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Influence of hail suppression systems over silver content in the environment in Aragón (Spain). I: Rainfall and soils

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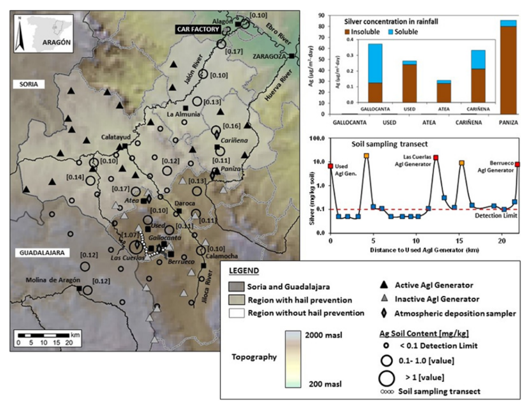
HIGHLIGHTS

- Silver content in rain and soils in Aragón (NE-Spain) from hail suppression systems
- Two-years of atmospheric deposition at 5 sites and soil samples at 72 sites
- Silver content decreases when samples are collected far from ground-based generators.
- Higher silver concentration in regions with hail suppression systems

GRAPHICAL ABSTRACT



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ABSTRACT

In several countries, hail is considered as the most harmful climatic phenomenon from an agricultural perspective. The surroundings of the Gallocanta Lake (North-East Spain), is one of the areas where the storms affecting the Ebro Valley are formed. For this reason, silver iodide from hail suppression systems has been emitted to the atmosphere for half a century.

Nowadays, there is an increasing social concern about the potential environmental consequences of this activity, which has promoted the analysis of the influence of hail suppression systems regarding the amount of silver concentration in the ecosystem. This study focuses on silver atmospheric deposition and its accumulation in soils.

To this end, silver concentrations in rainfall (5 gauges, 16 samples per site, from April 2017 to March 2019) and soils (72 samples) distributed across the hail suppression network managed by the Anti-hail Consortium of Aragón, were analysed.

The results show that the amount of silver is much higher in rainfall gauges and soils close to ground-based silver iodide generators (85 μg/m^2·day and 10 mg/kg soil, respectively), but concentrations considerably decrease when samples are collected far from them (downing to 0.3 μg/m^2·day and 0.1 mg/kg soil).

Apart from the samples obtained nearby silver iodide generators, most of the other soil samples display silver concentrations below the legal threshold established for the most vulnerable activities (1 mg/kg soil in agricultural and forestry land uses). Nevertheless, silver content, both in precipitation and in soils, is higher in regions where hail suppression has been developed for decades when compared to nearby areas in which silver iodide emissions did not occur.

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Silver content observed in soils is not high, but their cumulative effect in sediments and biota should be analysed, which is the aim of the second part of the present study.

1. Introduction

Climatic phenomena have always been the main enemy of agricultural activities. Among the most harmful phenomena, hail causes 40% of the losses declared by agricultural insurances in countries such as Spain, where the risk is high (Agroseguro, 2020).

Burgaz (2009) stated that agricultural insurance is the economic model widely selected by farmers. According to the author, this is the best option for the proper management of meteorological risks. However, weather domination and modification have always been a human desire, so many initiatives have proliferated with this aim.

Hail is created in convective clouds vertically developed, or cumulonimbus, which are the most typical thunderstorm clouds (Vujović and Protić, 2017). Whereas the area affected by a storm ranges from 50 to 500 km^2, the one affected by a hailstorm is considerably smaller (30–50 km^2), and its length barely is longer than 15 min (Font, 2000).

The presence of mountain ranges enhances air mass uplifts, increasing the instability of the air mass, which is a key factor for the delimitation of areas prone to be affected by hailstorms. At the lower areas and valleys downwind the mountain ranges, the damages caused by hailstorms are greater (Font, 2000).

Hailstorms are a global phenomenon that has been reported across the world throughout history, from the most harmful hailstorm, reported in Moradabad (India), on April 30, 1888, which caused 246 casualties due to hailstone impact (De et al., 2005), until the recurrent intense hailstorms in Mendoza (Argentina), where the annual agricultural losses reach $80 million (Pérez, 2007).

In Spain, the North-Eastern region is the most affected area. The losses caused by hailstones reach 10% of the agricultural production (López et al., 2001). According to García-Ortega et al. (2014), the Ebro Valley recorded 50 storm days in 2006, being 32.6 storms/year the average storm occurrence in the period 2001–2010. Pascual (2002) reported that hailstorm events in the Ebro Valley occur 9.4 days/year, mostly between May and September, and generally happening after the solar radiation maximum (16:00 UTC).

