

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

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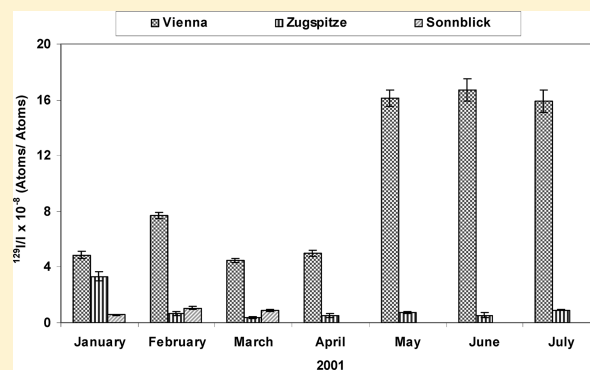
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S Supporting Information

ABSTRACT: Concentrations of gases and particulate matter have been proven to be affected by meteorological and geographical variables from urban locations to high mountain clean air sites. Following our previous research in Vienna, we summarize here new findings about concentration levels of iodine isotopes in aerosols collected at two Alpine meteorological stations, Sonnblick (Austria) and Zugspitze (Germany) during 2001. The present study mainly focuses on the effect of altitude on the anthropogenic concentration of ^{129}I and on the isotopic ratio $^{129}\text{I}/^{127}\text{I}$. Iodine was separated from matrix elements by using either an anion exchange method or solvent extraction, and was analyzed by ICP-MS and AMS. Over the altitude change from Vienna to Zugspitze and Sonnblick (202 m to 2962 m and 3106 m above sea level), stable iodine level decreased from an average of 0.94 ng m^{-3} to 0.52 ng m^{-3} and 0.62 ng m^{-3} , respectively. Similarly, ^{129}I concentrations at both Alpine stations were about 1 order of magnitude lower ($10^4 \text{ atoms m}^{-3}$) than values obtained for Vienna ($10^5 \text{ atoms m}^{-3}$) and reveal a strong vertical concentration gradient of ^{129}I . A high degree of variability is observed, which is due to wide variation in the origin of air masses. Furthermore, air trajectory analysis demonstrates the importance of large scale air transport mostly from southeast Europe for influencing Sonnblick whereas influence from northwest Europe is strong at Zugspitze. In contrast to ^{129}I , a higher concentration of ^7Be was found at higher altitude stations compared to Vienna which probably results from its production in the upper atmosphere.



1. INTRODUCTION

Iodine is an essential trace element that may influence climate through new aerosol formation and ozone destruction.¹ As sea represents the main source of iodine, coastal regions are expected to be more enriched with iodine than inland areas.² However, whether in fact such a correlation between iodine deposition flux on the soil and its distance from ocean exists is still disputed.³ Now it is generally accepted that high emission of iodine also results from bioactivity.⁴ On land, iodine emission from rice paddies and wetlands is considered most important. Still, few studies have been focusing on the latitude and altitude dependence of iodine levels in precipitation and snow.^{1,2,5–7}

The atmosphere is one of the most important media for iodine cycling in terms of iodine species transformations, climate influences, and transport of iodine from the ocean to the terrestrial ecosystems. It is difficult to understand the atmospheric distribution of iodine because of the short residence time and the complex iodine chemistry. In addition, it depends on factors such as type and size of aerosol, meteorological conditions (precipitation rate, wind speed, temperature, and wind pattern) and chemical parameters.⁸

These difficulties are also encountered in the studies of the environmental distribution of the long-lived radioiodine ^{129}I .

^{129}I is a major byproduct of nuclear fission that is of concern because of its mobility in the environment, excessive inventory, long half-life (~ 16 million years), and potential toxicity due to bioaccumulation through the food chain and bioconcentration in the thyroid gland. Indeed, spent nuclear fuel reprocessing facilities in northern Europe are the main global sources releasing ^{129}I both into effluent water and into the atmosphere. These facilities stand for more than 90% of the anthropogenic input into the environment. This is the main reason for the global variability of ^{129}I . Several studies suggest concentrations up to 1000 times higher in European atmosphere compared to North America.^{5,9,10} Recently, ^{129}I has been used as atmospheric tracer for radioiodine dispersion by nuclear accidents or atmospheric releases from reprocessing plants. Tracking the transport through different compartments of the global ecosystem provides new insights into the dynamics of

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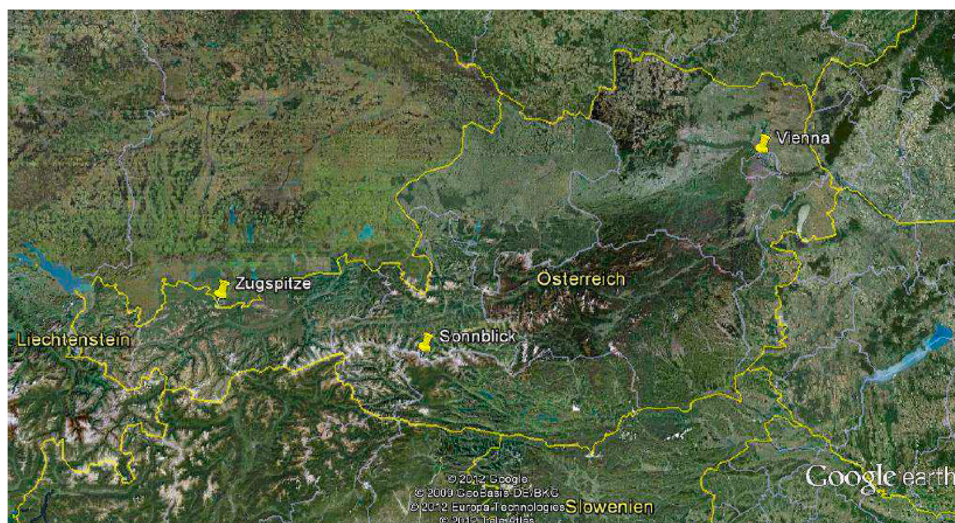


Figure 1. Location of sampling points.

the atmosphere and the biogeochemical cycle.¹¹ However, studies of ^{129}I in high altitude Alpine regions have been scarce until today.

In this study we have analyzed ^{129}I concentrations and $^{129}\text{I}/^{127}\text{I}$ isotopic ratios in aerosols sampled at the summits of the eastern Alps during 2001. Our study aims to shed light on variation of iodine isotopes (^{127}I and ^{129}I) on short time scales and on factors (meteorological and geographical) controlling this variation. The effects of vertical movements and scavenging processes in the atmosphere were checked by ^7Be concentration measurements. An important aspect of this study is to point out the variability of ^{129}I concentration over the altitude change of 2700 m (within a very small latitude difference of 1°) by comparing the ^{129}I Alpine concentrations with data from Vienna, Austria. The present study provides valuable data of the ^{129}I levels at high altitude Alpine stations, for which there was previously “almost no relevant data”.

2. MATERIALS AND METHODS

The aerosols from clean air regions in the eastern Alps were sampled at two weather observatories, Sonnblick (3106 m above sea level $12^\circ 58' \text{ E}$, $47^\circ 03' \text{ N}$, abbreviated SB) and Zugspitze (2962 m above sea level $10^\circ 59' \text{ E}$, $47^\circ 25' \text{ N}$, abbreviated ZS) (see Figure 1).¹² The eastern Alps have Atlantic influenced climate in their northern part, with continental influence in the east and Mediterranean influence in the south. The Sonnblick is located in the main ridge of the Austrian Alps, in the alpine massive “Hohe Tauern”. The surrounding area consists of a glacier to the south and a very steep 500-m drop to the north. Since there are no local pollution sources and the observatory itself is supplied with electricity through cable, the SBO has the ideal characteristics of a high alpine background station.¹³ The Zugspitze is the highest peak of the Wetterstein Mountains in the Bavarian Alps. It lies south of the town of Garmisch-Partenkirchen, and the border between Germany and Austria runs over its western summit. South of the mountain is the Zugspitzplatte, a high karst plateau with numerous caves. On the flanks of the Zugspitze are three glaciers.¹⁴ The samples had been collected during the first 3 months (SB) and 7 months (ZS) of 2001 within the STACCATO¹⁵ project and were made available to us for further investigations. Aerosols were sampled using

automatic high-volume samplers, which filtered about 1000–1200 standard cubic meter air per day on either glass fiber (SB) or cellulose nitrate (ZS) filters with a pore size of $8 \mu\text{m}$. Our samples represent the total particle bound iodine (^{127}I and ^{129}I). Therefore investigations of different particle size fractions were not possible and also iodine speciation was not achievable.

To depict the mechanism governing the removal and transport of aerosols, the air filters were first measured γ -spectrometrically to determine ^7Be concentrations before starting the iodine analysis¹⁵ (see Supporting Information (SI)).

