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ARTICLE *in* ENVIRONMENTAL SCIENCE & TECHNOLOGY · SEPTEMBER 2013

Impact Factor: 5.33 · DOI: 10.1021/es401973c · Source: PubMed

Environmental Science & Technology

Article

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Size Distributions of Airborne Radionuclides from the Fukushima Nuclear Accident at Several Places in Europe

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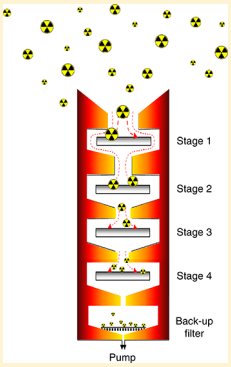
Supporting Information

ABSTRACT: Segregation and radioactive analysis of aerosols according to their aerodynamic size were performed in France, Austria, the Czech Republic, Poland, Germany, and Greece after the arrival of contaminated air masses following the nuclear accident at the Fukushima Dai-ichi nuclear power plant in March 2011. On the whole and regardless of the location, the highest activity levels correspond either to the finest particle fraction or to the upper size class. Regarding anthropogenic radionuclides, the activity median aerodynamic diameter (AMAD) ranged between 0.25 and 0.71 μm for ^{137}Cs, from 0.17 to 0.69 μm for ^{134}Cs, and from 0.30 to 0.53 μm for ^{131}I, thus in the "accumulation mode" of the ambient aerosol (0.1−1 μm). AMAD obtained for the naturally occurring radionuclides ^{7}Be and ^{210}Pb ranged from 0.20 to 0.53 μm and 0.29 to 0.52 μm, respectively. Regarding spatial variations, AMADs did not show large differences from place to place compared with what was observed concerning bulk airborne levels registered on the European scale. When air masses arrived in Europe, AMADs for ^{131}I were about half those for cesium isotopes. Higher AMAD for cesium probably results from higher AMAD observed at the early stage of the accident in Japan. Lower AMAD for ^{131}I can be explained by the adsorption of gaseous iodine on particles of all sizes met during transport, especially for small particles. Additionally, weathering conditions (rain) encountered during transport and in Europe in March and April contributed to the equilibrium of the gaseous to total ^{131}I ratio. AMAD slightly increased with time for ^{131}I whereas a clear decreasing trend was observed with the AMADs for ^{137}Cs and ^{134}Cs. On average, the associated geometric standard deviation (GSD) appeared to be higher for iodine than for cesium isotopes. These statements also bear out a gaseous ^{131}I transfer on ambient particles of a broad size range during transport. Highest weighted activity levels were found on the 0.49−0.95 μm and on the 0.18−0.36 μm size ranges in France and in Poland, respectively. The contribution from resuspension of old deposited ^{137}Cs was assessed for the coarse particle fractions only for the first sampling week.



INTRODUCTION

The accident that occurred at the Fukushima Dai-ichi nuclear power plant (FDNPP) following the earthquake and the tsunami on March 11, 2011 released a huge amount of radionuclides in the atmosphere. Among them, ^{134}Cs, ^{137}Cs (half-lives of 2.06 y and 30.17 y, respectively) and ^{131}I (half-life of 8.02 d) are of great concern for long- and short-term exposure, respectively. They were transported in the global atmosphere in the particulate form. Iodine-131 was also found in a gaseous form that accounted for most of the total (gaseous + particulate) ^{131}I throughout the world. Close to the damaged reactors (according to the daily measurements performed by the plant operator TEPCO[1] between March 19 and April 4), this gas to total ratio ranged between 53 and 99% with an average of 71%. This percentage varied from 52 to 71% in

Received: May 7, 2013
Revised: August 21, 2013
Accepted: September 3, 2013
Published: September 3, 2013

Chiba City[2] (220 km SSE from FDNPP) and from 30 to 67% in Fukuoka[3] (1000 km west to the FDNPP). Gaseous iodine predominance was found far from Japan: 77−81% in the U.S.A.,[4,5] 50−81% in Austria, [6] 77% in Greece[7] and the same, on average, on the European-wide scale.[8] After about 10 days following the beginning of the releases, contaminated air masses reached Europe and yielded to an unusual airborne concentration for 2−3 weeks,[8] even if this was of no concern for public health thanks to atmospheric dispersion and deposition along the route from Japan.

Rather few studies deal with the size distribution of airborne radionuclides in the environment in accident conditions. Most of them were published after the Chernobyl accident[9−12] (among others). It is generally considered that at some distance, the size distribution of the released radionuclides follows the size distribution of the ambient aerosol, i.e., belongs to the "accumulation mode" (0.1−1 μm). However, little is known about the size distributions of the volatile radionuclides that exist both under gaseous and particulate form with a possible transfer from one form to the other. This is especially the case for ^{131}I owing to its short half-life. The size distribution is of great concern when dealing with the subsequent ability of radionuclide-labeled aerosols to enter the respiratory tract and the aftermath dose calculation.

The aim of this study is to gather existing information on the European scale in order to characterize the aerosol distributions and the most radioactive aerosol sizes, especially for ^{131}I. The subsequent goal is to highlight and explain possible time and space variations in the size distributions of the Fukushima-labeled aerosols soon after the accident. According to the literature review dedicated to the FDNPP accident, few experimental determinations of the size distribution of the released radionuclides have been reported, three in Europe[6,13,14] and four in Japan: in Tokyo,[15] 220 km WSW; in Tsukuba,[16,17] 150−170 km SSW and in Fukushima city,[18] 60 km NW, respectively, from the FDNPP. An inhalation dose reduction effect for people that wore face masks against pollen allergies was attested.[15] This trial was conducted from 15 to 16 March 2011, when contaminated air masses were blowing over Tokyo and Ibaraki prefecture and when there were a lot of Japanese cedar pollens in the air. It was found that wearing a mask able to efficiently trap (99.6%) particles with an aerodynamic diameter (AD) > 3 μm reduced the inhalation of almost all of the ^{137}Cs and 35% of the particulate ^{131}I. [15] Japanese cedar produces pollen of some tens of micrometers and thus it can be supposed that ^{137}Cs-labeled aerosols were attached to cedar pollen of big sizes. Doi et al.[17] found an activity median aerodynamic diameter (AMAD) of 0.7 μm for ^{131}I whereas the AMAD was higher regarding cesium isotopes: 1.8−1.0 μm for ^{134}Cs-labeled particles and 1.5−1.0 for ^{137}Cs-labeled particles. Kaneyasu et al.[16] showed that the mass distribution of chemical pollution aerosols (sulfate aerosols) matches the ^{137}Cs distribution with a similar maximum on the "0.49−0.7 μm" stage and thus non-sea-salt sulfate could potentially act as a carrier for ^{137}Cs at that time. Koizumi et al.[18] found that 74% of the ^{134}Cs and 81% of the ^{137}Cs were attached to particles with an AD < 0.49 μm. A bimodal distribution,[13] obtained from the values reported in the Koizumi's study,[18] shows evidence of a weak contribution of resuspended ^{137}Cs attached to coarse particles three months after the accident and an AMAD of about 0.5 μm for the smaller mode. This last value was close to the value measured in the Czech Republic shortly after the Fukushima accident.[13] The same authors have also shown that the size distributions of the Fukushima-labeled aerosols observed in the Czech Republic were similar to those registered locally after the Chernobyl accident.[13]