Bearing this in mind, climate change may increase the number of storms, since it has been observed that the higher the average minimum temperature, the more frequent storms, and thus, the likelihood of hail increase. Dessens (1995) detected that for the period 1946–1992, the losses caused by hail in France rose 40% per each degree in the average minimum temperature.

From mid-20th century onwards, several hail suppression systems/networks have been designed all over the world: in France (Dessens, 1986a; Dessens, 1998), USA (Henderson, 2006), China (Wang et al., 2006) or Israel (Levin, 2011). Esteban (1975) already described how many of the hail suppression systems are based on cloud seeding by emitting silver iodide (AgI) nuclei to the atmosphere. The aim is to multiply the number of potential deposition nuclei within the clouds, so the number of hail particles would increase, but the size is smaller, and thereby, the potential hail damage is reduced. The hail suppression systems have been usually developed in areas where hail risk is high, and several methods have been applied: rockets (Abshaev et al., 2006), ground-based generators (Dessens et al., 2016), or even aircrafts (Mather et al., 1997; Krauss and Santos, 2003; Wang et al., 2006).

Silver biochemical cycles include its liberation to the atmosphere, water, or soils, from natural and anthropogenic sources. Once silver is in the atmosphere, the long distance transport of fine particles redistribute the AgI nuclei, which finally fall back to the ground by wet and dry deposition over water bodies and sediments (ATSDR, 1990). It has been quantified that around 50% of the silver liberated to the atmosphere by industrial activities is transported more than 100 km, and it is deposited thanks to precipitation (ATSDR, 1990). Additionally, cloud seeding events scatter silver downwind hundreds of kilometres (Freeman, 1979).

Once silver reaches the soil, it is mainly immobilised by salt precipitation, complexing, or absorbed by organic matter, clays, and iron or manganese oxides (Smith and Carson, 1977). Not in vain, it has been already proved that silver emissions from electric plants fuelled with carbon can produce silver accumulation in the surrounding soils (Fowler and Nordberg, 1986).

During the last decades, the expansion of the hail suppression systems across the world and the increasing concern about the consequences of weather modification over the environment and human health have led to the development of several studies. Most of them were focus on an environmental perspective (Sokol and Klein, 1975; Howell, 1977; Klein, 1978; Potapov et al., 1996; Williams and Denholm, 2009; Fajardo et al., 2016), whereas some of them faced a human health approach (Standler and Vonnegut, 1972; Sánchez et al., 1999).

In this context, only a few countries have established legal thresholds related to the silver content in soils. In Spain, the Regional Governments are responsible for setting reference values according to the land use, but silver is not concerned in all regional regulation in Spain. In Aragón, the reference level of heavy metals content in soils for protecting human health are based on the report published by IGME (2008), where the background levels including a list of metals are determined (BOA, 2008). That report, and therefore the regional law, establishes that the silver reference value RV90 in soils in Aragón is 0.97 mg/kg soil. It also establishes 1 mg/kg soil as the reference level for agriculture, livestock and forestry activities, 10 mg/kg soil for urban areas and playgrounds, and 100 mg/kg soil for industrial activities.

The long-term effects of hail suppressions systems have been previously focused on their effectiveness (Dessens, 1986b), so in the present research, the effects were analysed from an environmental approach. The potential environmental effects of silver accumulation from hail suppression systems are expected to be observed both in soils and rainwater from an area under the influence of hail suppression systems for the last fifty years.

2. Experimental

2.1. Study area

The hail suppression policy in Aragón (Spain) was the reason for the creation in 2016 of a social movement (*Who dry our lands?*) worried about the environmental consequences of the silver iodide emissions. This movement was born in Used (Zaragoza), one of the villages in the surroundings of the Gallocanta Lake, in the Iberian Range (Fig. 1). This zone is the most preferential area in which thunderstorms affecting the Ebro Valley are developed (Font, 1983; BOA, 2016).

The hail suppression in Aragón was firstly initiated in this area in 1971. Initially, by using carbon-fuelled generators, and, from 1973 onwards, by the installation of ground-based generators that emit silver iodide dissolved in acetone (BOA, 2016). After the noon meteorological forecast, the farmers activated themselves the generators if hail risk was expected.