The anion exchange method for iodine extraction from glass fiber filter was similar to that used previously.¹⁶ A detailed description is presented in the Supporting Information. Stable iodine concentration was measured on an aliquot by ICP-MS Agilent 7500ce, Waldbronn, Germany, equipped with a CETAC ASX-520 auto sampler (using a standard addition method in 2% ammonia solution) before adding potassium iodide carrier (5 mg of I^-) to the sample. Iodine was separated using Dowex 1x 8 (100–200 mesh Cl^- form) with 0.5 M HNO_3 and precipitated as AgI by addition of AgNO_3 solution. However, separation of iodine was failed by anion exchange for cellulose nitrate filters. Therefore, solvent extraction with chloroform followed by sodium bisulphate was used as given in the literature.¹⁷ The chemical yield in this procedure ranged from 60 to 70%. Finally, the dried precipitates of AgI from both procedures were mixed with silver powder ($\text{AgI}:\text{Ag} = 1:1$ by weight) and pressed into the copper sample holders used for accelerator mass spectrometry (AMS) measurements at the Vienna Environmental Research Accelerator (VERA; see Supporting Information). The uncertainty was estimated from counting statistics and from the reproducibility between the several measurements. Ratios were normalized using a standard material “ETH-D2” provided by the ETH Zürich with a nominal isotopic ratio of 4.73×10^{-11} . Technical details are given elsewhere.¹⁸ This material was produced by dilution of the NIST reference material SRM 4949B-79.¹⁹ Chemical blanks prepared with the same procedure as samples were used for background correction. The measured $^{129}\text{I}/\text{I}$ ratio in blank samples ($4 \pm 0.5 \times 10^{-13}$) was at least 1 order of magnitude lower than in samples ($0.1\text{--}4.7 \times 10^{-11}$).

However, very low negative iodine current was observed for the samples derived from cellulose nitrate filters (ZS). This may have been caused by reduced negative ion yields in the cesium sputter source due to the presence of impurities in the AgI precipitates, most likely in the form of Ag_2SO_3 or AgCl . This assumption was further confirmed by acquiring a full mass spectrum with AMS, which revealed peaks only at mass 16 (oxygen), 32 (sulfur), 107 and 109 (silver), and 127 (iodine, however too little), but not the typical chlorine peaks at mass 35 and 37. Since sulfur is known to impair negative ion formation in the cesium sputter source,¹⁷ we assume that we were not successful in removing it completely. However, even a strong reduction in negative ion yield is not expected to influence the isotopic ratios measured, therefore we decided to use the already measured data, despite its significantly larger uncertainty. For a few samples, measurements at both low and high current were possible, which showed good agreement. Contrary to observations by Lopez-Gutierrez et al.¹⁷ we found only sulfur peaks in our samples; tellurium contamination is completely suppressed at VERA.

3. RESULTS

The concentrations of total particle-bound ^{127}I measured by ICP-MS are shown in Tables 1 and 2. The concentrations

Table 1. Concentration of Iodine Isotopes and Be-7 in Aerosols from Sonnblick

period 2001	^{127}I ng m ⁻³	$^{129}\text{I} \times 10^4$ atoms m ⁻³	$^{129}\text{I}/^{127}\text{I} \times 10^{-9}$ atoms/atoms	^7Be mBq m ⁻³
01–08 Jan.	0.47 ± 0.01	0.5 ± 0.1	2.3 ± 0.2	4.3 ± 0.8
09–15 Jan.	0.41 ± 0.01	1.0 ± 0.1	5.5 ± 0.3	9.4 ± 1.2
16–22 Jan.	0.55 ± 0.01	1.1 ± 0.1	4.1 ± 0.2	5.7 ± 0.8
23 Jan.–01 Feb.	0.38 ± 0.01	1.9 ± 0.1	10.4 ± 0.4	3.0 ± 0.6
02–08 Feb.	0.68 ± 0.01	2.5 ± 0.1	7.9 ± 0.3	4.3 ± 0.7
09–15 Feb.	0.65 ± 0.01	0.9 ± 0.1	2.9 ± 0.2	6.1 ± 0.8
16–22 Feb.	1.67 ± 0.01	1.7 ± 0.1	2.1 ± 0.1	5.3 ± 0.8
23 Feb.–01 Mar.	0.55 ± 0.01	7.6 ± 0.3	29.5 ± 1.4	2.5 ± 0.5
02–08 Mar.	0.24 ± 0.01	2.8 ± 0.1	24.6 ± 1.2	9.4 ± 1.2
09–15 Mar.	0.45 ± 0.01	0.7 ± 0.1	3.4 ± 0.4	3.0 ± 0.6
16–23 Mar.	0.69 ± 0.01	1.0 ± 0.1	3.2 ± 0.2	3.5 ± 0.7
24 Mar.–01 Apr.	0.75 ± 0.01	1.3 ± 0.1	3.8 ± 0.2	3.4 ± 0.8

varied from 0.24 to 1.67 ng m⁻³ (mean value 0.62 ± 0.36 ng m⁻³) and 0.15 to 1.43 ng m⁻³ (mean value 0.52 ± 0.29 ng m⁻³) during 3 and 7 months of monitoring at Sonnblick and Zugspitze, respectively, while in Vienna we had found 0.94 ± 0.21 ng m⁻³.

For ^{129}I we found even larger differences between high altitude Alpine stations and the lowland area of Vienna. At altitudes of 3106 and 2962 m above sea level, the concentrations of ^{129}I in aerosols ranged between 0.3 and 7.6×10^4 atoms m⁻³ with averages of 1.9×10^4 atoms m⁻³ and 1.6×10^4 atoms m⁻³ (Tables 1 and 2), respectively, compared to 3.8×10^5 atoms m⁻³ in Vienna. The average isotopic ratio for Sonnblick and Zugspitze was found to be around 8.2×10^{-9} , compared to 10.2×10^{-8} in Vienna. The results of ^{129}I in the

Table 2. Concentration of Iodine Isotopes and Be-7 in Aerosols from Zugspitze

period 2001	^{127}I ng m ⁻³	$^{129}\text{I} \times 10^4$ atoms m ⁻³	$^{129}\text{I}/^{127}\text{I} \times 10^{-9}$ atoms/atoms	^7Be mBq m ⁻³
01–08 Jan.	0.21 ± 0.01	1.1 ± 0.2	11 ± 1.7	3.1 ± 0.3
09–15 Jan.	0.20 ± 0.01	0.7 ± 0.1	7.5 ± 0.8	8.9 ± 0.9
16–22 Jan.	0.15 ± 0.01	4.2 ± 0.1	58 ± 5.5	5.2 ± 0.5
23 Jan.–01 Feb.	0.17 ± 0.01	4.4 ± 0.1	56 ± 5	4.2 ± 0.4
02–08 Feb.	0.53 ± 0.01	0.5 ± 0.1	2 ± 0.3	3.6 ± 0.4
09–15 Feb.	0.56 ± 0.01	0.64 ± 0.03	2.4 ± 0.1	4.9 ± 0.5
16–22 Feb.	0.38 ± 0.01	3.3 ± 0.9	18.5 ± 4.9	4.8 ± 0.5
23 Feb.–01 Mar.	0.17 ± 0.01	0.30 ± 0.05	4 ± 0.6	1.6 ± 0.2
02–08 Mar.	0.30 ± 0.01	0.7 ± 0.1	5.1 ± 0.5	4.6 ± 0.5
09–15 Mar.	0.22 ± 0.01	0.11 ± 0.02	1.1 ± 0.3	1.5 ± 0.2
16–23 Mar.	0.24 ± 0.01	0.20 ± 0.01	1.4 ± 0.1	2.3 ± 0.2
24 Mar.–01 Apr.	0.40 ± 0.01	1.4 ± 0.2	7.4 ± 1	2.6 ± 0.3
02–06 Apr.	0.79 ± 0.01	1.8 ± 0.2	4.8 ± 0.8	6.9 ± 0.7
08–14 Apr.	0.33 ± 0.01	0.6 ± 0.1	3.8 ± 1.1	1.6 ± 0.1
15–23 Apr.	0.31 ± 0.01	2.2 ± 0.2	15.4 ± 1.5	2.1 ± 0.2
24–30 Apr.	0.61 ± 0.02	1.2 ± 0.4	4.3 ± 1.2	5.0 ± 0.5
01–07 May	0.75 ± 0.02	7.5 ± 0.8	21 ± 2.3	5.4 ± 0.5
08–15 May	0.66 ± 0.01	2.8 ± 0.1	0.9 ± 0.1	5.6 ± 0.6
16–23 May	0.50 ± 0.01	1.0 ± 0.2	4.2 ± 1.1	4.9 ± 0.5
25–31 May	1.02 ± 0.02	2.2 ± 0.2	4.6 ± 0.5	6.1 ± 0.6
01–07 June	0.52 ± 0.01	1.6 ± 0.2	6.6 ± 0.7	3.8 ± 0.4
09–15 June	0.39 ± 0.01	1.8 ± 0.6	10 ± 3.3	4.4 ± 0.4
16–24 June	0.39 ± 0.01	2.5 ± 0.2	13.5 ± 1.1	3.5 ± 0.3
25–30 June	0.82 ± 0.02	1.4 ± 0.5	3.7 ± 1.4	6.9 ± 0.7
01–07 July	1.43 ± 0.02	0.3 ± 0.1	0.5 ± 0.1	5.8 ± 0.6
08–21 July	0.55 ± 0.01	0.5 ± 0.1	2.0 ± 0.4	4.6 ± 0.5
22–30 July	0.69 ± 0.01	0.8 ± 0.1	2.4 ± 0.3	6.9 ± 0.7

aerosols indicated a larger variation in the concentrations compared with that of ^{127}I .

