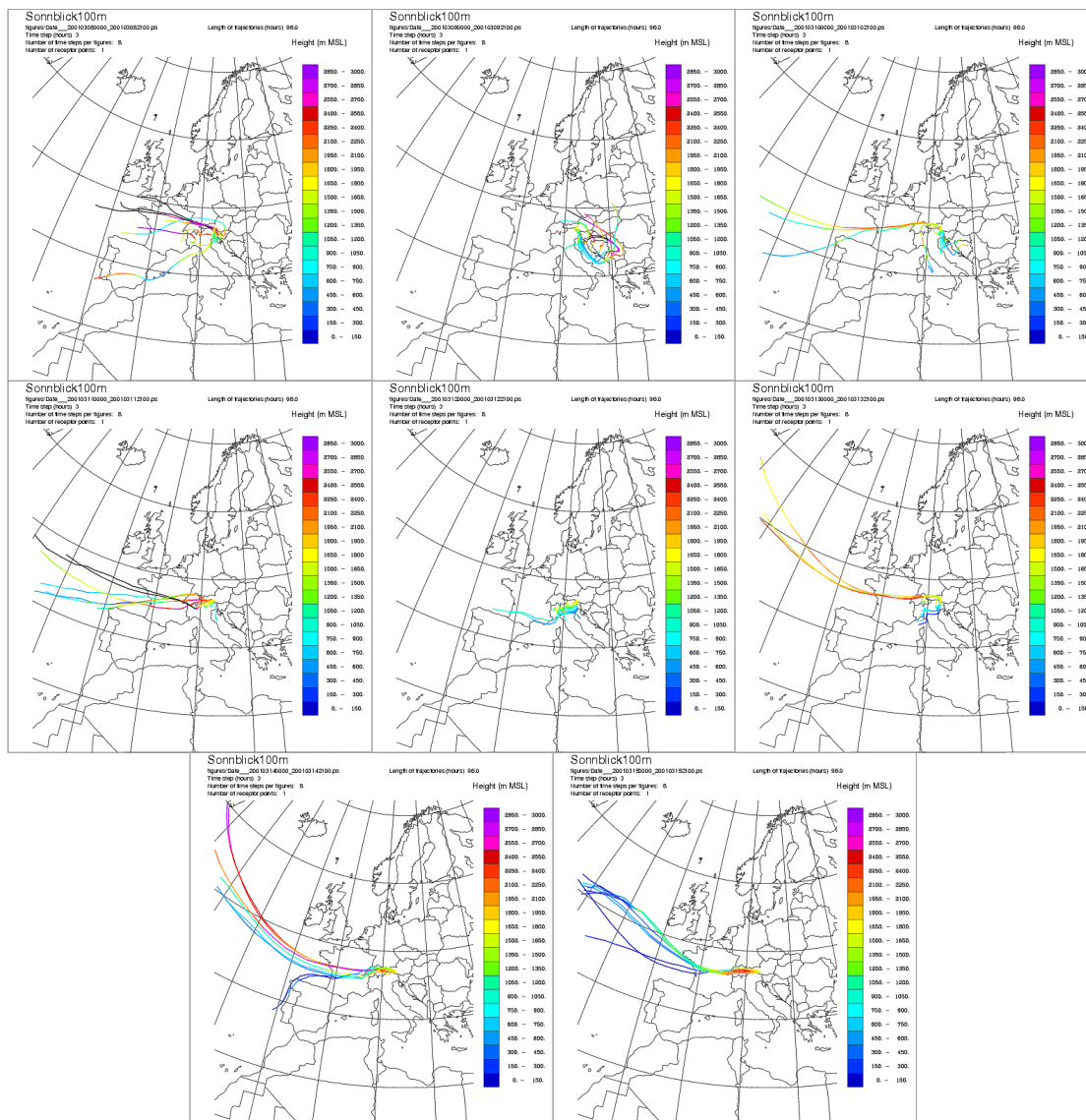


Fig. S-3 b

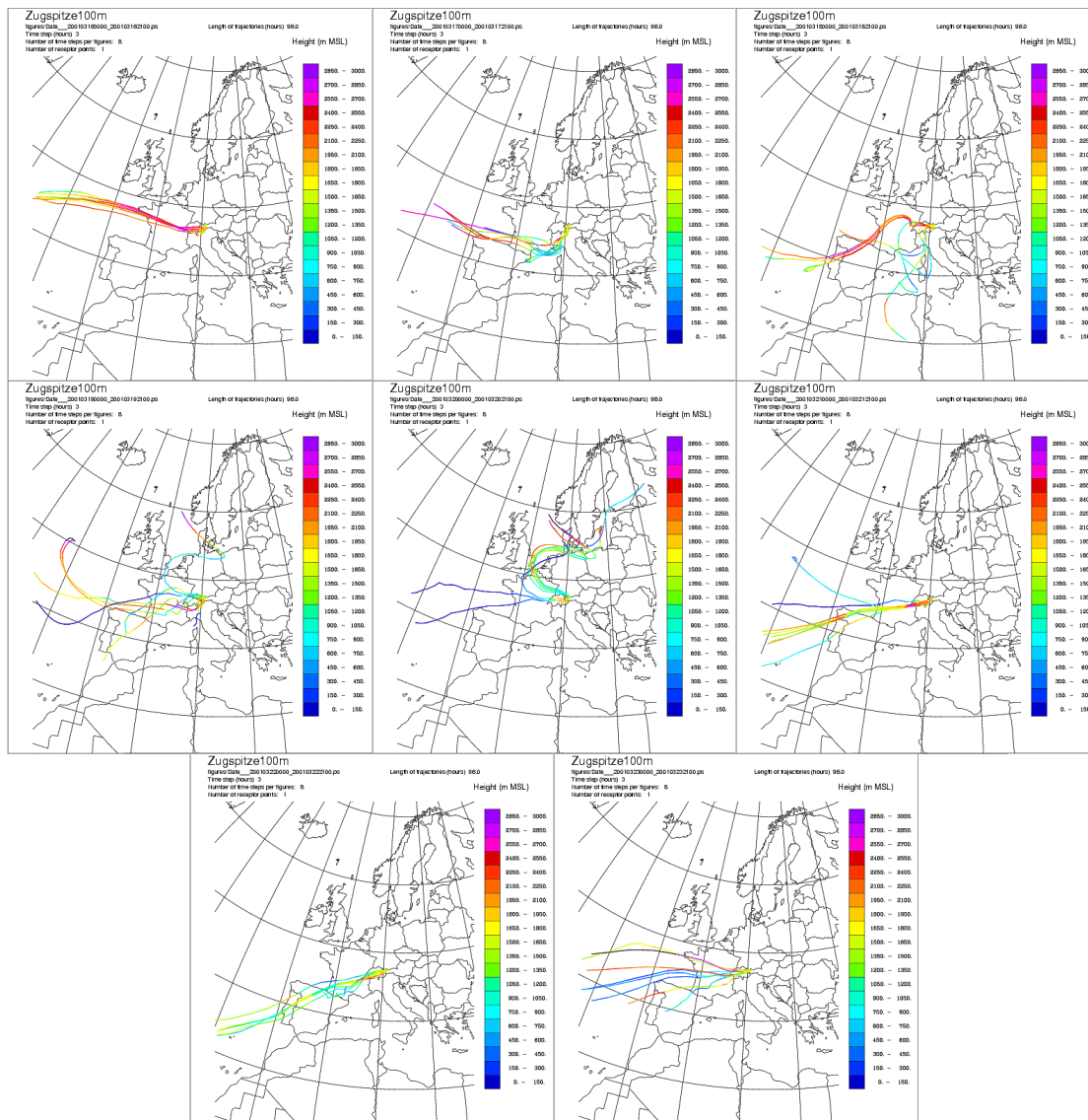