The next step was the creation of the Anti-Hail Consortium of Aragón (Official Journal of the Cortes de Aragón, 2001) in 2001, which gathered

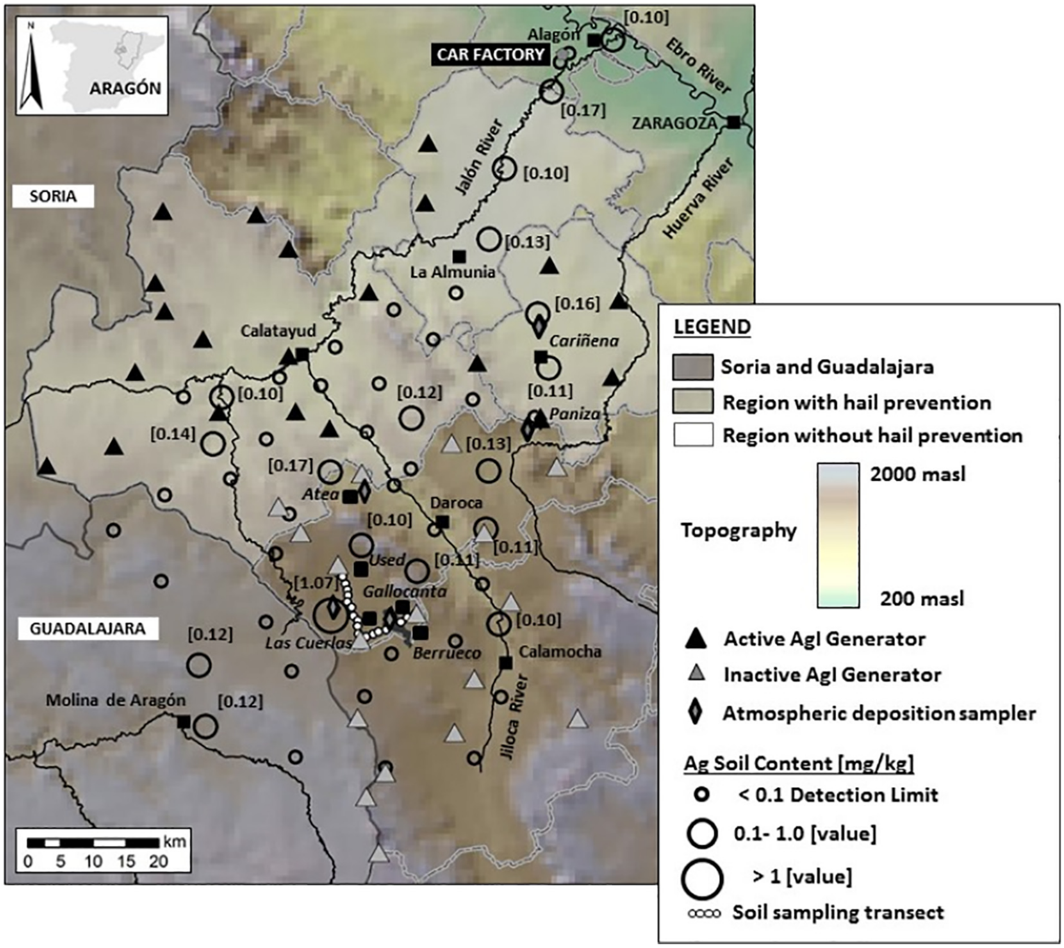

Fig. 1. Location of ground-based generators (actives/inactives in 2017–2019), rainfall collectors and soil samples (regional samples and inter-generators transect).

on a voluntary basis to the regions usually affected by hailstorms. The initial network was formed by 51 ground-based generators (10 × 10 km: Fig. 1), which were operative between April 15th and September 30th. The activation of the generators is based on the daily storm risk (Dessens et al., 2016; Anti-Hail Consortium of Aragón, personal communication). The regions being part of the consortium have been variable since 2001. Thus, new regions joined the consortium in 2007 (Bajo Aragón-Caspe), whereas others decided to leave thereafter (Jiloca, in 2008; Daroca, in 2017).

Between the 70s of the 20th century and the creation of the Anti-Hail Consortium of Aragón in 2001, the Government of Aragón have supported programmes such as cloud seeding by aircrafts during 1984 and 1985, as it was recorded in the Official Journal of the Aragón Congress (1985). Likewise, in 1983, a car factory was settled in Figueruelas (Zaragoza), in the central part of the Ebro Valley. Since then, rumours about the use of hail suppression methods by the factory with the aim of protecting hundreds of new cars parked outdoors have been incessant. Finally, according to personal communications from AVIMON (Moncayo's Aircraft Ecologist Association, from its Spanish acronym), in nearby areas belonging to Castilla, were hail suppression was also used in the early seventies, requests for the installation of new anti-hail generators have not been conceded by water authorities.