SAMPLING AND MEASUREMENTS

Specific samplings were taken in France (Cadarache), Austria (Linz), Czech Republic (Prague), Poland (Lodz), Germany (Munich) and Greece (Athens) (Supporting Information Figure SI-1) using different cascade impactors (Andersen or Berner type). All in all, at least one impactor was operating from March 22 until April 26, 2011. The impactor model, the flow rate and the cutoff points are summarized in Supporting Information Table SI-1. Collection substrates and back-up filters used with high volume impactors (HVI) were made of quartz or glass-fiber, whereas cellulose-based or aluminum foil substrates and filters were used with low volume impactors (LVI). All sampling sites were located at lowland altitudes, between 200 and 500 m above sea level (a.s.l.). Sampling durations were about one to two weeks and the starting date of sampling differs according to sites (Supporting Information Table SI-2).

For each sampling site, collection substrates and back-up filters were analyzed by gamma spectrometry. Conventional or well-type detectors, in all cases low-level, low-background high purity Germanium (HPGe) detectors were used. Counting times were extended from 80 000 s to 600 000 s. More details regarding sampling and measurement conditions applied in the Czech Republic, in Poland and in Greece can be found in references 13, 14 and 19, respectively. A coincidence summing correction (also called peak sum correction) was applied for the ^{134}Cs determination.[20] The nonconsideration of this correction for ^{134}Cs can lead to differences 15% less using a conventional detector and up to a bias factor of 3 when using a well-type detector due to its very high detection efficiency.

COMPUTATION METHOD

Beside the size distribution of airborne activity levels, the results are expressed in terms of the activity median aerodynamic diameter (AMAD) and the associated geometric standard deviation (GSD), in order to get an all-encompassing idea of the most contributing size fraction. By default, this computation assumes a log-normal distribution according to the aerodynamic diameter (AD). The AMAD is defined so that 50% of the activity bound to aerosols belongs to particles with ADs larger than AMAD and the remaining 50% to ADs lower than the AMAD. Relevance of the log-normal distribution can be concluded if a high cumulative percentage of the total activity is well adjusted by a log-normal law. As a matter of common sense, it can be estimated that when this corresponds to at least 90%, this requirement is fulfilled. Several more or less sophisticated methods ("inverse" methods) can be used to check the log-normal adjustment but it was found that the Probit method or its equivalent Henry law adjustment is valid to compute AMAD and GSD values.[21] The same authors also pointed out the negative effect of results having a high level of uncertainty. Most of the 86 gamma spectrometry results were determined above detection limits (DL): 67% for ^{134}Cs, 75% for ^{137}Cs, 85% for ^{131}I, and 100% for ^{7}Be and ^{210}Pb. The AMAD determination requires having the most complete size distribution. For this purpose, missing ^{134}Cs values (i.e., values < DL) were estimated using ^{137}Cs levels significantly

determined on the same sample and a $^{134}Cs/^{137}Cs$ average ratio based on significant pairs of results (see next section). This can be considered as the best estimate. When the ^{137}Cs result was lower than the DL, its value was estimated by taking half of the DL value.[22]

RESULTS

Airborne levels lower than DLs were mainly obtained for coarse particles. Generally speaking, such particles are not expected to be suspended for a long time or travel over long distances but produced close to where they are sampled. Lastly, for a given mass of particles, the surface exchange is naturally lower when considering a big particle than for a small one. Thus, the chance for the biggest particles (typically with AD > 3 μm) to carry a significant part of the emitted radionuclides was poor regarding the distance from Japan. The average percentage of activity supported by particles with an AD > 3 μm ranged between less than 1% to a few percent of the total, for both cesium isotopes. ^{131}I was slightly better distributed over the whole size range since up to 10% of the total activity was found for particles with an AD > 3 μm. Conversely, for all locations and all sampling periods, at least 75% of the total activity of both cesium isotopes and ^{131}I were found on the small particles, i.e., having an AD < 1 μm. For radionuclides of natural origin (i.e., ^{7}Be, ^{210}Pb, ^{228}Ac, ^{234}Th) the coarse fractions were associated with 7−35% of their respective total activity. Typical differential size distributions of ^{137}Cs, ^{134}Cs and ^{131}I obtained in Linz, Austria are shown for example (Figure 1). Depending on the location,

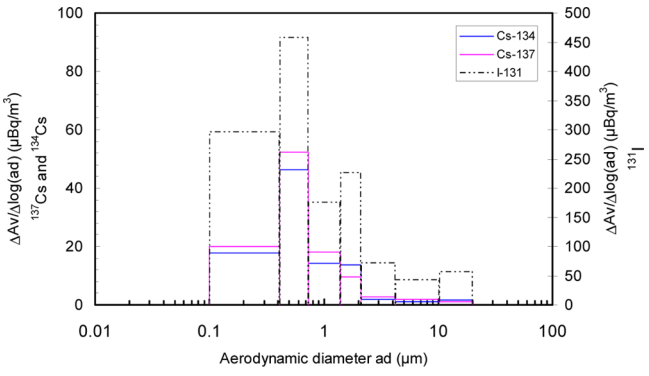


Figure 1. Typical size distribution of ^{134}Cs, ^{137}Cs and particulate ^{131}I. Results for Linz, Austria from March 31 to April 11, 2011.

the highest activity level was found either on the back-up filter (i.e., the smallest size fraction) or on the stage located just above it (Supporting Information Table SI-1) depending on the lower and upper bounds of the considered stages, but in all cases refers to the fine fractions.

^{137}Cs has a particular status since it was already measurable at ultratrace airborne levels in Europe before the FDNPP accident. The presence of "old" ^{137}Cs can be ascribed to its rather long half-life (30.17 y.) and physical processes like resuspension of soil particles and emission of flying ashes from sporadic or seasonal biomass burnings; both carrying some traces of ^{137}Cs originating from former deposits (global fallout from atmospheric nuclear weapon tests and Chernobyl fallout). Before the FDNPP accident, average ^{137}Cs levels were typically of 1 μBq m^{-3} in Central Europe[23] and lower average values (<0.3 μBq m^{-3}) were characteristic of northern,[24] western and southern Europe.[25] Those levels depended both on the location and meteorological conditions, as well as the deposition received especially after the Chernobyl accident according to the course of the radioactive plume and the rains that occurred at the same time. During the passage of contaminated air masses from Fukushima, airborne ^{137}Cs levels were globally enhanced by 2 to 3 orders of magnitude.[8] Conversely, ^{134}Cs had not been measured in the atmosphere since the middle of the 1990s due to its fairly short half-life of 2.06 years. Generally speaking, the $^{134}Cs/^{137}Cs$ ratio found in the air in Japan[3,26] or at worldwide scale after the dissemination of the Fukushima releases, was considered as close to 1 and in accordance with the source term assessment,[27] (among others). A more precise determination is available through all the European bulk aerosol data[8] with an average of 0.95. For the present study, an average $^{134}Cs/^{137}Cs$ ratio of 0.92 ± 0.01, consistent with the previous "bulk aerosol" value, was obtained from significant pairs of cesium data (Figure 2). As a first estimate, it can be assumed that this ratio also stands for the size stages on which only ^{137}Cs was quantified above the DL (see Computation Method). It can be seen that this ratio seems rather constant whatever the location and the size range considered. Data for Greece yield to a lower ratio on certain stages that can be ascribed to a more intense local resuspension of "old" ^{137}Cs.