The ^{129}I time series was analyzed in combination with the weekly pattern of ^7Be and precipitation data. Basic statistics of ^7Be activity concentrations at Sonnblick and Zugspitze are shown in Tables 1 and 2. The values found for ^7Be were in the range of 1.5–9.4 mBq m⁻³. Generally they were about a factor 2 higher than the respective values measured in Vienna. ^7Be maxima and trends were very similar at both high altitude stations (e.g., an abrupt increase of ^7Be up to 9.4 and 8.9 mBq m⁻³ was found during second week of January) and followed the same pattern, indicating that the vertical movement of air masses from the stratosphere to the troposphere happened simultaneously at both locations.

Using deposition velocity ranges ν_d of 0.001–0.02 and 0.004–0.074 ms^{-1} for ^{129}I and ^7Be , respectively, and the concentration of the respective isotope $C(t)$, the dry fallout $F_d(t)$ (given in atoms or mBq cm^{-2}) was estimated by Englund et al.^{20,21} as

$$F_d(t) = C(t) \cdot \nu_d \cdot \text{tr}$$

where tr is the conversion factor from $\text{m}^{-2} \text{s}^{-1}$ to cm^{-2} . The upper limit of the deposition velocity $\nu_d = 0.02 \text{ ms}^{-1}$ assumes that iodine is attached to particles of $>1 \mu\text{m}$.²⁰ However, dry deposition is critically dependent on precipitation (the higher the amount of precipitation, the fewer aerosols are left for dry deposition) and particle size. Particles varying from submicrometer to intermediate 2–4 μm deposit via diffusion, impaction, and interception, and large particles greater than 10 μm deposit through gravitational setting.²² The average weekly dry deposition of ^{129}I obtained in present work is approximately $2 \times 10^4 \text{ atoms cm}^{-2}$ (Figures S-1 and S-2). A plot of dry deposition of iodine isotopes at Sonnblick and Zugspitze versus precipitation did not reveal any significant correlation. However, correlations of -0.38 and -0.3 between ^7Be dry deposition and precipitation indicated the importance of wet scavenging as controlling mechanism in the case of this nuclide.

4. DISCUSSION

The purpose of the present investigation was to determine atmospheric deposition of ^{129}I at the remote areas of high altitude Alp stations. At both Alpine stations ^{127}I concentrations were about a factor of about 1.5 lower than the mean value found in Vienna.¹⁶ This is probably due to the fact that anthropogenic sources (as, e.g., heating emissions and traffic) of ^{127}I do not exist in the surroundings of Sonnblick and Zugspitze. Another explanation is that alpine regions are covered with snow most of the time, which can prevent resuspension of iodine from soil.⁵ However, due to lack of statistical data from literature, this assumption remains uncertain. Moreover, a removal of “foreign” iodine with increasing altitude might be possible because of scavenging by clouds and precipitation in the lower troposphere. Such a gradient was also observed for stable iodine with a 60% lower concentration in air at an altitude of 1000 m above sea level compared to that at sea level. A similar decrease in iodine concentration of a factor of 2 was observed by Gilfedder et al. at a horizontal distance of only 5 km and over the 838 m height change from Ottenhöfen (326 m above sea level) to Hornisgrinde (1164 m above sea level).^{23,24} Interestingly, Reithmeier et al. also measured 70% depletion of stable iodine at the Fiescherhorn glacier compared to stable iodine in rainwater collected from Stierberg, Upper Bavaria.⁶ In the present study, the concentration of stable iodine was somewhat higher (20%) for Sonnblick than Zugspitze. A possible explanation for the observed deviation may be the different collection efficiencies of glass fiber (SB) and cellulose nitrate (ZS) filters, since membrane filters have higher flow resistance and lower loading capacity than fiber filters.²⁵ However, different origins of the air masses at the two stations or differing wash out rates of aerosols can also explain such different iodine concentrations.

Our high altitude data indicate a decrease of 1 order of magnitude in ^{129}I concentration over an altitude change of about 2800 m as compared to Vienna. A possible reason for the

low ^{129}I concentration at high altitude (compared to other nuclides originating from the nuclear weapon tests and also from the nuclear accident in Chernobyl) might be the fact that the injection of ^{129}I into the atmosphere from the reprocessing facilities does not reach high altitudes.^{6,9} According to Aldahan et al. ^{129}I may reach up to a few hundred meters and thus its spreading is strongly dependent on wind strength, direction, and moisture content.⁹ The depletion of ^{129}I with increasing altitude could also be caused by clouds scavenging and precipitation (in the same way as for the stable ^{127}I), as also observed in decreasing ^{129}I concentrations between Zürich and the Fiescherhorn ($\sim 4000 \text{ m}$ above sea level) glacier in Switzerland by Reithmeier et al.⁶

Due to the larger decrease of ^{129}I compared to ^{127}I the isotopic ratios $^{129}\text{I}/^{127}\text{I}$ were lowered by a factor of 10 if compared to Vienna. At the Alp stations these values were on the order of 10^{-9} (Tables 1 and 2). The observed isotopic ratio is 2 orders of magnitude higher than the value obtained for snow from Mt. Erebus, Antarctica, at a height of 3794 m in the Southern Hemisphere reflecting that the main source of ^{129}I lies in the mid latitudes of the Northern Hemisphere.²⁶

Generally speaking, our data support the opinion that single values measured for ^{129}I deposition or for the $^{129}\text{I}/^{127}\text{I}$ ratio require information on the sampling site altitude, and cannot be considered representative for a whole region if it covers different elevations. Reithmeier observed that the ^{129}I concentration at the Fiescherhorn glacier must be multiplied by a certain factor (6) to derive wet deposition fluxes at the nearby lowland. From our measurements we calculate that the dry fallout at high altitudes is about a factor of 18 lower than the weekly value of $4.36 \times 10^5 \text{ atoms cm}^{-2}$ reported for Vienna ($48^\circ 15' \text{ N}$ and $16^\circ 21' 50'' \text{ E}$; 202 m above sea level).²⁷ This factor (for dry deposition) is clearly higher than that given by Reithmeier (for wet deposition) and may have an uncertainty related to the different pore sizes of the filters (Alps 8 μm , and Vienna 1.6 μm). According to Tsukada et al., the particle size distribution of iodine isotopes (^{127}I and ^{129}I) showed similar pattern, rich in fine mode.²⁸ Therefore, a part of the high depletion factor might be attributed to loss of fine particles in the filters from the high altitude site. However, considering the above cited similarity for the distribution of the nuclides, the loss of fine particles would not change the isotopic ratio. The weekly dry deposition value observed for Vienna is on the same order of magnitude as calculated for Northern Sweden ($67^\circ 50' \text{ N}$ and $20^\circ 20' \text{ E}$; 408 m above sea level) and Seville, southwest Spain ($37^\circ 23' \text{ N}$, $5^\circ 58' \text{ W}$; 12 m above sea level)²⁹ with values of $3.07 \times 10^5 \text{ atoms cm}^{-2}$ and $1 \times 10^5 \text{ atoms cm}^{-2}$ (using average ^{129}I concentration of $0.85 \times 10^5 \text{ atoms m}^{-3}$ from ref 29), respectively, but an order of magnitude lower than 12.69×10^5 reported for southern Sweden ($56^\circ 5' \text{ N}$ and $13^\circ 14' \text{ E}$; 42 m above sea level, 250 km from the coast).²⁰

Our results show that the temporal fluctuation of ^{129}I is more pronounced than that of ^{127}I , indicating an alternating source term. Today the most extensive sources of ^{129}I are marine discharges and gaseous emissions from the nuclear fuel reprocessing plants at Sellafield (UK), started in 1951, and La Hague (France), started in 1966, in western Europe. The marine discharges from Sellafield (1380 kg up to 2005) spread around Irish Sea. This ^{129}I is then further transported with the water masses northerly around Scotland, enters the North Sea, and mixes into the water current coming out of the English Channel, which carries the marine discharges from La Hague (3330 kg up to 2005); the water then flows along the Belgian,