Therefore, as shown in Fig. 1, the present research focus on the Gallocanta Lake surroundings, but it also partially includes areas of the regions member of the Anti-Hail Consortium of Aragón, from the Ebro River, to Guadalajara (Castilla).

The ultimate aim of this research is to carry out an environmental diagnosis, based on reliable silver content data, about the influence of the hail suppression policy applied in Aragón. This is the first part of a larger research, and it is focused on silver atmospheric deposition and its content in soils.

2.2. Materials and methods

2.2.1. Atmospheric deposition

Five bulk atmospheric deposition collectors were installed across the study area. The collector network was installed following some of the criteria described by Pey et al. (2020). Samples were collected from April 2017 to March 2019. Two out of five sites were in the region of Cariñena, which is member of the Anti-Hail Consortium of Aragón. One of these collectors was next to a ground-based generator in Paniza, and the other one, equidistant to several generators, in Cariñena (Fig. 1). Three collectors were placed in the region of Daroca, which left the Consortium in 2017. One of them was installed next to Gallocanta Lake, another in an agricultural plot, and the third one in the outskirts of Atea, a small village on the downwind side of the Sierra de Santa Cruz.

During the period in which the hail suppression systems are potentially operative (from April 15th to September 30th), samples were collected on a monthly basis, whereas samples out of the hail season were obtained usually every two or three months (three samples between October 2017–March 2018), except for the period October 2018–March 2019, only one sample.

The collected samples are treated through a two-step filter method, as stated in Pey et al. (2020). Firstly, the very large particles are removed by using a 100 μm size filter. Secondly, 47 mm pre-heated quartz fibre filters are used to individually filter each sample. To do so, a filtration ramp connected to a vacuum pump was used. Therefore, from each sample, one soluble sample (collected filtered water, which is quantified) and one insoluble sample (particles in the filter) are obtained. Those samples are analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The insoluble samples were previously digested by using HF, HNO_3 and $HClO_4$, evaporated to dryness and the residual was dissolved by using HNO_3 6%. The samples were measured using the Agilent 7500ce system with ORS (Octopolar Reaction System) technology, which use helium collision mode, and its measurement procedures are based on the U.S. EPA 200.8 (1994) guidelines for liquids samples and the U.S. EPA 6020B (2014) for solid samples.

The samples were classified according to date when they were collected. They were examined by a multivariate Cluster analysis (Statgraphics Centurion XVI, 2010), and they were binary categorised depending on if they were collected when the generators were potentially in operation or not (0–1), on the amount of sampled water, and on the silver content. Data were standardised, the square Euclidean distance was used to measure similarity and the Ward's method was considered to obtain hierarchical associations.

2.2.2. Soils

According to Badía et al. (2007), Calcisols, Cambisols and Regosols are the most common types of soils within the vast study area. These types of soils are commonly encountered in arid and Mediterranean areas. Calcisols are characterized by a layer of calcium carbonate at some depth; Cambisols are rich in minerals and good for agricultural activities; and Regosols are mineral soils, slightly developed and related to arid and dry conditions.

Two sampling campaigns were carried out following a number of criteria: 1) samples had to be taken from the first 2–3 cm, where silver from atmospheric deposition could be found, and 2) they had to be taken in well-known uncultivated lands, with the aim of avoiding silver mixing during till. In any case, in order to verify that the silver in soils came from atmospheric deposition and that the vertical transport was not relevant, as stated by Tsiouris et al. (2003), a deeper sample (30 cm) was taken next to a generator in Used, together with a superficial one.

The first campaign was carried out in 2016. The samples were regularly collected each kilometre (21 samples) between the generators in Used, Las Cuerlas and Berrueco. Those generators are separated by 10 km and draw a "L", which cross the Gallocanta Lake (Fig. 1). A second sampling campaign was carried out in June 2018 and the study area was extended. The samples collected during this campaign (51 samples) were separated around 20 km, from the Ebro River, where the car factory is located, to Guadalajara, where hail suppression systems have not been used since the 70s of the 20th century. The lab analysis of these samples followed the aforementioned method used for the insoluble part of the samples from the collectors.