Even if the size distributions observed in Europe after the Fukushima accident reflect the FDNPP releases, it is interesting to check if a contribution of "old ^{137}Cs" on certain size stages is possible, especially for coarse particles. This may be partly attributed to local resuspension, i.e., resuspension of ^{137}Cs deposited by global fallout and after the Chernobyl accident. For this purpose we used a specific ^{137}Cs reference size distribution obtained in the south of France in July 2010. Care was taken to check that during this period no intrusion of desert dust occurred. It is known that such high dusty events are prone to convey soil particles, labeled with ^{137}Cs traces originating from global fallout.[28−30] Since large amounts of particles are transported during such events, this can easily lead to increased airborne activity levels. This trial was conducted using six HVIs simultaneously, equipped with 5 + 1 stages, for a two-week sampling period. The overall flow rate was around 430 m^3/h. Thanks to the high volume of sampled air (~92400 m^3) and very sensitive measurements, reference activity levels of 14, 13, 8, 10, and 14 nBq m^{-3} for stages 1, 2, 3, 4 and 5, respectively plus a detection limit of 45 nBq m^{-3} for the back-up filter, were obtained. The resulting total activity level was thus at least 0.059 μBq m^{-3} and at most 0.104 μBq m^{-3} and in accordance with the lowest values obtained locally during a one-year bulk aerosol monitoring. This attempt also assumes that during sampling, resuspension of freshly deposited Fukushima-labeled ^{137}Cs can be neglected. This assumption holds since the cumulative ^{137}Cs deposition from Fukushima in Europe was of the order of 1 Bq m^{-2} on soils still having some hundreds to thousands Bq m^{-2}. The ratio between the "old ^{137}Cs" levels to those obtained when air masses reached Europe shows that this past contribution could still represent up to 45% for the coarse particles during the first sampling period (March, 22−27) when the ambient ^{137}Cs airborne level was 2.5 μBq m^{-3} on average and not more than 5% at most for the coarse particles (>7.2 μm) during the second sampling period (March 27 to April 4) when the average ambient level had increased by a factor of 10 (Figure 3). Conversely, for both periods, the contribution of resuspended "old ^{137}Cs" on particle sizes ranging from less than 0.49 to 1.5 μm is almost negligible (0.7 to 3% of the total ^{137}Cs). In Japan, this "old ^{137}Cs" contribution

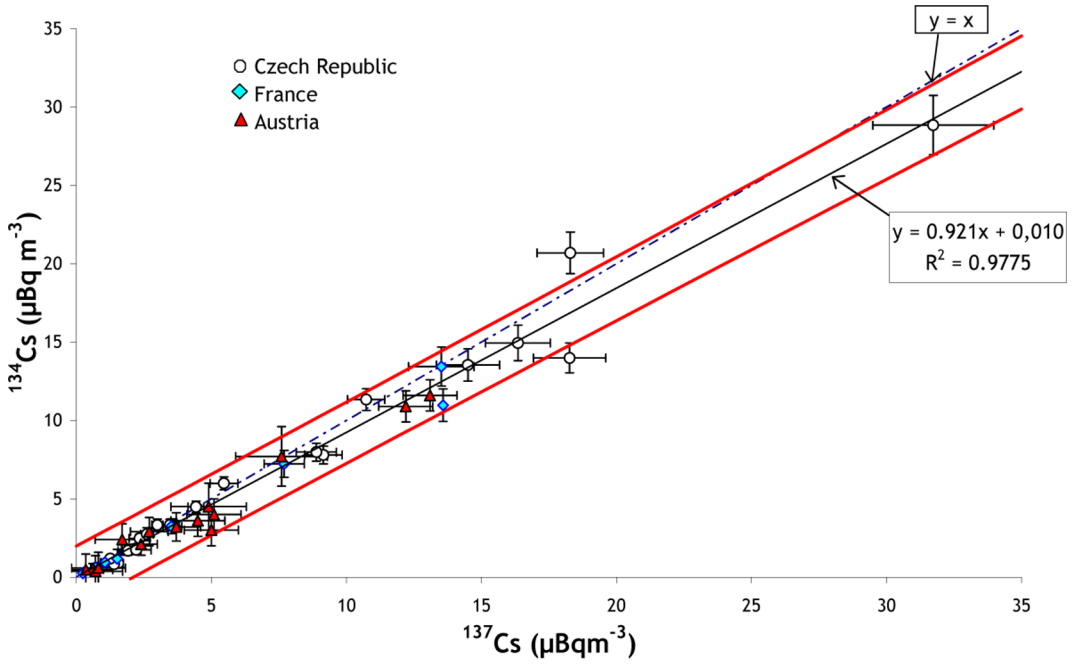


Figure 2. ^{134}Cs vs ^{137}Cs from aerosol size segregated results. The linear fit with its 95% confidence band is delimited in red.

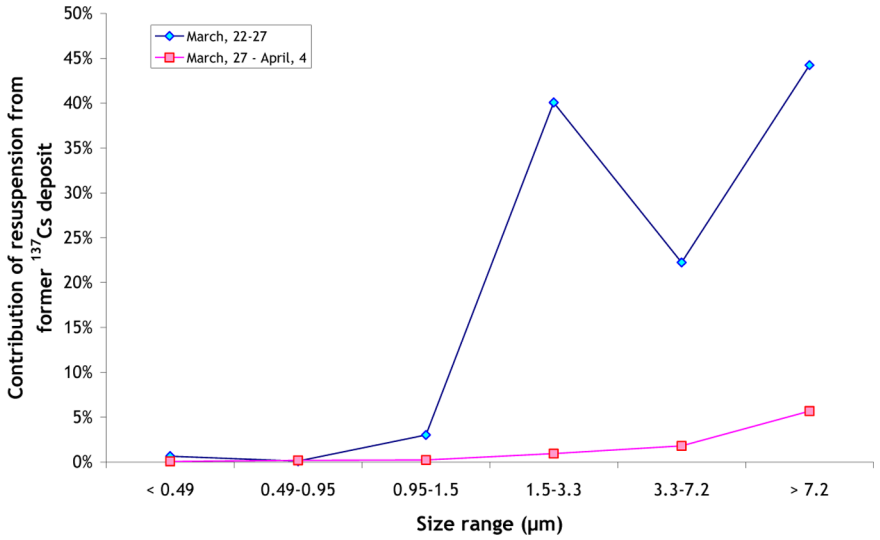


Figure 3. Contribution of the resuspension of "old" ^{137}Cs to the ^{137}Cs size distribution in France during the first two weeks after the arrival of the Fukushima-labeled air masses.

was estimated to be less than one percent.[26] Using the ^{134}Cs results as representative of the Fukushima-labeled ^{137}Cs ("fresh ^{137}Cs"), it can be stated that the released particulate radionuclides did not correspond to the coarse fractions of aerosols sampled in Europe but were mainly transported on the fine fractions.