Fig. S-4 a

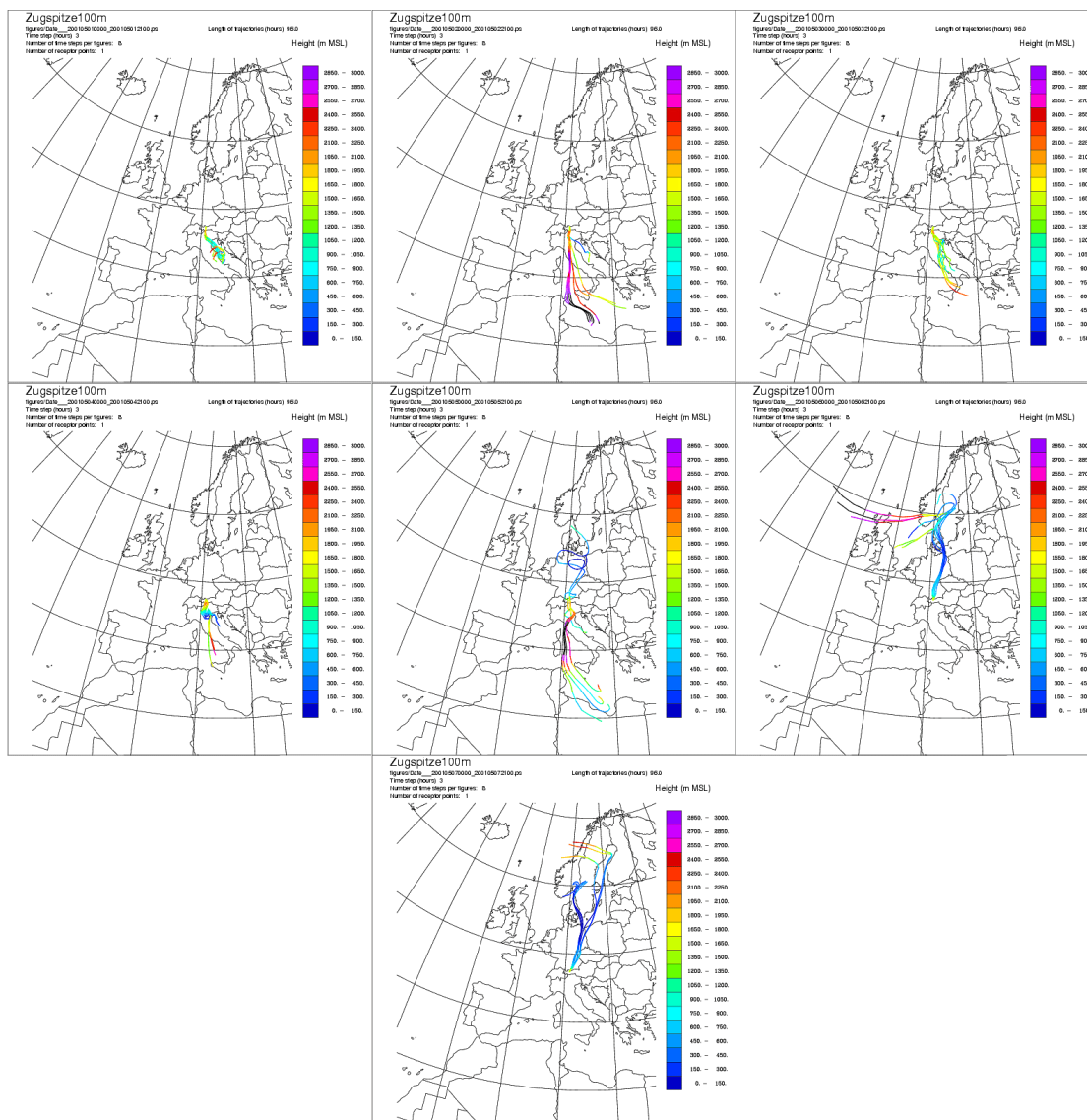