3. Results

3.1. Atmospheric deposition

The multivariate analysis divided the sixteen samples into two groups (10 and 6 samples, respectively), as shown in Table 1 and Fig. 2. The first group is characterized by more water (more rain) and silver content in all the collectors. 90% of the samples in this group were collected between April and September, when the generators are potentially activated. Only one sample in this group was collected out of the hail season. However, that sample was collected a few days before the 15th April 2018. It is not discarded that it could be affected by the preliminary tests annually done before the hail suppression campaign starts.

The second group is composed by three samples collected between October and April, and three samples collected during the hail suppression period. Rainfall collected in the latter samples is low, which directly influence low silver emissions and thus, silver content in collectors. Anyway, two sub-groups distinguishing between the samples collected during the hail suppression period and the rest can be observed (Fig. 2).

Therefore, it seems clear that silver content in our samples is strongly related to silver iodide emissions from the hail suppression network. Wet deposition associated to thunderstorms developed during the hail suppression period, and identified with hailstone risk, is the most likely process behind these observations. Regarding the spatial

Table 1
Silver content and rainfall in each sampling period. Multivariate Cluster Analysis. Samples were divided into two groups depending on the hail suppression period (codes 0–1), silver content and rainfall collected in Gallocanta, Used, Atea, Cariñena and Paniza.

From	To	Gallocanta		Used		Atea		Cariñena		Paniza	
Date (dd/mm/yyyy)		Ag ($\mu g/m^2 \cdot day$)|rainfall (mm/day)									
07/04/2017	10/05/2017	0.01	0.4	0.00	0.4	0.01	0.7	0.02	0.3	14	0.3
10/05/2017	02/06/2017	0.19	1.5	0.00	1.2	0.07	1.4	1.13	0.9	89	1.4
02/06/2017	16/06/2017	0.10	2.0	0.02	2.8	0.00	3.4	0.11	1.9	24	2.1
16/06/2017	10/07/2017	0.45	1.5	0.17	1.2	0.27	1.4	0.18	1.4	63	1.7
10/07/2017	08/08/2017	0.05	0.1	0.01	0.1	0.01	0.0	0.05	0.3	8	0.1
08/08/2017	01/09/2017	0.83	1.4	0.15	2.0	0.17	1.9	0.36	1.3	264	1.2
01/09/2017	28/09/2017	0.83	0.5	0.27	0.4	0.37	0.4	0.04	0.3	109	0.5
28/09/2017	07/11/2017	0.12	0.0	0.03	0.1	0.04	0.0	0.04	0.1	22	0.1
07/11/2017	25/01/2018	0.13	0.4	0.06	0.3	0.12	0.1	1.61	0.4	6	0.7
25/01/2018	26/03/2018	0.12	1.3	0.12	1.2	0.44	1.8	0.02	1.6	192	2.0
26/03/2018	27/04/2018	4.26	2.5	0.08	2.2	0.25	3.3	1.41	4.5	5	3.6
27/04/2018	14/06/2018	0.67	2.8	1.04	3.6	0.47	4.0	0.11	2.6	299	2.3
14/06/2018	13/07/2018	0.29	1.0	1.29	1.7	0.16	2.5	0.02	0.2	167	1.1
13/07/2018	30/08/2018	0.03	0.6	1.44	1.1	0.07	0.6	0.17	0.8	35	0.5
30/08/2018	26/09/2018	0.24	1.0	0.05	1.9	0.07	1.6	0.07	0.7	311	0.9
26/09/2018	02/04/2019	0.01	0.9	0.01	0.9	0.01	1.0	0.03	0.4	31	0.7

Hail-suppression period[a]	Variable	Gallocanta	Used	Atea	Cariñena	Paniza
Group 1	Ag ($\mu g/m^2 \cdot day$)	0.72	0.44	0.20	0.36	144.89
0.9	Rainfall (mm/day)	1.56	1.89	2.19	1.59	1.68
Group 2	Ag ($\mu g/m^2 \cdot day$)	0.19	0.06	0.09	0.30	31.55
0.5	Rainfall (mm/day)	0.38	0.37	0.37	0.30	0.40

[a] 0 = Sampled when generators are not installed (October 1st–April 14th); 1 = Sampled when generators are installed (April 15th–September 30th).