AMADs for ^{134}Cs and ^{137}Cs in Europe ranged from 0.17 to 0.69 μm and from 0.25 to 0.71 μm, respectively (Table 1 and Figure 4). The associated GSDs were ranging from 1.2 to 4.9 μm. Due to a likely contribution of "pre-Fukushima" resuspended ^{137}Cs as well as high uncertainties found on certain stages, AMADs for cesium isotopes were not computed for the samples taken in Greece as being representative of the Fukushima releases.

^{131}I also has a particular status due to its coexistence under particulate and gaseous forms. Similarly to what was noticed after the Chernobyl accident,[31] in Europe and in Japan,[32] ^{131}I was also predominantly found under gaseous form on a worldwide scale after the Fukushima accident (see Introduction). Regarding the particulate form, the highest contributions (in %) of the total airborne level were found on average on the back-up filters and represented around 60% for AD < ~0.5 μm. Thanks to the LVI used in Poland[14] and in Germany, around 45% and 63% of the airborne particulate ^{131}I activity belonged to the particles with AD < 0.3 μm, respectively. AMADs for ^{131}I in Europe were ranging from 0.30 to 0.53 μm with an average of 0.39 μm (Table 1). Over the studied period, this is 15% less on average than for cesium isotopes. The associated geometric standard deviation (GSD) was 20% higher on average than for cesium isotopes. This shows that the distribution of iodine was more uniform over a wider range of particle sizes than for cesium isotopes, as already depicted.[14] This was also noticed in

Table 1. AMAD and GSD for Airborne Radionuclides in Europe after the Arrival of Air Masses Labeled by the FDNPP Atmospheric Releases in Comparison with Data from Japan

		^{134}Cs		^{137}Cs		^{131}I		^{210}Pb		^{7}Be		^{234}Th		^{228}Ac	
sampling location	sampling period	AMAD	GSD	AMAD	GSD	AMAD	GSD	AMAD	GSD	AMAD	GSD	AMAD	GSD	AMAD	GSD
Cadarache, France	22 - 27 March	0.64	1.22	0.64	1.23	[a]	[a]	0.29	3.37	0.39	2.99	3.24	2.71	3.48	2.98
	27 March -4 April	0.42	2.73	0.44	2.71	0.30	4.16	0.41	2.81	0.52	2.93	[a]	[a]	[a]	[a]
Linz, Austria[6]	31 March −11 April	0.38	3.75	0.39	3.59	0.42	5.27	0.52	5.51	0.43	3.47	2.38	3.51	2.57	3.31
	11 April −18 April	0.37	3.76	0.34	4.27	0.39	4.97	0.39	5.32	0.41	3.37	2.36	3.86	2.40	3.95
	18 April −26 April	0.48	4.83	0.44	4.91	[a]	[a]	0.19	4.93	0.27	3.42	1.70	4.35	1.40	6.44
Lodz, Poland[14]	30 March −5 April	[a]	[a]	[a]	[a]	0.34	9.1	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]
Prague, Czech Republic[13]	24 - 27 March	0.69	3.10	0.48	4.26	0.38	3.55	[a]	[a]	0.53	2.63	[a]	[a]	[a]	[a]
	27 - 30 March	0.66	2.56	0.71	2.32	0.36	3.33	[a]	[a]	0.45	2.69	[a]	[a]	[a]	[a]
	30 March -3 April	0.36	4.64	0.41	4.20	0.35	3.81	[a]	[a]	0.44	3.17	[a]	[a]	[a]	[a]
	3 - 8 April	0.25	3.74	0.31	3.48	0.47	3.35	[a]	[a]	0.34	3.29	[a]	[a]	[a]	[a]
	8 - 13 April	0.17	4.00	0.27	4.27	0.53	3.45	[a]	[a]	0.28	3.29	[a]	[a]	[a]	[a]
Munich, Germany	28−31 March	[a]	[a]	[a]	[a]	0.42	2.18	[a]	[a]	0.61	2.01	[a]	[a]	[a]	[a]
	31 March -4 April	[a]	[a]	[a]	[a]	0.45	2.95	[a]	[a]	0.45	2.32	[a]	[a]	[a]	[a]
	4−11 April	[a]	[a]	0.33	2.67	0.33	2.59	[a]	[a]	0.43	1.99	[a]	[a]	[a]	[a]
Athens, Greece	6 - 7 April	[a]	[a]	[a]	[a]	0.49	2.50	[a]	[a]	0.66	2.30	[a]	[a]	[a]	[a]
	13 - 14 April	[a]	[a]	[a]	[a]	0.43	2.60	[a]	[a]	0.50	2.40	[a]	[a]	[a]	[a]
Tsukuba, Japan[16]	28 April -12 May	0.54	1.4	0.53	1.4	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]
	12 - 26 May	0.63	1.4	0.63	1.4	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]
Tsukuba, Japan[17]	4 - 11 April	1.8	*	1.5	[a]	0.7	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]
	14 − 21 April	1.0	[a]	1.0	[a]	0.7	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]
Fukushima Pref.[18]	2 - 8 July	0.52	1.52	0.48	1.57	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]

[a]Not determined.

Japan after the Chernobyl accident since the ^{131}I size distribution did not obey to a log-normal distribution.[32]

DISCUSSION

The time variation of AMAD for a given radionuclide was more pronounced than its variation from place to place (Figure 4). This statement makes it possible to draw a synthetic spatially averaged time trend on the European scale (Figure 5). Differences of AMAD for cesiums and iodine were most pronounced when air masses arrived at the sampling locations in Europe. Cs-bearing particles sampled in Japan at different intervals after the initial release make possible the following scenario: at the early stage of the accident, when air masses blew toward Tokyo on March 15, 2011, spherical ^{137}Cs-bearing particles were found with a diameter up to 2.6 μm.[33] From April 4 to 11, AMADs for ^{134}Cs and ^{137}Cs-bearing particles were 1.8 and 1.5 μm, respectively, while they decreased down to 1.0 μm for both isotopes from April 11 to 21.[17] According to Doi et al.[17] such AMADs could still be representative of hot particles. From April 28 to May 26, an AMAD of 0.53 to 0.63 μm was mostly found for ^{137}Cs-bearing particles that were assumed to be sulfate aerosol.[16] On the basis of these statements, it can be supposed that the higher AMADs for cesium-bearing particles when air masses reached Europe resulted from the higher AMADs initially found in Japan. The same assumption holds for the decreasing time trend observed in Japan and the decreasing time trend in Europe, the only difference being the lower starting value in the case of Europe due to the loss of the biggest particles during transport. The decrease observed for both cesium isotopes was also noticed for ^{7}Be (Figure 5). The AMAD decreasing trend for both cesium isotopes is also accompanied with an increase of their GSD (Figure 4, graphs A and B), at least during the first week after the arrival of the labeled air masses. This behavior and the likeness with ^{7}Be probably results from the removal effect induced by rain that occurred over Europe at that time.