Fig. S-4 b

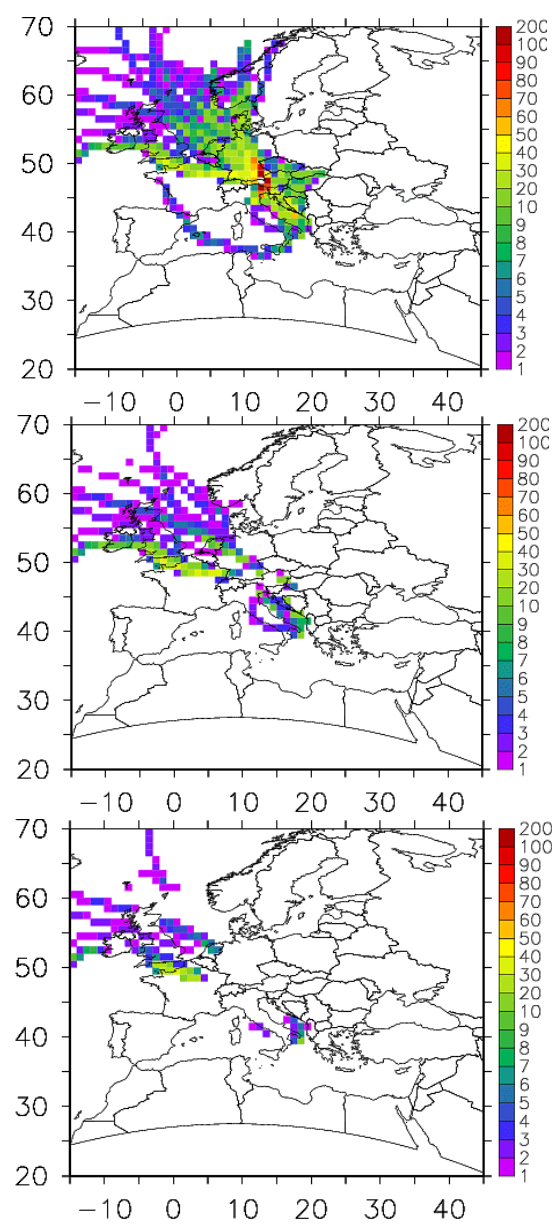


Fig. S-5 a