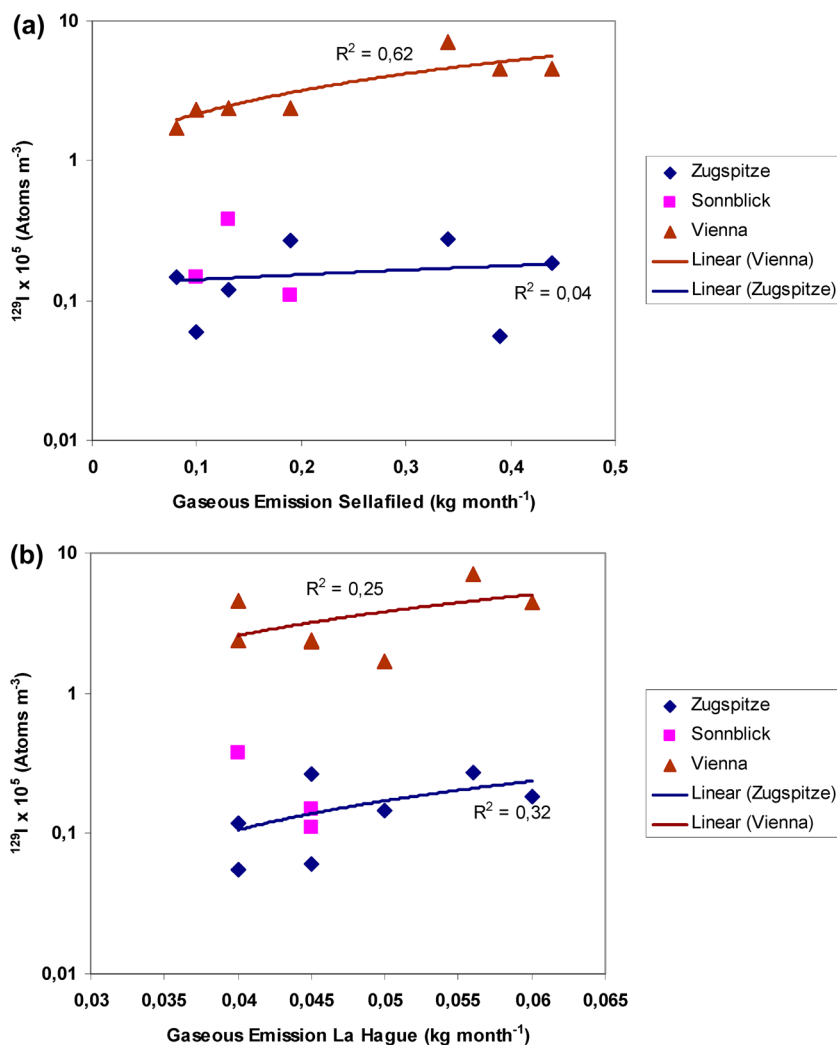


Figure 2. Scatter plot of ^{129}I concentrations (log scale) in the air (Zugspitze, Sonnblick, and Vienna) versus gaseous emissions from Sellafield (a) and La Hague reprocessing plants (b). The measured values of Vienna were taken from Jabbar et al.¹⁶

Dutch, German, and Danish Shores to the southern Baltic Proper through Skagerrak-Kattegat basin.³⁰ The ^{129}I pool in the Kattegat represents a mixture of surface and intermediate water of Skagerrak and Baltic Proper water out flowing via the Öresund.³¹ Finally, ^{129}I is transported along the Norwegian coast into the Nordic Sea and further into the Arctic Ocean.³⁰ In addition to that Marcoule (operated during 1959–1997) discharged a comparatively small amount of liquid ^{129}I (45 kg) to the Mediterranean Sea via the Rhone River.⁶ The impact on the Mediterranean Sea was confined to the proximity of the Rhone Estuary where isotopic ratios of about 5×10^{-7} were observed.³⁰ During 2001, NRP at Sellfield also released ^{129}I in air at a relatively higher rate (3 kg) than La Hague (0.68 kg). Statistical analysis was used to assess the influence of gaseous emissions of ^{129}I at Alp stations from the release points on the concentrations measured at our sampling sites. As already depicted in Jabbar et al.,¹⁶ the aerosol time series from Vienna shows a strong correlation with the Sellafield emissions ($r^2 = +0.62$). Contrary to that, monthly trends from Zugspitze depicted very weak correlation ($r^2 = +0.1$) with gaseous emissions from Sellafield. The respective temporal trend of ^{129}I at Zugspitze ($r^2 = +0.3$) suggests a higher contribution from La Hague, which does not agree with the fact that gaseous emissions from La Hague were 1 order of magnitude lower

than that of Sellafield (see Figure 2a and b). We think that the statistical analysis supports the opinion that ^{129}I in air has multiple sources. Most authors agree that the contribution of liquid releases partly re-emitted from the ocean surface is almost as important as direct gaseous emissions since 1990.^{3,6,30} Reithmeier et al. estimated the total ^{129}I amount re-emitted from the ocean's surface to be 27.54 kg until the year 2004,⁶ which is much less than the directly released ^{129}I to the atmosphere (140 and 69 kg from Sellafield and La Hague until 2005).³⁰ In the context of this work, we observed that iodine in aerosols originates from sources with isotopic ratios between 10^{-10} and 10^{-8} . These values are significantly lower than $^{129}\text{I}/^{127}\text{I}$ ratios of 10^{-6} in the highly contaminated North Sea water (in very restricted areas closer to the shore including also Skagerrak and Kattegat basin). The lowest $^{129}\text{I}/^{127}\text{I}$ ratio of 10^{-8} was found in the middle of northern North Sea and in the Baltic Sea.^{30,31} The aerosols with the highest isotopic ratios of 10^{-8} may originate from sea spray water from such regions, while the lower isotopic ratio down to 10^{-10} has been observed in the northeast Atlantic Ocean.³⁰ The Mediterranean Sea is isolated from direct liquid discharges, however, influence from Mediterranean Sea can not be totally neglected because in Mediterranean mussel tissue isotopic ratios as high as 10^{-9} have been found.³² The probable source is deposition of gaseous

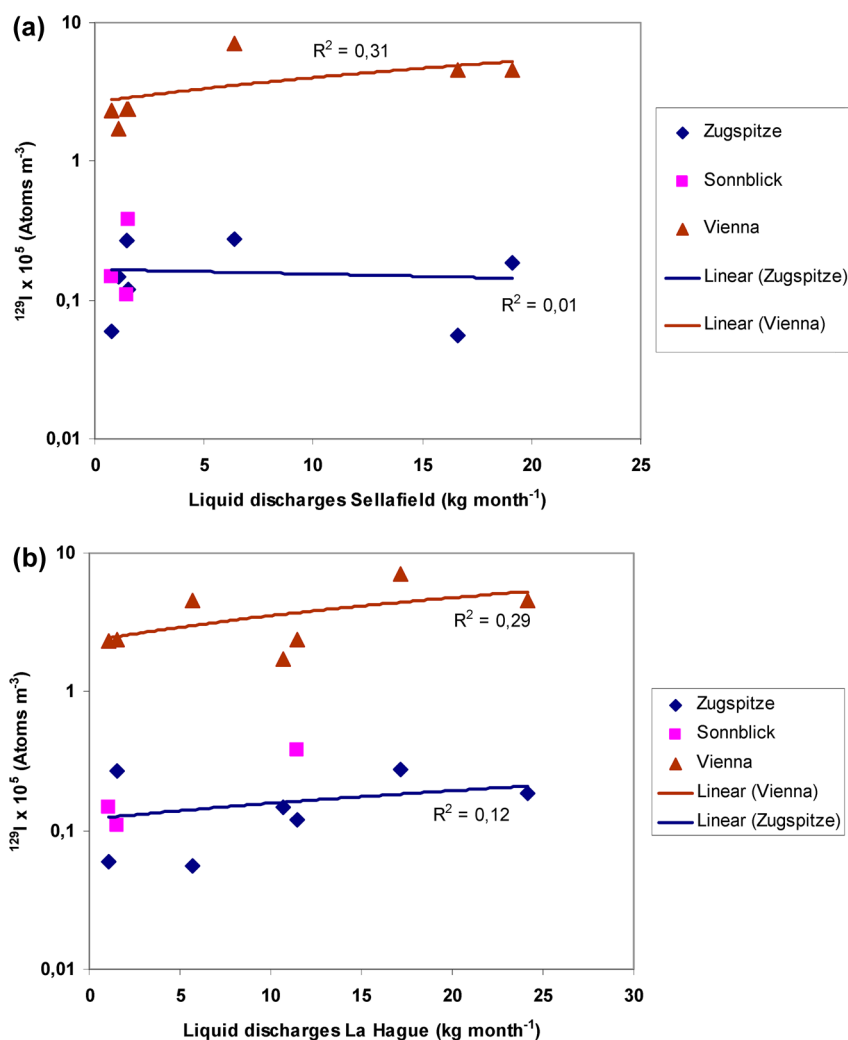


Figure 3. Scatter plot of ^{129}I concentrations (log scale) in the air (Sonnblick, Zugspitze, and Vienna) versus marine discharges from Sellafield (a) and La Hague reprocessing plants (b).

releases from the Sellafield and La Hague into the Mediterranean.