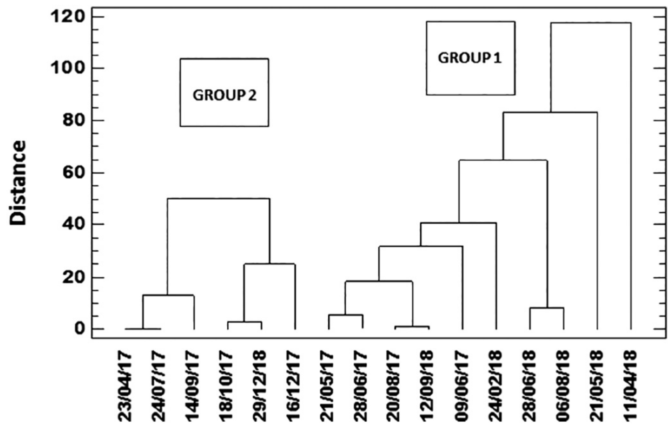

Fig. 2. Dendrogram of the samples collected in Gallocanta, Used, Atea, Cariñena and Paniza for the period April 2017–March 2018.

variability (Fig. 3), the results highlighted that silver in the collector next to a generator (Paniza), is significantly higher if compared to the rest of the collectors (85 μg/m^2·day and 0.14–0.37 μg/m^2·day, respectively). Silver has mainly been found in the insoluble part (94%) of the samples, since larger and insoluble silver particles should usually be deposited in the surroundings of the generators.

The silver content in the collector placed in Cariñena was significantly lower (0.33 μg/m^2·day), and the percentage of silver in the insoluble part of the sample was also lower (64%). Surprisingly, the collectors placed in the region of Daroca, where generators were not installed, had similar silver content than Cariñena. Even the collectors in Used and Atea reached similar silver content in the solid portion of the samples than Paniza. Finally, the collector in Gallocanta reached more silver than the Cariñena one, even with a lower percentage of silver in the solid portion of the sample (Fig. 3).

According to the results, two conclusions may be reached: (1) atmospheric deposition of silver is notably depleted at a certain distance of the emission source (10 km), but (2) atmospheric dynamics may scatter silver pollution over extensive regions even located hundreds of kilometres away, as stated by Freeman (1979), DeFelice et al. (2014) and Jing et al. (2016). These conclusions are also supported by the results found by Pey et al. (unpublished data), who observed that silver from atmospheric deposition in remote and pristine areas, such as in the Ordesa and Monte Perdido National Park (at around 200 km away, and frequently downwind during the warm season), may be up to one order of magnitude lower (0.03 μg/m^2·day) than contents in areas covered by the hail suppression network.

The high percentage of silver in the insoluble part of the samples in Used and Atea may suggest an additional source of silver apart from silver iodide emissions from the network. It is noteworthy that an invert relationship between rainfall in Gallocanta, Used, and Atea, and the silver content in these collectors (Eq. (1)) has been observed, which led to question the influence of silver iodide emissions over rainfall. Further research is currently in progress in this matter by the authors.

$$\text{Silver } (\mu g/m^2 \cdot day) = -0.83 \cdot \textit{Rainfall}\ (mm/day) + 1.22, R^2 = 0.9998; P<0.05 \quad (1)$$

3.2. Soils

The samples collected in the transect between the generators in Used, Las Cuerlas and Berrueco (Figs. 1 and 4) showed that the highest silver content (around 10 mg/kg soil) was found close to the generators. One kilometre away from the generator, where some samples were collected, silver content is considerably lower, even below the detection limit (0.1 mg/kg soil).

The deeper sample collected next to the generator in Used had 0.34 mg/kg soil, whereas the superficial sample had 6.67 mg/kg soil. This difference confirms the atmospheric deposition as the main silver source, but also its limited vertical mobility.

Most of the samples between the generators had low values (around the detection limit). However, unexpectedly, two of the samples had silver contents of the same order or magnitude of those collected next to the generators. The analysis of 5 additional samples collected at the surroundings of the fifth sample between Used and Las Cuerlas (18 mg/kg soil) showed that the mean silver content was 0.16 mg/kg soil (standard deviation 0.07 mg/kg soil). Therefore, the spatial variability at the surroundings of a sample is narrow, and the outliers may be explained by local and punctual sources of pollution (e.g. the aforementioned sample between Used and Las Cuerlas is close to an abandoned illegal dump).

Regarding to the regional sampling, only 18 out of 51 samples (35%) were above the detection limit (0.1 mg/kg soil). The maximum value (1.07 mg/kg soil) was found in a sample close to a former generator in Used, which was operational until the Anti-Hail Consortium of Aragón installed its generators. The rest of the samples were below 0.17 mg/kg soil.