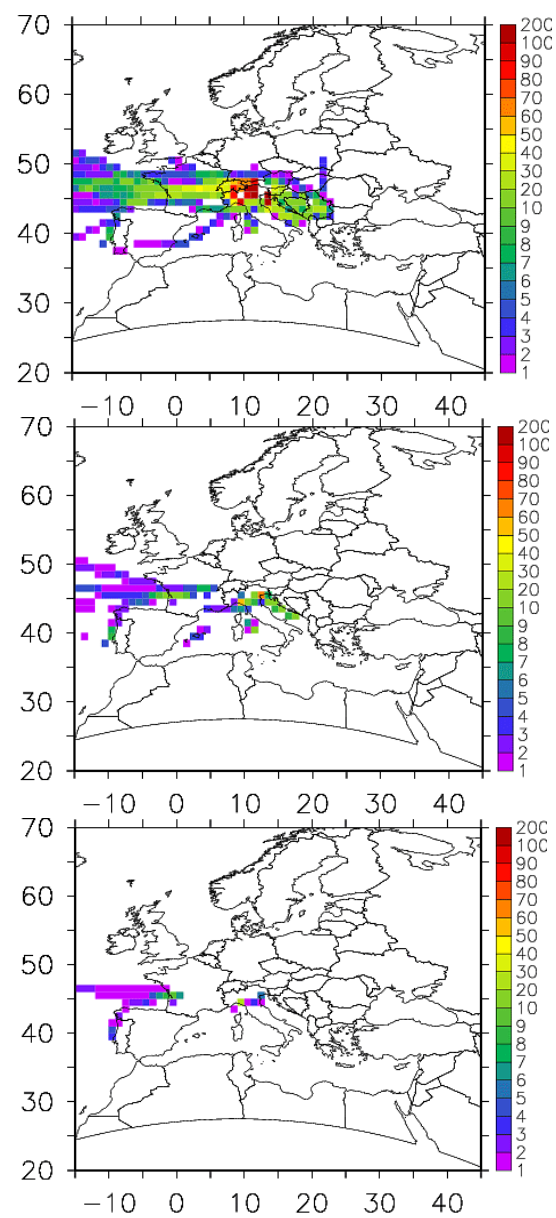


Fig. S-5 b

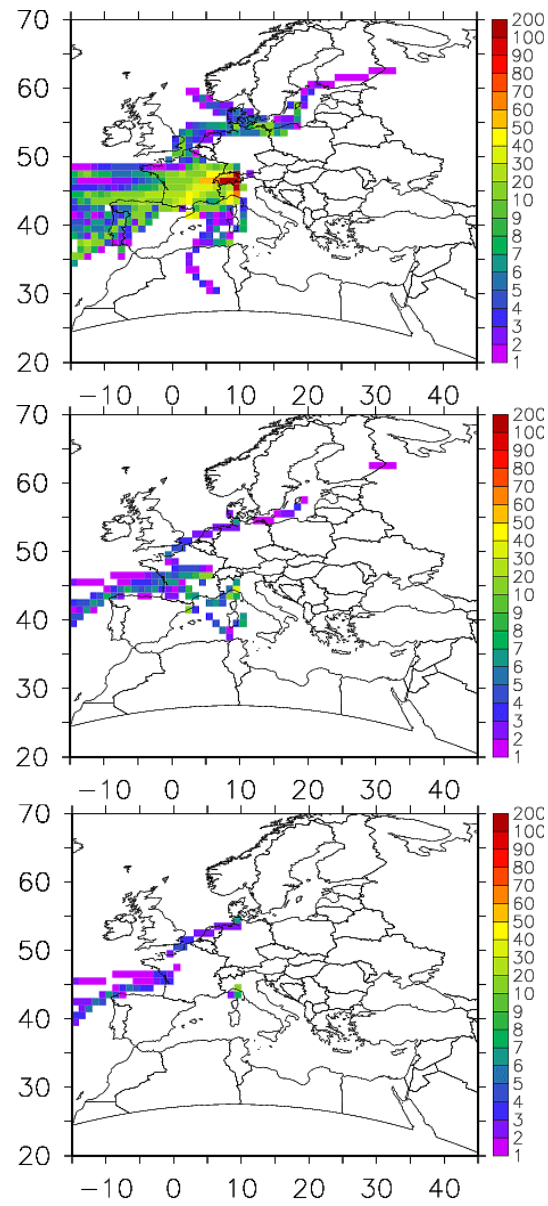