Similar to for the gaseous releases, monthly marine discharges from Sellafield and La Hague were plotted against our measured monthly ^{129}I concentrations (Figure 3a and b). No correlation is found for Zugspitze. In contrast to that, for Vienna, correlations with monthly marine discharges from Sellafield (+0.3) and La Hague (+0.3) exist. The data clearly depict that the Vienna and Zugspitze ^{129}I inventory in air had more influence from gaseous emissions (Vienna: +0.25 for La Hague and +0.6 for Sellafield, and Zugspitze: +0.3 for La Hague and +0.1 for Sellafield). However, the correlations obtained for Sonnblick in both cases (gaseous emissions and liquid discharges) could not be supported statistically due to lack of a sufficiently large amount of data (Figures 2 and 3).

Cosmogenic ^7Be is a marker for the exchange of air between stratosphere and troposphere. At high-altitude Alpine stations, the highest ^7Be concentration observed might be attributed mainly to vertical air mixing and to dry conditions.³³ Weather data verified dry conditions during the ^7Be maxima we observed for the Sonnblick and Zugspitze sites (see Supporting Information). By correlating the data on the weekly deposition of ^{129}I and ^7Be we therefore might extract information on stratospheric ^{129}I . However, the statistical analysis does not

show any significant correlation (Figures S-1 and S-2). This finding may be explained by the different properties of the two isotopes, since iodine is strongly linked to wet deposition²⁰ (precipitation) whereas ^7Be is linked to dry deposition (aerosols). Furthermore, ^{129}I is mainly transported by large-scale horizontal air flow while ^7Be is controlled by downward movement of air masses.

At the Zugspitze sampling station the atmospheric concentration of ^{129}I exhibited maxima in the last week of January, in the third week of February, and in the first week of May, always correlated with winds from west to northwest. Interestingly, the temporal behavior of ^{129}I at Sonnblick was similar to that of Zugspitze but showed a week delay, which seems rather long for a distance of only 160 km. However, one must take into account that we combined 7 daily filters, so the delay may also be smaller (one week is the time resolution limit of our measurement).

Large-scale wind air flow can be studied with backward trajectory calculations. The possible sources of ^{129}I lie to the northwest of the investigated sites. In the period of Jan 16 to Feb 1 (first ^{129}I maximum at Zugspitze) the winds came mainly from southeast to southwest, but beginning with Jan 29 the main wind direction was from northwest to west. During the second maximum (Feb 16–22 at Zugspitze) a storm from

northwest was observed beginning at Feb 20; during the third period with high ^{129}I levels at Zugspitze (May 1–7) wind from north was reported from May 6–7. Generally, the area of Zugspitze is exposed directly to northern or northwestern winds, while the Sonnblick area might be a little bit shielded from them. Also we would expect influence from air masses with southern origin at Sonnblick, while at Zugspitze the air flow should be mainly from northwest with the exception of foehn situations (which occur more frequently during spring).

Calculated air trajectories support our assumption that measured high concentrations of ^{129}I correspond to air masses which were in contact to seawater affected by liquid discharges of the reprocessing plants (see Figures S-3 to S-6). Trajectories were calculated using a 0.5 degree grid for the weeks with the highest and lowest ^{129}I concentrations measured at both sites (see Supporting Information). The investigation period for Sonnblick is Feb 22 to Mar 1 (highest concentration of ^{129}I) and Mar 8–15. The trajectories corresponding to the maximum concentrations of ^{129}I showed contact with seawater in the suspected source regions, whereas the trajectories corresponding to minimum concentration had no contact to such regions in the previous 96 h. Similarly, in the case of Zugspitze the lowest measured concentration of ^{129}I during Mar 16–23 was due to air most of the time descending from high elevation, which was also evidenced by a high ^7Be concentration of 12 mBq m^{-3} on March 16. During May 1–7 the highest concentration of ^{129}I was measured at Zugspitze. While the trajectories showed transport from the south or from the vicinity of Alps until May 4, air masses which had last surface contact with the Baltic Sea arrived on May 6 and 7.

The elucidation of air transport processes is challenging at high altitude Alpine sites. It seems that long-range air transport causes concentration peaks of ^{129}I , but due to increasing washout by precipitation with height, a strong altitude gradient develops. The influence of liquid discharges and atmospheric emissions from nuclear reprocessing facilities on the concentration of ^{129}I in the studied region is captured through statistical analysis. The first results for two alpine stations (Sonnblick and Zugspitze) show that even though two stations are situated close to each other, air from northeast and southeast Europe mostly affect Sonnblick whereas Zugspitze had more frequently air from northwestern Europe.

This study will fill the gap in ^{129}I data for high-altitude stations and we think this information is helpful for not only the prediction of the distribution of ^{129}I in the environment, but also for the transport of ^{131}I after a nuclear accident. Because of the observed complex variation of ^{129}I , more measurements would be eligible to understand fallout of ^{129}I at Alpine stations. Further, speciation studies will be helpful to better understand the mechanisms of iodine transport.

■ ASSOCIATED CONTENT

📄 Supporting Information

Details of extraction method and measurement of iodine by AMS, and some extended discussions including air trajectories, and 6 figures as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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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).

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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
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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.