For ^{131}I, AMADs found in Japan were smaller by a factor of 1.5 to 2.5 compared with AMAD for cesium-bearing particles observed at the same time.[17] Similar differences were noticed after the Chernobyl accident between ^{137}Cs aerosol carriers and more volatile radionuclides such as ^{131}I.[11,13] Differences of AMAD between cesium and iodine in Japan could thus be sufficient to explain the difference of AMAD in Europe even if in a less pronounced way. Due to its high volatility ^{131}I was largely emitted and observed under gaseous form in Japan.[17] Part of this ^{131}I gaseous fraction can adsorb onto particles, among them small particles, thus lowering the AMAD. From laboratory-scale experiments, it was shown that up to 5% (mass) of iodine in the air rapidly attached to particles over interaction periods ranging between 1 and 10 min.[34] The same author also found that most of the adsorbed iodine was found on submicronic particles. During transport, the gaseous form partly reacts with naturally present aerosols of all origins and sizes and part of the ^{131}I-labeled particles among them the

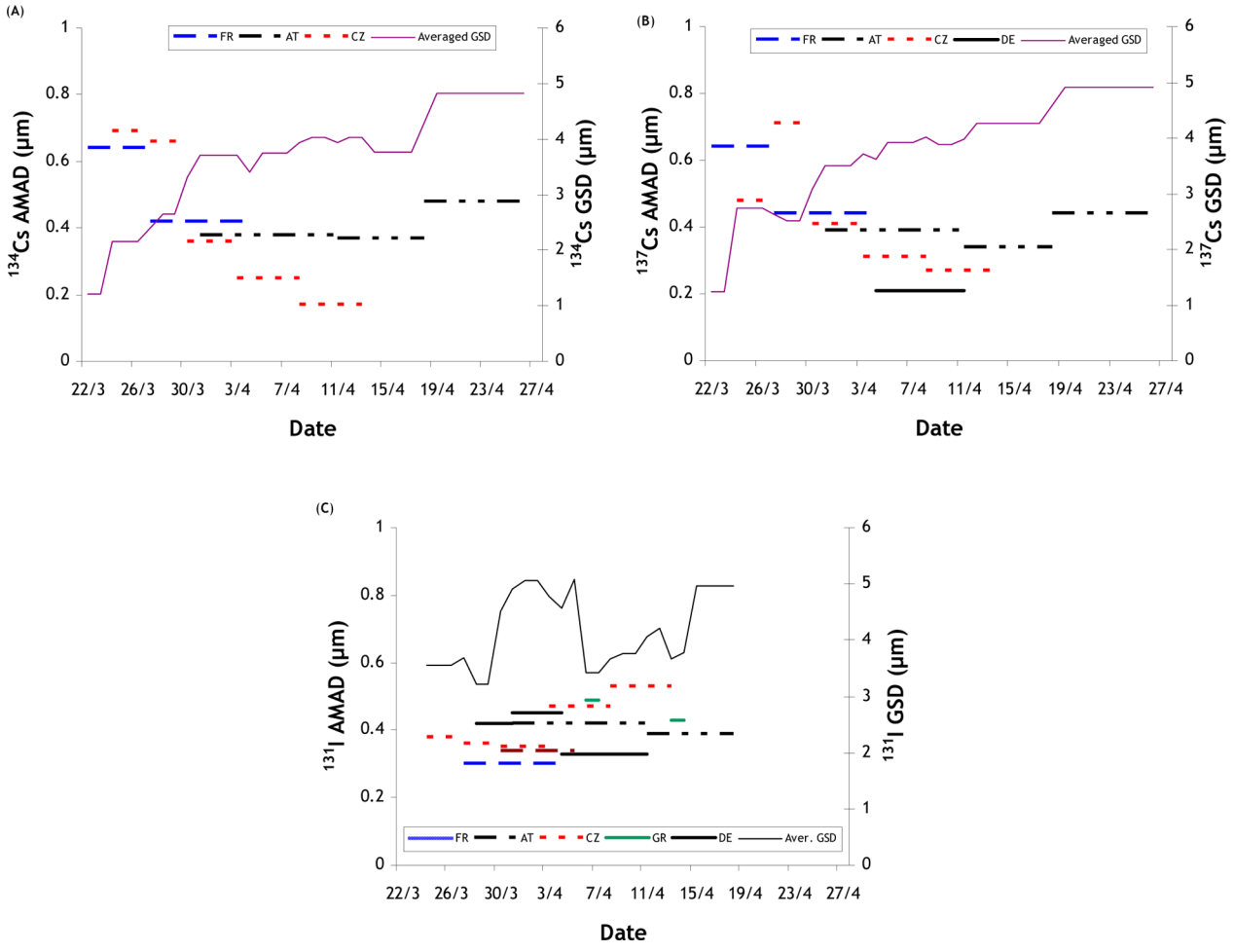


Figure 4. Time variation of AMAD and GSD of aerosols carrying ^{134}Cs (graph A), ^{137}Cs (graph B) and ^{131}I (graph C) in several European countries from March, 22 to April, 26 2011.

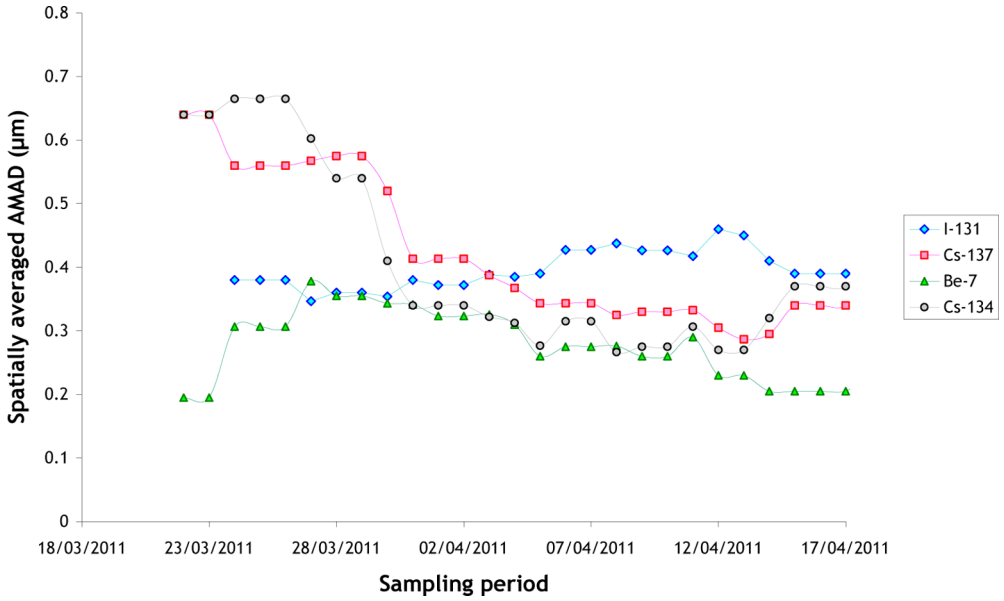


Figure 5. Time trends of spatially averaged AMAD for ^{134}Cs, ^{137}Cs, ^{131}I and ^{7}Be.