Fig. S-6 a

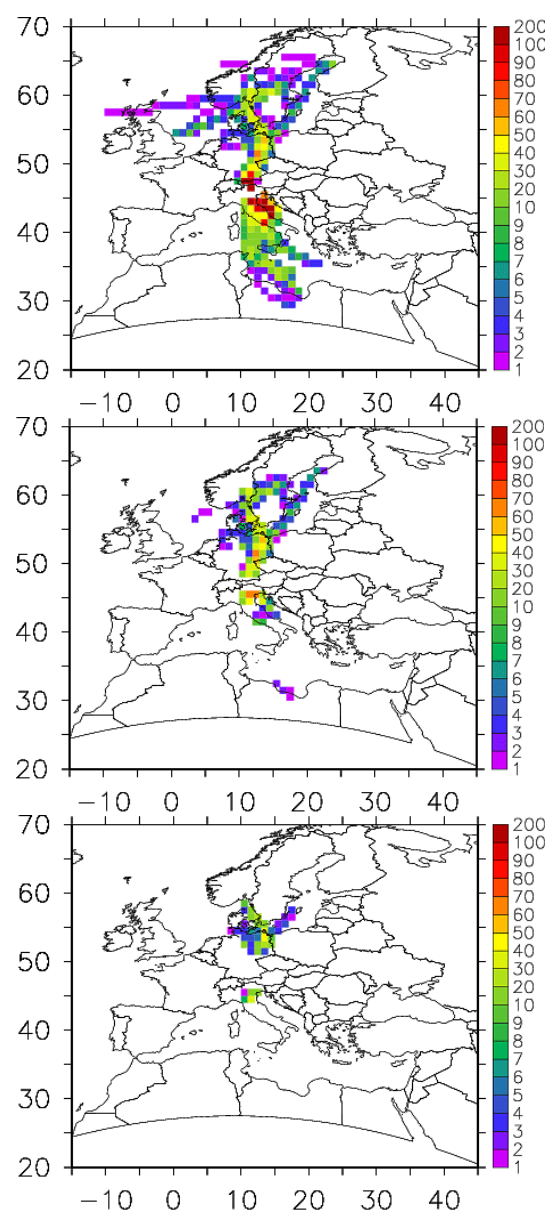


Fig. S-6 b