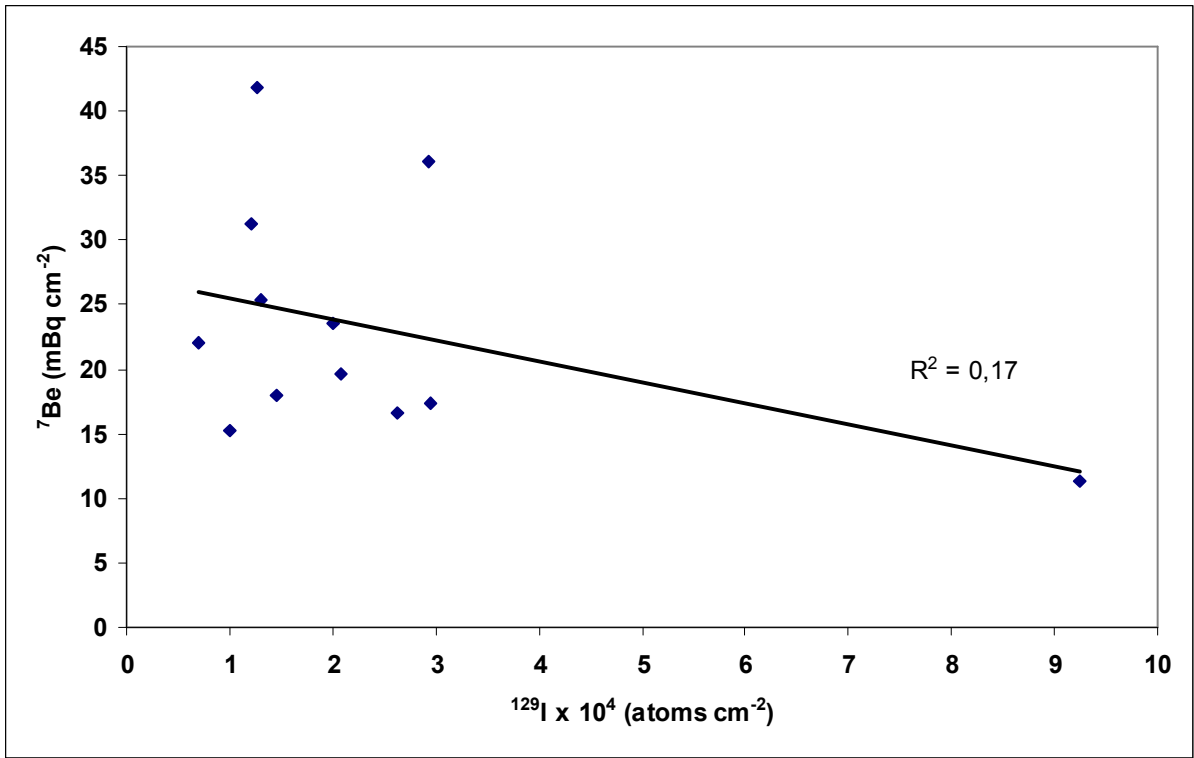


Fig. S-1

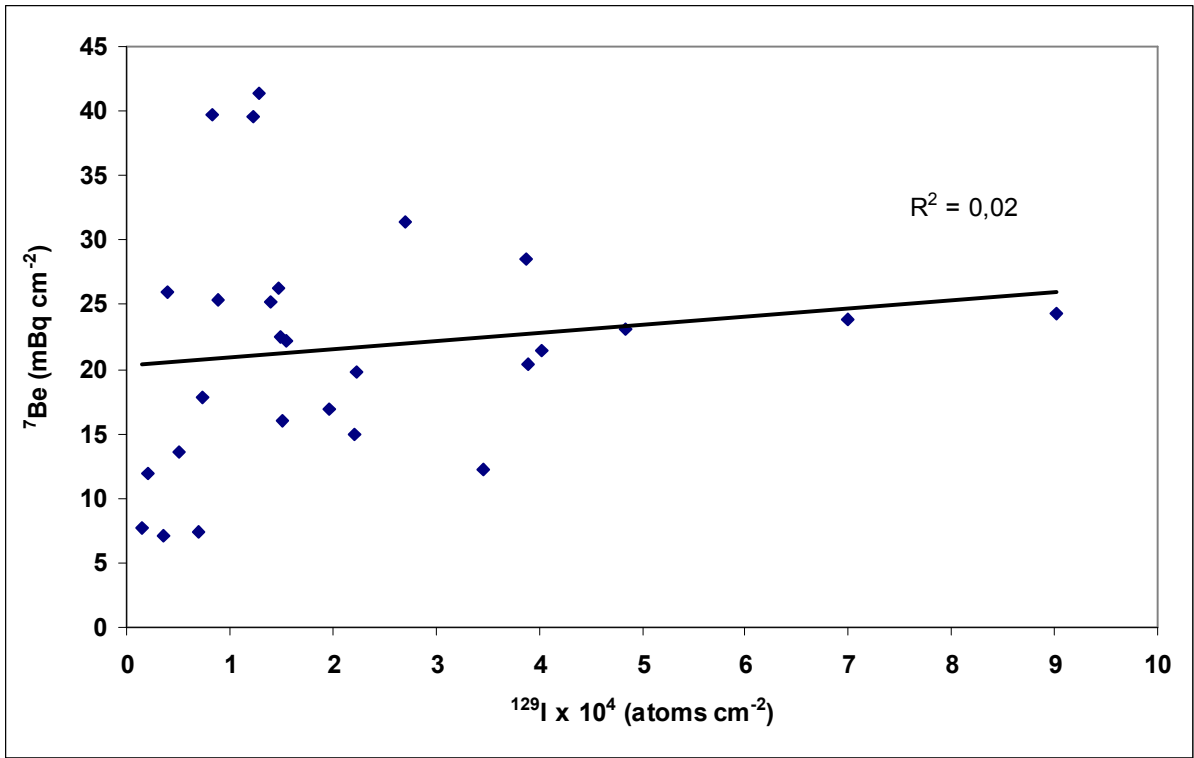


Fig. S-2

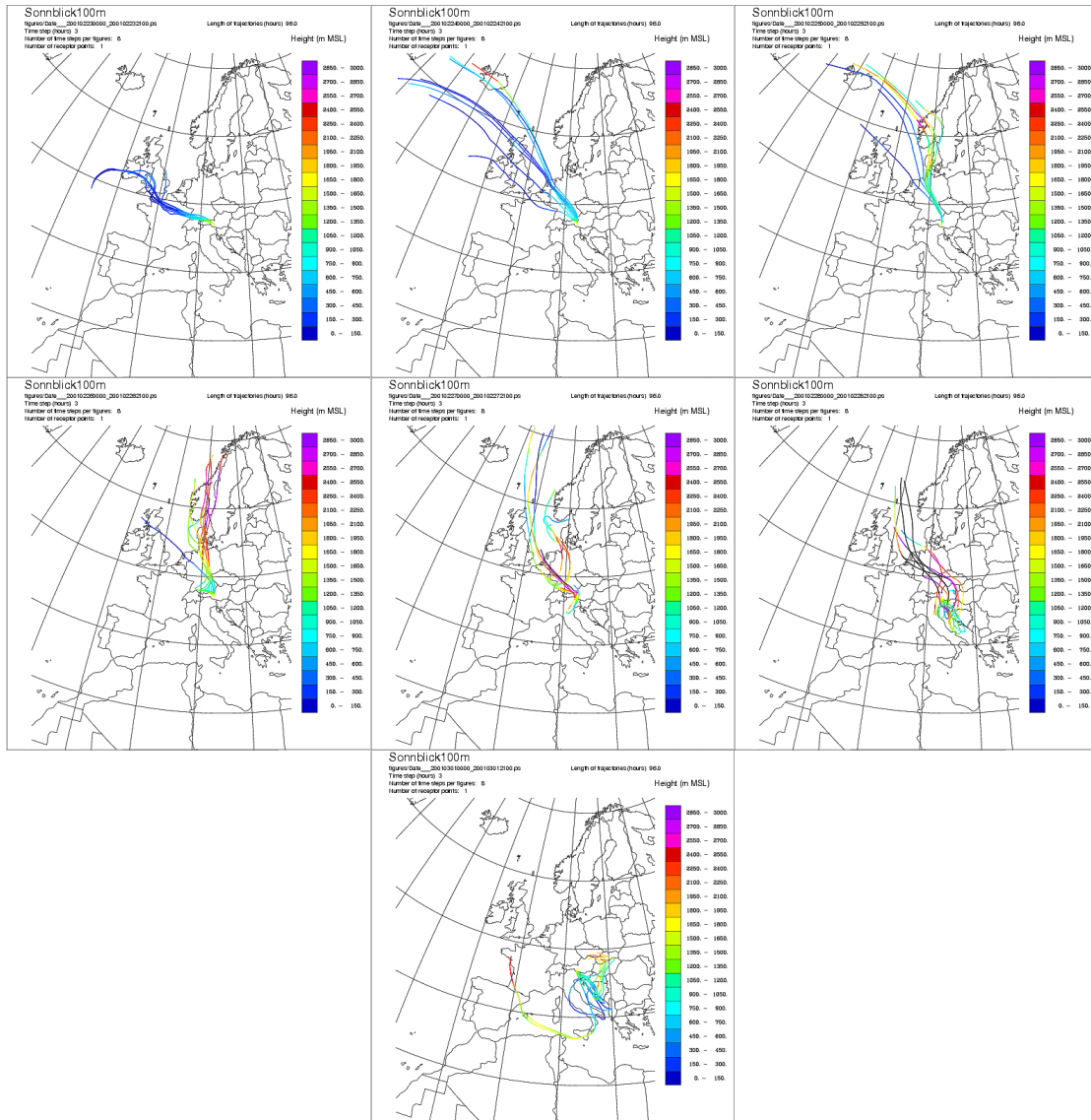


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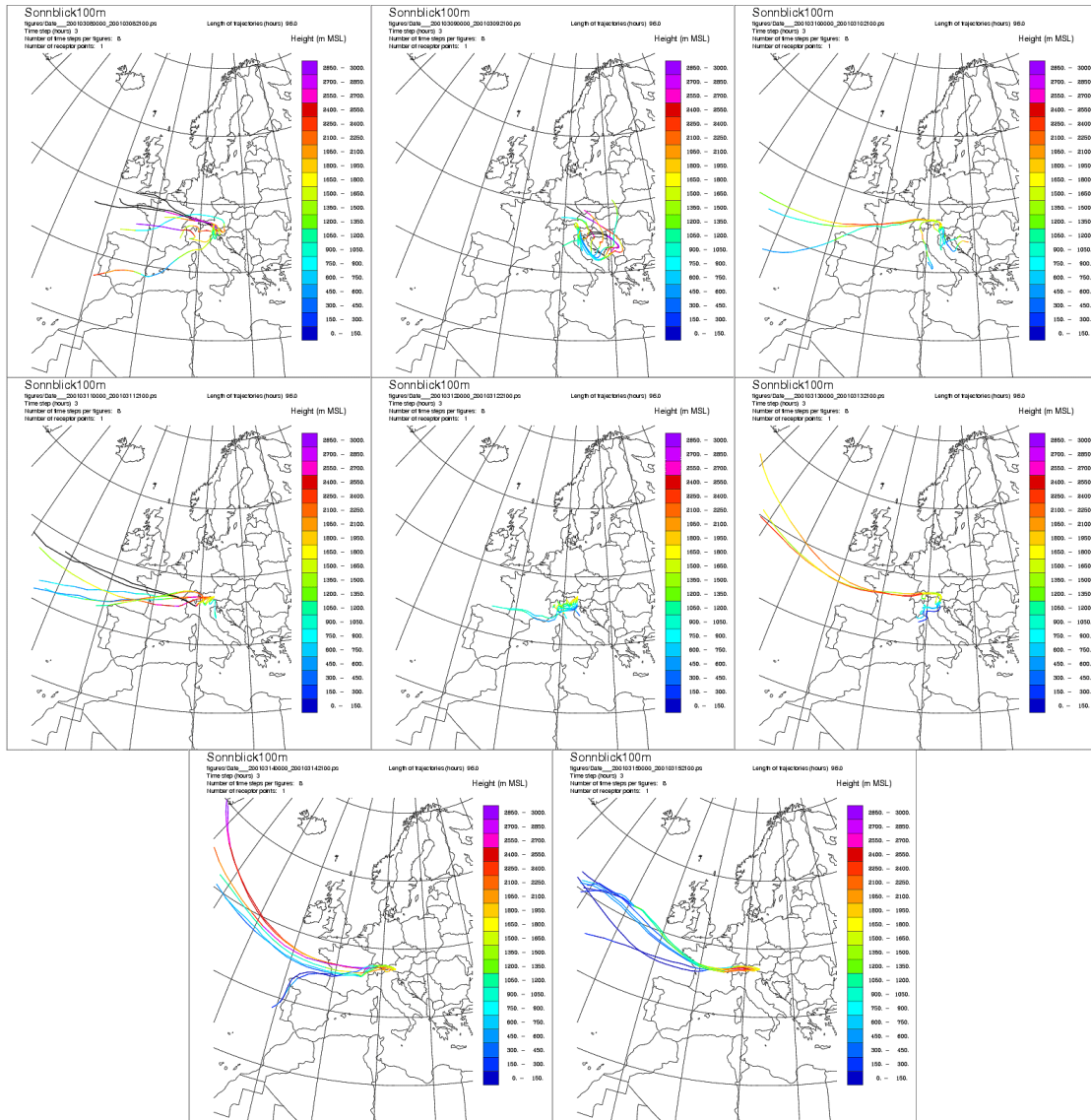