biggest may have been preferentially deposited while those in the range of the accumulation mode (0.1−1 μm) kept going. It is also known that after a certain residence time in the atmosphere, ultrafine particles no longer exist as they coalesce between them to form larger particles or grow due to vapor condensation. This can thus indicate why the finest particles

dx.doi.org/10.1021/es401973c | Environ. Sci. Technol. 2013, 47, 10995−11003

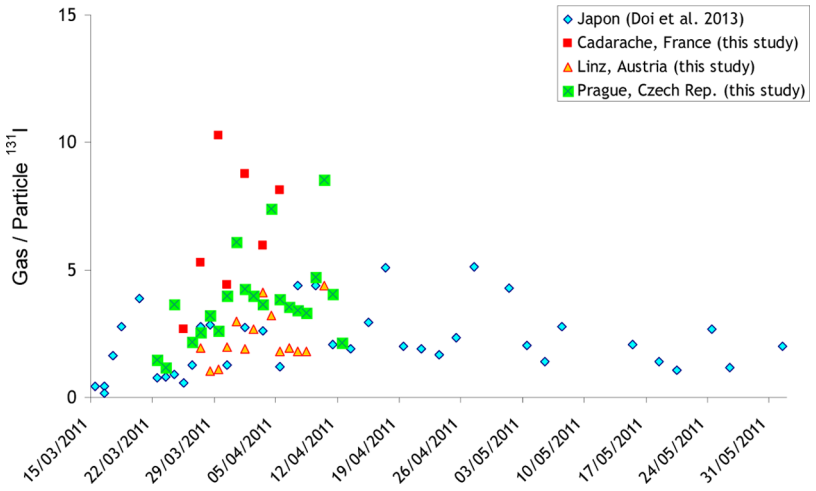


Figure 6. Time trends of the gas/particle ^{131}I ratio in Japan[17] and at the sampling locations depicted in this study.

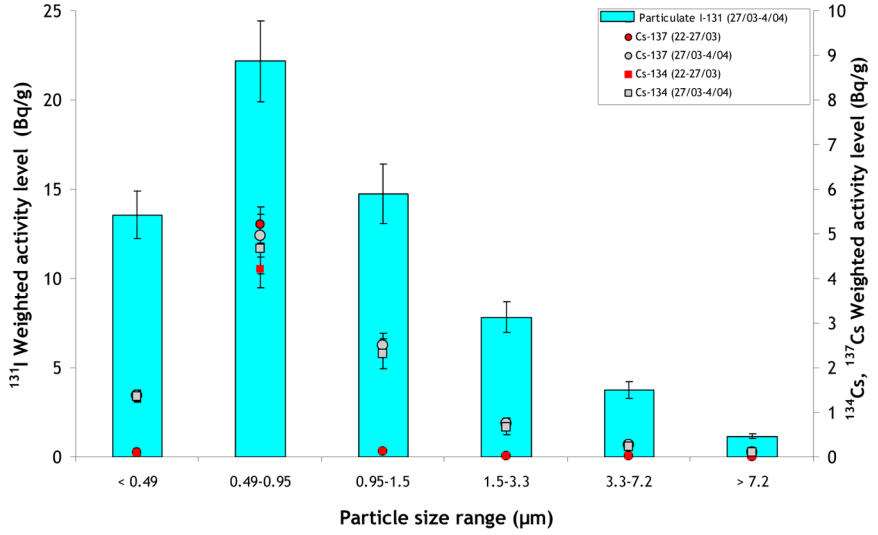


Figure 7. Size distribution of the weighted activity levels for ^{131}I (left *y*-axis) and ^{134,137}Cs (right *y*-axis) in France. Error bars correspond to expanded uncertainties (k = 2).

that have adsorbed gaseous iodine close to the FDNPP or soon after the releases may not correspond necessarily to the finest ones labeled with ^{131}I in Europe. Comparison of the gas-to-particle ^{131}I ratio in Japan and at the European sampling locations used in this study shows an increasing trend that probably results from the particulate iodine removal during transport and at the sampling locations, by dry and wet deposition processes (to which particles are very sensitive) and the previously mentioned gas-to-particle attachment (Figure 6).

Despite a slow possible desorption, a large proportion is expected to remain in the vapor phase at equilibrium. From *in situ* measurements, a "gas-to-particle" conversion time was estimated to be at least 12 days after the Chernobyl accident with a mean time of 2 to 3 weeks.[35] In our opinion this "gas-to-particle conversion" results mainly from the adsorption of gas on particles. After the Fukushima accident, a ^{131}I removal time varying between 17.1 to 24.2 days was found for a reasonably well-mixed aerosol.[36] The mean residence time for aerosols was estimated at 10 days from simultaneous measurements of ^{210}Po, ^{210}Pb and ^{210}Bi performed in Poland[14] in the period between end of March and beginning of April. Larger aerosol residence or removal times for ^{131}I than for a purely aerosol-bound radionuclide such as ^{137}Cs, can be ascribed to the gaseous ^{131}I transfer that permanently produces ^{131}I-labeled aerosols. Newly ^{131}I-labeled aerosols thus increases the apparent residence time. All those time lapses match with the arrival time over Europe, thus signifying that this process had already started but was probably not completely finished when the air masses reached Europe. As time went by, the ^{131}I AMAD showed a slight increase or at least a constant trend. Moreover, the averaged GSD of aerosol carriers of ^{131}I is higher than that for cesium as a probable result of the adsorption of ^{131}I on particles of all sizes. Additionally, the difference of AMAD with time could reflect, even if minimized by homogenization during transport, the different release phases that were representative of different problems: scrubbing, melting, venting and explosion.

For ^{129}Te, the trial performed in France between March 27 and April 4 gave significant results for all stages of the HVI from which an AMAD of 0.44 μm and a GSD of 2.1 μm were computed. Regarding radionuclides of crustal origin determined in French and Austrian samples (see Table 1), larger AMADs were obtained for ^{234}Th (at least 1.7 and up to 3.2 μm) and ^{228}Ac (at least 1.4 and up to 3.5 μm); both radionuclides resulting from a more or less local suspension of particles

dx.doi.org/10.1021/es401973c | *Environ. Sci. Technol.* 2013, 47, 10995−11003

induced by wind erosion of soil surfaces and that produces coarse aerosols.