When data are regionally analysed (Table 2), it can be concluded that the regions of Daroca and Cariñena display the highest amount of samples above the detection limit (67%), and record the most elevated mean silver content in soils (0.2 and 0.11 mg/kg soil, respectively). Both regions have been under silver iodide emissions since the 70s of

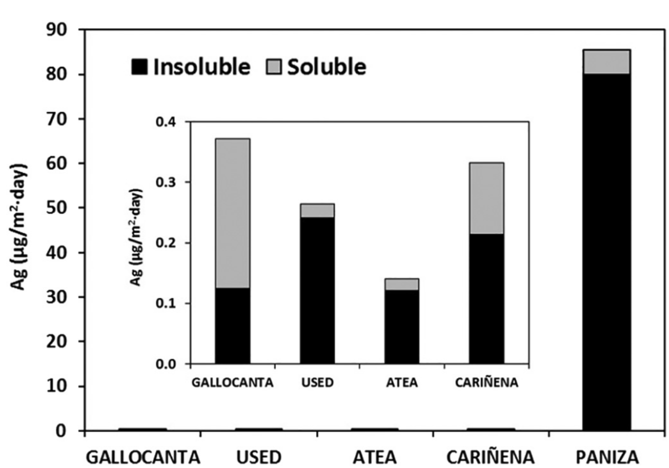

Fig. 3. Silver content in water (soluble) and filters (insoluble) of the collectors in Gallocanta, Used, Atea, Cariñena and Paniza for the period April 2017–March 2019.

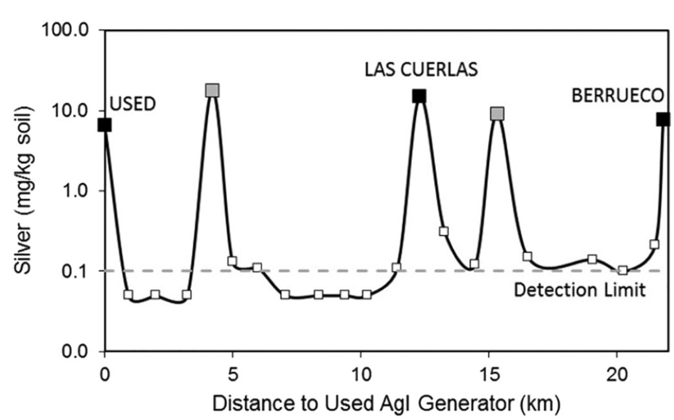

Fig. 4. Silver content in the samples collected in the transect between Used-Las Cuerlas-Berrueco.

Table 2
Number of soil samples, % of samples above the Detection Limit (DL), and mean silver content at the studied regions.

Region	Number of samples	Ag > DL[a]	Mean Ag[b]
		%	mg/kg soil
Castilla	7	29	0.07
Jiloca	8	13	0.06
Daroca	9	67	0.20 (0.10)[c]
Cariñena	3	67	0.11
Calatayud	16	19	0.07
Valdejalón	5	60	0.10
High Ebro Banks	3	33	0.07

[a] DL: detection limit Ag = 0,1 mg/kg soil.
[b] When silver content is <DL, silver content is considered as 0.05 mg/kg soil for calculation.
[c] Mean value excluding the sample collected next to a former generator.

the 20th century, although Daroca left the Anti-Hail Consortium of Aragón in 2017.

Conversely, other regions such as Jiloca (left the Anti-Hail Consortium of Aragón in 2008), or Guadalajara (not participating in such weather-modification practices), show the lower portion of samples above the detection limit (13% and 29%, respectively), and the lower mean silver content in soils (0.06 and 0.07 mg/kg soil, respectively).

It can be also highlighted that only 19% of the samples collected at the region of Calatayud (member of the Anti-Hail Consortium of Aragón) were above the detection limit, whereas in the region of High Ebro Banks (where the car factory is located), showed one of the lowest silver content in soils (0.07 mg/kg soil). It cannot be concluded that silver content in soils was clearly associated to the type of soil.

Except for the sample collected next to a former generator in Used, all the samples are clearly below 1 mg/kg soil, which is the legal threshold established by the Government of Aragón (BOA, 2008) for agricultural and forestry activities. Nevertheless, it must be mentioned that the threshold was based on the analysis of 403 samples collected across Aragón (IGME, 2008). The results of that work show that mean silver content in Aragón was 0.48 mg/kg soil, and 0.71 mg/kg soil in the regions studied in this research.