Fig. S-3 b

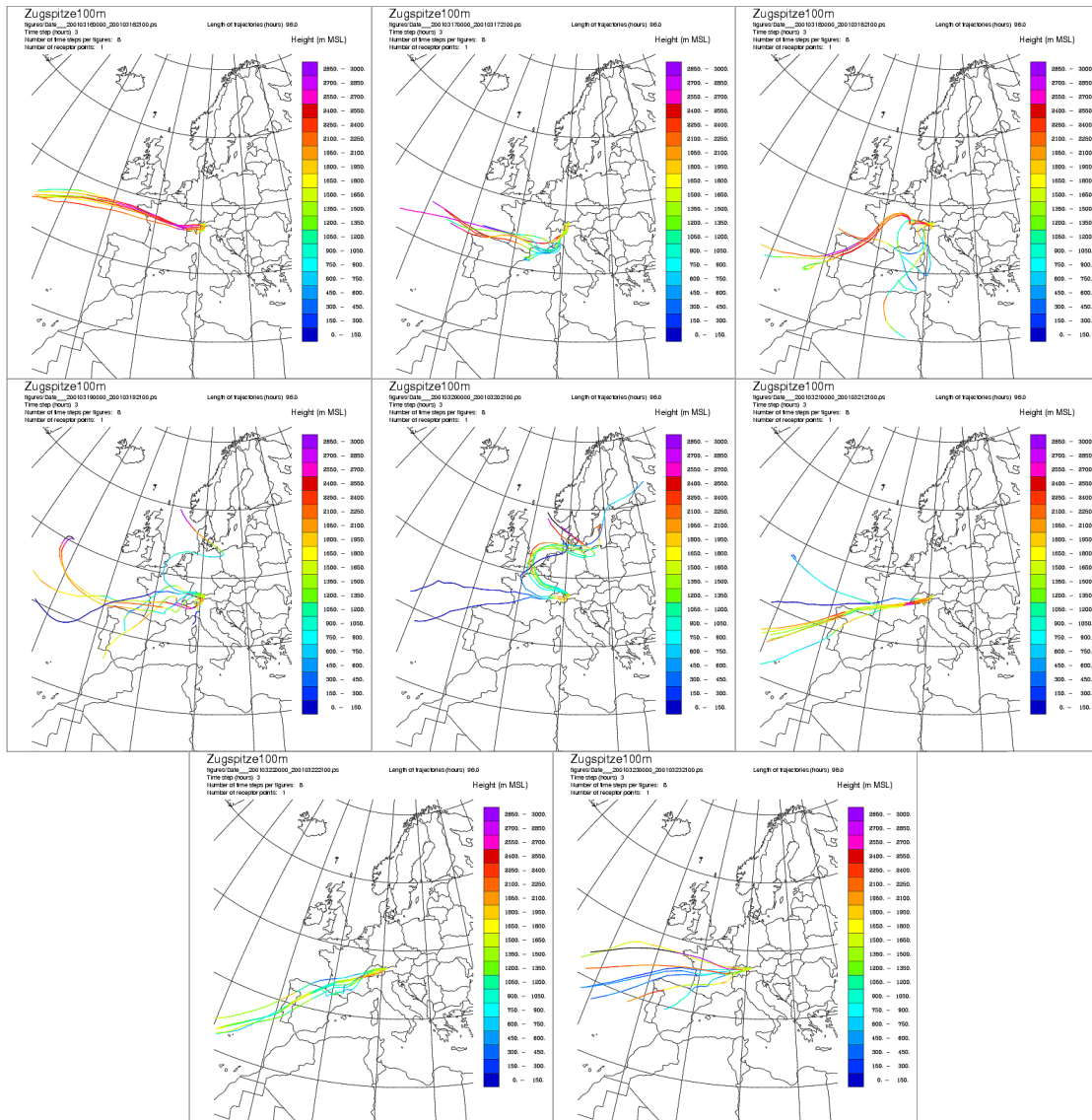


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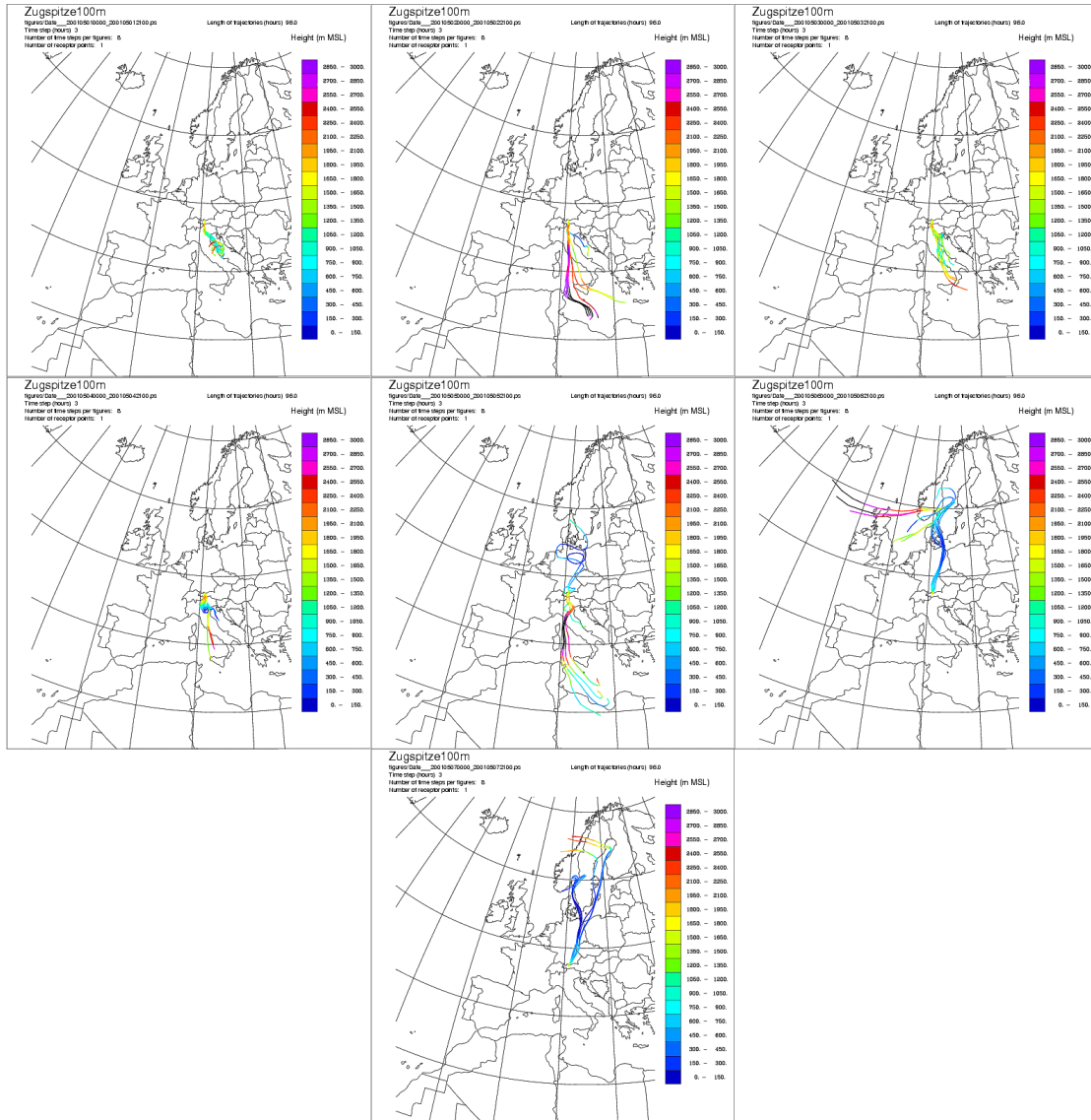