Weighted activity levels of the Fukushima-labeled aerosols can also provide some information regardless of the dust concentration. This was performed in France and in Poland (Figure 7). Higher weighted activity levels were found for the size fractions 0.49−0.95 μm in France and 0.18−0.36 μm in Poland. This information are complementary and differences in the size recovery area may result from the assembly of the collection substrates from Poland in the ranges 0.36−1.8 μm and 1.8−10 μm, before radioactive measurements. The maximum ^{131}I weighted activity levels were up to 22 and 15.5 Bq/g in France and in Poland, respectively. In France, weighted activity levels for cesium varied from 4.2 to 4.6 Bq/g for ^{134}Cs and 5 to 5.2 Bq/g for ^{137}Cs. In comparison, the averaged weighted ^{137}Cs activity level found in France over the 2000−2010 decade was 0.009 Bq/g. For cesium isotopes, the highest weighted activity levels found for the 0.49−0.95 μm fraction did not increase with time, whereas it was the case for smaller and bigger particles, between the first sampling period and the second one. At least for the French samplings, this explains why the GSD of the aerosol carriers of cesium isotopes increases with time. Unfortunately, the ^{131}I measurement for the first sampling period was performed too late according to the half-life period to give significant results.

In case of an accidental radioactive release into the atmosphere, it is highly recommended to perform such sampling and size distribution analysis as soon as possible after the release and especially at short and medium distances (i.e., in all cases before the aerosol carriers of radionuclides get so diluted that their size distribution becomes similar to that of ambient aerosols) and to maintain such analysis as long as possible. This will make the inhalation dose assessment more robust. It is also important to perform size distribution analysis in long-term post-accidental situations and in routine monitoring to determine the influence of resuspension of soil particles or ash emission in case of biomass burnings and to get reference values for such situations.

This study also highlights the need to develop a high volume impactor, to improve the chance of significant determinations, coupled with lower cutoff points than available for most of the current high volume impactors since the AMAD is regularly found outside the aerosol size range accessible through the size sorting.

■ ASSOCIATED CONTENT

Supporting Information

Two tables and one figure. Tables summarize theoretical cut-offs (μm) of equivalent aerodynamic diameter, according to the type of impactor and sampling conditions. The figure corresponds to the map of sampling locations. 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.

■ ACKNOWLEDGMENTS

Co-authors are thanked for their participation through data exchange, discussion about AMAD computation and their helpful comments. Reviewers are acknowledged for their relevant comments.

■ REFERENCES

(1) TEPCO. Monitoring measurements following the Fukushima Accident. www.tepco.co.jp/en/press/corp-com/release/index1103-e.html.

(2) Amano, H.; Akiyama, M.; Chunlei, B.; Kawamura, T.; Kishimoto, T.; Kuroda, T.; Muroi, T.; Odaira, T.; Ohta, Y.; Takeda, K.; Watanabe, Y.; Morimoto, T. Radiation measurements in the Chiba Metropolitan Area and radiological aspects of fallout from the Fukushima Dai-ichi Nuclear Power Plants accident. *J. Environ. Radioact.* **2012**, *111*, 42−52.

(3) Momoshima, N.; Sugihara, S.; Ichikawa, R.; Yokoyama, H. Atmospheric radionuclides transported to Fukuoka. Japan remote from the Fukushima Dai-ichi nuclear power complex following the nuclear accident. *J. Environ. Radioact.* **2012**, *111*, 28−32.

(4) Thakur, P.; Ballard, S.; Nelson, R. Radioactive fallout in the United States due to the Fukushima nuclear plant accident. *J. Environ. Monit.* **2012**, *14* (5), 1285−1492.

(5) Ten Hoeve, J. E.; Jacobson, M. Z. Worldwide health effects of the Fukushima Daiichi nuclear accident. *Energy Environ. Sci.* **2012**, *5*, 8743−8757.

(6) Ringer, W.; Klimstein, J.; Bernreiter, M. Long-term time series and activity size distribution of beryllium-7 in the atmospheric environment time series and activity size distribution of iodine-131 in Austria after the Fukushima NPP accident. *Radioprotection* **2011**, *46* (6), S7−S10.

(7) Potiriadis, C.; Kolovou, M.; Clouvas, A.; Xanthos, S. Environmental radioactivity measurements in Greece following the Fukushima Dai-ichi nuclear accident. *Radiat. Protect. Dosimetry* **2011**, *150* (4), 441−447.

(8) Masson, O.; Baeza, A.; Bieringer, J.; Brudecki., Bucci, S.; Cappai, M.; Carvalho, F. P.; Connan, O.; Cosma, C.; Dalheimer, A.; Didier, D.; Depuydt, G.; De Geer, L. E.; De Vismes, A.; Gini, L.; Groppi, F.; Gudnason, K.; Gurriaran, R.; Hainz, D.; Halldórsson, O.; Hammond, D.; Hanley, O.; Holey, K.; Homoki, Zs.; Ioannidou, A.; Isajenko, K.; Jankovic, M.; Katzlberger, C.; Kettunen, M.; Kierepko, R.; Kontro, R.; Kwakman, P. J. M.; Lecomte, M.; Leon Vintro, L.; Leppänen, A.-P.; Lind, B.; Lujaniene, G.; Mc Ginnity, P.; Mc Mahon, C.; Malá., H.; Manenti, S.; Manolopoulou, M.; Mattila., A.; Mauring., A.; Mietelski, J. W.; Møller, B.; Nielsen, S. P.; Nikolic, J.; Overwater, R. M. W.; Pálsson, S. E.; Papastefanou, C.; Penev, I.; Pham, M. K.; Povinec, P. P.; Ramebäck, H.; Reis, M. C.; Ringer, W.; Rodriguez, A.; Rulík, P.; Saey, P. R. J.; Samsonov, V.; Schlosser, C.; Sgorbati, G.; Silobritiene, B. V.; Söderström, C.; Sogni, R.; Solier, L.; Sonck, M.; Steinhauser, G.; Steinkopff, T.; Steinmann, P.; Stoulos, S.; Sýkora, I.; Todorovic, D.; Tooloutalaie, N.; Tositti, L.; Tschiersch, J.; Ugron, A.; Vagena, E.; Vargas, A.; Wershofen, H.; Zhukova, O. Tracking of Airborne Radionuclides from the Damaged Fukushima Dai-Ichi Nuclear Reactors by European Networks. *Environ. Sci. Technol.* **2011**, *45* (18), 7670−7677.

(9) Ooe, H.; Seki, R.; Ikeda, N. Particle-size distribution of fission products in airborne dust collected at Tsukuba from April to June 1986. *J. Environ. Radioact.* **1988**, *6*, 219−223.