The different silver content between the aforementioned study and the present research may be explained by the different analysis method used in each work. In IGME (2008), the samples were analysed by using ICP-AES, whose detection limit is five time higher than the ICP-MS used in the present work (0.5 mg/kg soil versus 0.1 mg/kg soil). In order to verify the obtained results, 5 samples were sent to another lab (Actlabs, Canada), where they were analysed by using ICP-MS (detection limit = 0.002 mg/kg soil). The results corroborated the results obtained in previous analysis (four out of five samples below the detection limit and one out of five 0.16 mg/kg soil).

Based on this, it would be recommendable that laws that establish reference levels of silver content also include sampling conditions and analytical techniques. In any case, both IGME (2008) and the present study have found higher silver concentration in soils from the regions covered by the hail suppression network.

4. Discussion and conclusions

During this research, data about the amount of silver emitted by the Anti-Hail Consortium of Aragón was not available. However, BOA (2010) reports that in 2009 the generators were activated 67 days, during 316 h (4.7 h per day).

The design of the hail suppression network in Aragón is supported by Dessens et al. (2016), who also act as advisor for activating the generators. Based on several study cases, for a ground-based network similar to the one installed in Aragón (10 × 10 km), Dessens et al. (2016) recommend the emission of 9 g of AgI per hour, starting at least 3 h before storm occurrence. If that emission rate is applied to 2009, each generator would have emitted 1.3 kg of silver, which means 1.3 mg/m^2 in 100 km, that is, the area covered by each generator. Obviously, atmospheric dynamics distribute silver pollution across wider areas beyond the generators and therefore actual deposition rates should be lower than this value.

Silver collected by the atmospheric deposition collectors during the study period (2017–2018) ranged between 30 mg/m^2·year in Paniza and 0.05–0.13 mg/m^2·year in the rest of the collectors. Given that important deposition rates are only detected in Paniza, next to the generator, the low silver content in the other four collectors could be explained by the dispersion of the particles once in the atmosphere, as stated by previous researches (Freeman, 1979; Tsiouris et al., 2003).

For an average deposition rate of 0.10 mg/m^2·year during the last 50 years, in the upper three centimetres of a soil, whose density is 1.4 g/cm^3, silver concentration in that soil would be 0.12 mg/kg soil. This concentration is in the same order of magnitude that the observed in the soil samples collected across the study area.

Tsiouris et al. (2002) found similar silver concentration in soils in Greece, additionally, no significant differences were found between areas with and without hail suppression systems. Nevertheless, the hail suppression network was in operation for twelve years in Greece, whereas silver concentrations were significantly lower (up to 155 μg/m^2) in Serbia after a 6 year-period of emissions by using rockets (Ćurić and Janc, 2012). In relation to silver content in water, it is well known that silver is mostly insoluble, so concentrations were significantly lower than in soils. Our results are in line with findings from previous studies in Spain (Sánchez et al., 1999), and Moldova (Cazac et al., 2017), which determined that silver concentration in water were below legal thresholds. The higher silver concentration observed in collectors close to ground generators it can be explained by silver iodide emissions, and it is supported by previous findings observed by Sánchez et al. (1999) in Spain, who stated that silver concentration in rainwater was higher during seeding days; and Ćurić and Janc (2013), who estimated wet deposition of silver in Serbia.

If we consider that the emission rate during the last 50 years is similar to the one calculated for 2009 (1.3 mg/m^2·year), and that the silver iodide is entirely and homogeneously deposited within the study area, silver concentration in the upper three centimetres in soils should be around 1.5 mg/kg soil, but this is not the case. Outflows of silver are probably occurring. The silver mobility once it reaches soils due to lixiviation, its accumulation in sediments of water bodies, or its assimilation by biota are analysed in the second part of this research (Causapé et al., 2021).

It seems evident that silver observed both in collectors and soils has an anthropogenic source: the emission of silver iodide by hail suppression systems. Besides, silver concentration is higher in the regions with those systems, but further areas are also under its influence.

Silver content both in rainfall and soils are considerable high in the surroundings of the ground-based generators, thus, it would be necessary further research for assessing its spatial range. Once the samples are taken a dozen of metres away from the generators, the atmospheric deposition significantly decrease and it is accumulated in soils, although the content remain below the legal threshold even for the most restrictive activities.

CRediT authorship contribution statement

Jesús Causapé: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization, Supervision, Project administration. **Jorge Pey:** Conceptualization, Methodology, Resources, Data curation, Writing – review & editing. **José María Orellana-Macías:** Formal analysis, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Jesús Reyes:** Data curation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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