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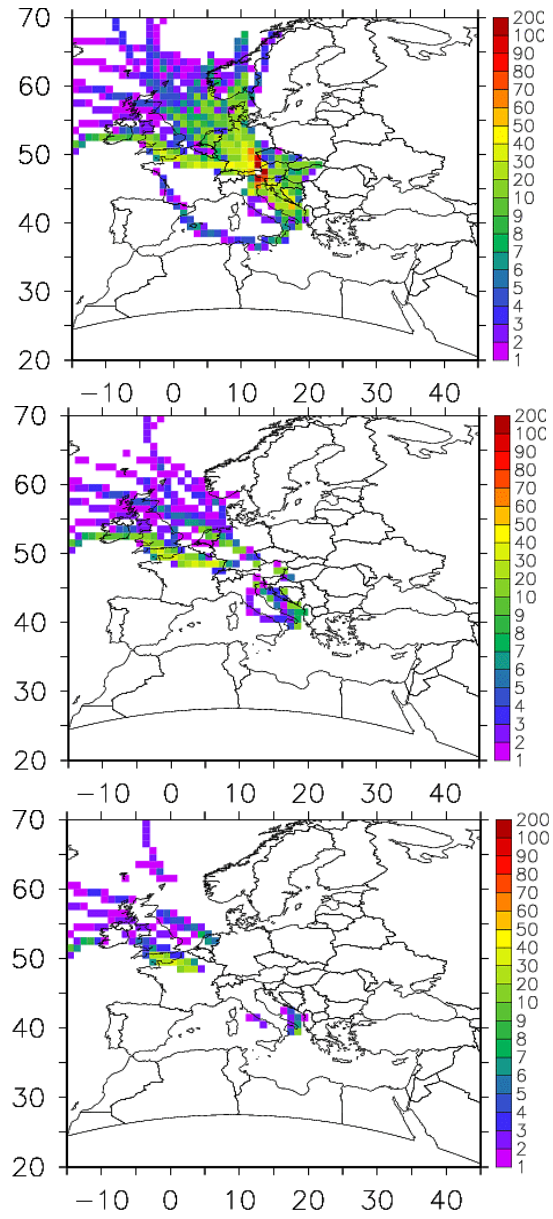


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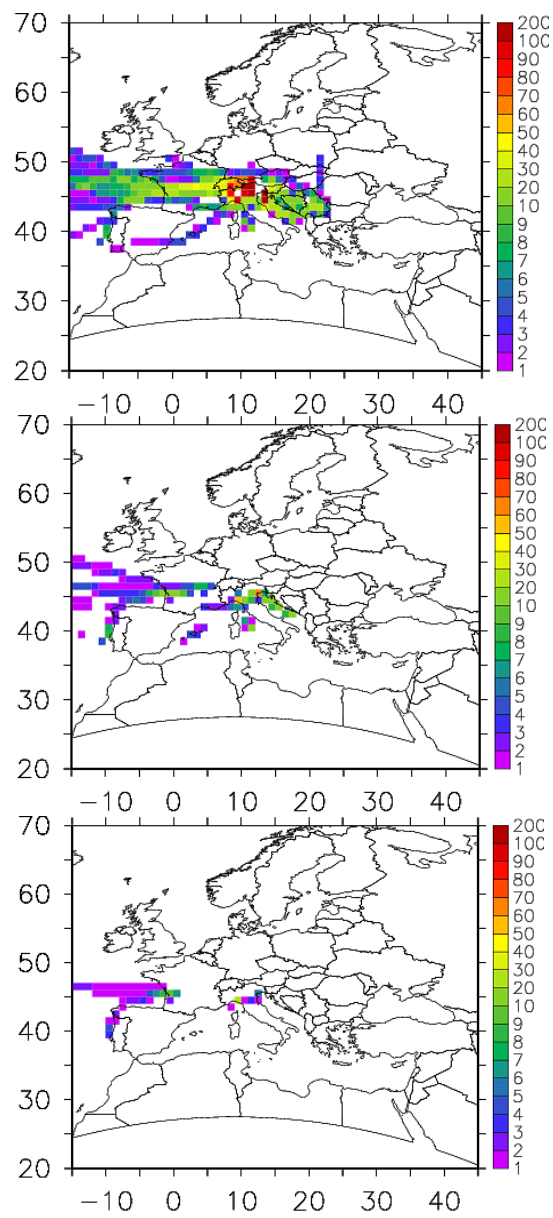


Fig. S-5 b

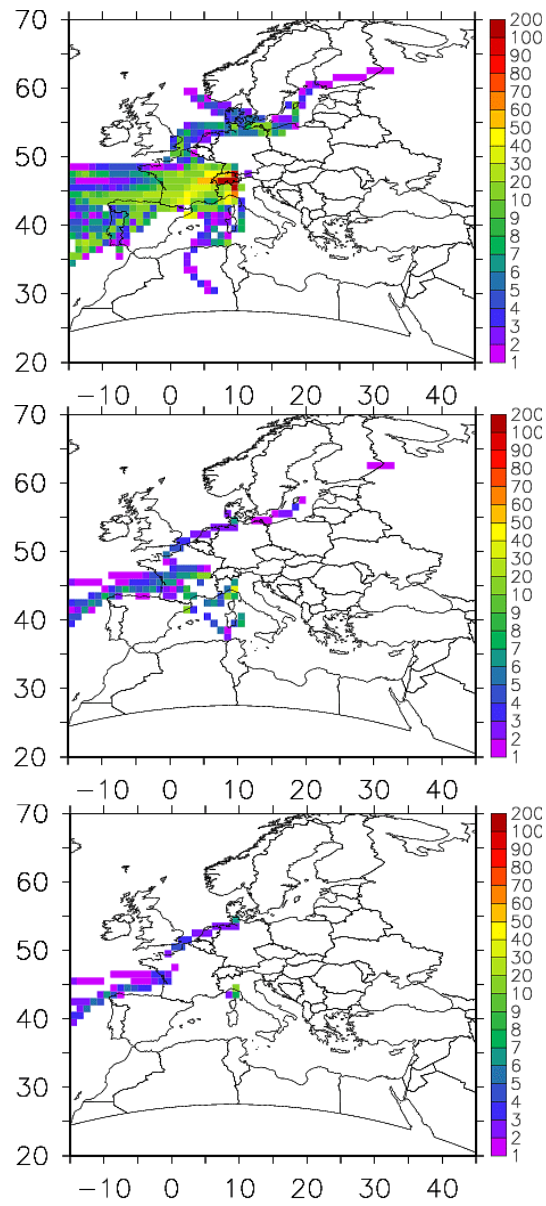


Fig. S-6 a

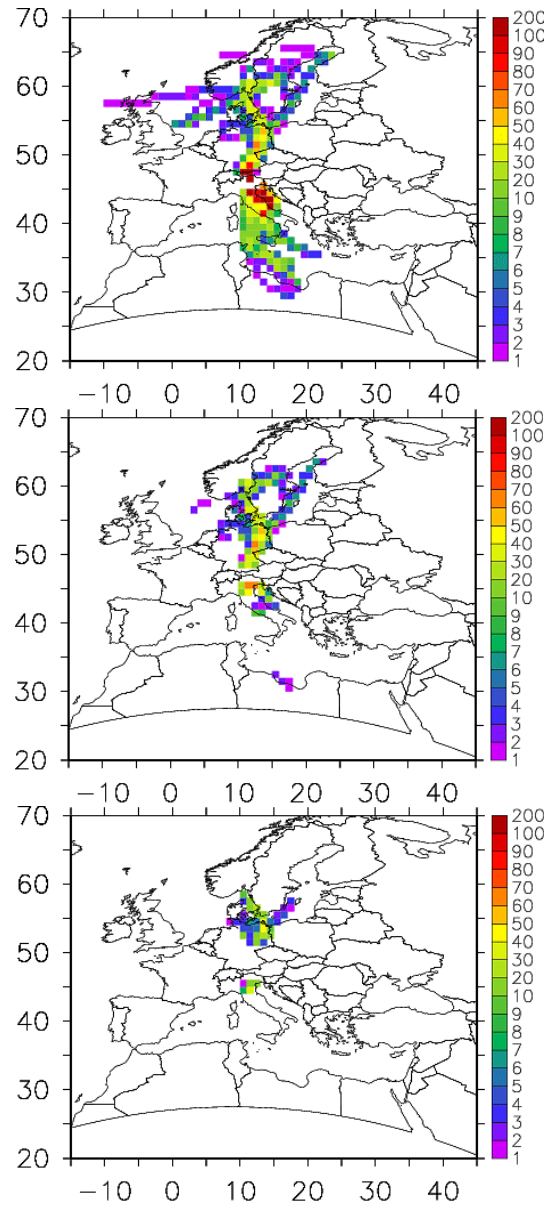


Fig. S-6 b