(10) Reineking, A.; Becker, K. H.; Postendorfer, J.; Wicke, A. Air activity concentrations and particle size distributions of the Chernobyl aerosol. *Radiat. Protect. Dosimetry* **1987**, 159−163.

(11) Tschiersch, J.; Georgi, B. Chernobyl fallout size distribution in urban areas. *J. Aerosol Sci.* **1987**, *18*, 689−692.

(12) Dorrian, M.-D. Particle size distributions of radioactive aerosols in the environment. *Radiat. Protect. Dosimetry* **1997**, *69* (2), 117−132.

(13) Malá, H.; Rulík, P. Particle size distribution of radioactive aerosols after the Fukushima and Chernobyl accidents. *J. Environ. Radioact.* **2013**, *126C*, 92−98.

(14) Dlugosz-Lisiecka, M.; Bem, H. Aerosol residence times and changes in radioiodine-^{131}I and radiocaesium-^{137}Cs activity over Central Poland after the Fukushima-Daiichi nuclear reactor accident. *J. Environ. Monit.* **2012**, *14*, 1483−1489.
(15) Higaki, S.; Hirota, M.; Nogawa, N. The reductive effect of an anti-pollinosis mask against internal exposure from radioactive materials dispersed from the Fukushima Daiichi nuclear disaster. *Health Phys.* **2013**, *104* (2), 227−231.
(16) Kaneyasu, N.; Ohashi, H.; Suzuki, F.; Okuda, T.; Ikemori, F. Sulfate aerosol as a potential transport medium of radiocesium from the Fukushima nuclear accident. *Environ. Sci. Technol.* **2012**, *46*, 5720−5726.
(17) Doi, T.; Kazuyoshi, M.; Toyoda, A.; Tanaka, A.; Shibata, Y.; Hirose, K. Anthropogenic radionuclides in the atmosphere observed at Tsukuba: characteristics of the radionuclides derived from Fukushima. *J. Environ. Radioact.* **2013**, *122*, 55−62.
(18) Koizumi, A.; Harada, K. H.; Niisoe, T.; Adachi, A.; Fujii, Y.; Hitomi, T.; Kobayashi, H.; Wada, Y.; Watanabe, T.; Ishikawa, H. Preliminary assessment of ecological exposure of adult residents in Fukushima Prefecture to radioactive cesium through ingestion and inhalation. *Environ. Health Prev. Med.* **2012**, *17* (4), 292−298.
(19) Kritidis, P.; Florou, H.; Eleftheriadis, K.; Evangeliou, N.; Gini, M.; Sotiropoulou, M.; Diapouli, E.; Vratolis, S. Radioactive pollution in Athens, Greece due to the Fukushima nuclear accident. *J. Environ. Radioactivity* **2012**, *114*, 100−104.
(20) Sima, O.; Arnold, D. Accurate computation of coincidence summing corrections in low level gamma-ray spectrometry. *Applied Radiat. Isot.* **2000**, *53*, 51−56.
(21) O'Shaughnessy, P. T.; Raabe, O. G. A comparison of cascade impactor data reduction methods. *Aerosol Sci. Technol.* **2003**, *37*, 187−200.
(22) Hecht, H.; Honikel, K. O. Assessment of data sets containing considerable values below the detection limits. *Z. Lebensm.-Unters. Forsch.* **1995**, *201* (6), 592−597.
(23) Franić, Z.; Šega, K.; Petrinec, B.; Marović, G. Long-term investigations of post-Chernobyl radiocaesium in fallout and air in North Croatia. *Environ. Monit. Assess.* **2009**, *148*, 315−323.
(24) Lujaniene, G.; Aninkevicius, V.; Lujanas, V. Artificial radionuclides in the atmosphere over Lithuania. *J. Environ. Radioact.* **2009**, *100*, 108−119.
(25) Valles, I.; Camacho, A.; Ortega, X.; Serrano, I.; Blazquez, S.; Perez, S. Natural and anthropogenic radionuclides in airborne particulate samples collected in Barcelona (Spain). *J. Environ. Radioact.* **2009**, *100*, 102−107.
(26) Kanai, Y. Monitoring of aerosols in Tsukuba after Fukushima Nuclear Power Plant incident in 2011. *J. Environ. Radioact.* **2012**, *111* (2012), 33−37.
(27) Povinec, P. P.; Sýkora, I.; Holý, K.; Gera, M.; Kovácik, A.; Brest'áková, L. Aerosol radioactivity record in Bratislava/Slovakia following the Fukushima accident - A comparison with global fallout and the Chernobyl accident. *J. Environ. Radioact.* **2012**, *114*, 81−88.
(28) Igarashi, Y.; Aoyama, M.; Hirose, K.; Miyao, T.; Nemoto, K.; Tomita, M.; Fujikawa, T. Resuspension: Decadal monitoring time series of the anthropogenic radioactivity deposition in Japan. *J. Radiat. Res.* **2003**, *44* (4), 319−328.
(29) Pham, M. K.; La Rosa, J. J.; Lee, S.-H.; Oregioni, B.; Povinec, P. P. Deposition of Saharan dust in Monaco rain 2001−2002: Radionuclides and elemental composition. *Phys. Scr., T* **2005**, *T118*, 14−17.
(30) Masson, O.; Piga, D.; Gurriaran, R.; D'Amico, D. Impact of an exceptional Saharan dust outbreak in France: PM10 and artificial radionuclides concentrations in air and in dust deposit. *Atmos. Environ.* **2010**, *44*, 2478−2486.
(31) Nedveckaite, T.; Filistovic, V.; Mastauskas, A.; Thiessen, K. Thyroid dosimetry in the western trace of the Chernobyl accident plume. *Radiat. Protect. Dosimetry* **2004**, *108* (1), 1−9.
(32) Hirose, K.; Takatani, S.; Aoyama, M. Wet deposition of radionuclides derived from the Chernobyl accident. *J. Atmos. Chem.* **1993**, *17* (1), 61−71.
(33) Adachi, K.; Kajino, M.; Zaizen, Y.; Igarashi, Y. Emission of spherical cesium-bearing particles from an early stage of the Fukushima nuclear accident. *Sci. Rep.* **2013**, *3*, 2554.
(34) Garland, J. A. The adsorption of iodine by atmospheric particles. *J. Nucl. Energy* **1967**, *21*, 687−700.
(35) Uematsu, M.; Merrill, J. T.; Patterson, T. L.; Duce, R. A.; Prospero, J. M. Aerosol residence times and iodine gas/particle conversion over the North Pacific as determined from Chernobyl radioactivity. *Geochem. J.* **1988**, *22*, 157−163.
(36) Kristiansen, N. I.; Stohl, A.; Wotawa, G. Atmospheric removal times of the aerosol-bound radionuclides ^{137}Cs and ^{131}I measured after the Fukushima Dai-ichi nuclear accident − a constraint for air quality and climate models. *Atmos. Chem. Phys.* **2012**, *12*, 10759−10769.