# Concentrations of three rare elements in the hydrological cycle and soil of a mountainous fir forest

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Abstract In this work, the concentrations of three rare trace elements, antimony (Sb), selenium (Se), and vanadium (V) were determined in the hydrological cycle and soil of a mountain fir forest. The three elements were significantly enriched in throughfall compared to the bulk deposition. Dry deposits, either in particles or vapor form, are probably the cause of this. It was found that for the enrichment of rain with Sb and Se long range transport played a more important role compared to V. The latter had a significant relation with marine derived ions, a rather unexpected finding. Apart from dry deposition coming from long distances, all elements were enriched with continental material. The concentrations of the three elements in soils were close to the average values reported in literature. In addition, their concentrations in the streamflow water were far below the tolerable drinking water limits set up by the World Health Organization and national authorities.

**Keywords:** Sb, Se, V, bulk deposition, throughfall, soil solution, streamflow, soil.

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### Introduction

Research on heavy metals in forest ecosystems has mainly focused on lead, cadmium, arsenic, copper and other heavy metals. Remote forests have low concentrations of these minerals in water, soils and plant tissues and therefore serve as a comparison with agricultural or forest ecosystems having a history of pollution. There are also the so-called rare trace elements for which there is little work done. Antimony,

selenium and vanadium are three of them.

Antimony (Sb) is a metalloid that has a wide range of uses, including the construction of semiconductors, lead hardeners, batteries, missile trackers, car brake liners and pigments (Filella et al. 2009). Important anthropogenic sources of antimony in soils are vehicle (Huang et al. 1994, Dietl et al. 1996) and foundry emissions (Hammel et al. 2000). Steinnes (1997) reported that antimony emissions can be transported into the atmosphere over

long distances, e.g., from Central Europe to Norway. Sb occurs in trivalent and pentavalent oxidation states. The trivalent condition may be associated with carcinogenicity (Gebel 1997). It usually occurs in oxides, hydroxides or oxo anions either in the (+5) state in relatively toxic environments (antimonates) or in the (+3) state in anoxic environments. It has (like As, another metalloid) strong affinity for thiol groups and can replace phosphorus in biological reactions, which explains their inhibitory role in DNA replication and metabolic processes (Wilson et al. 2010).

Selenium is a nonmetal, present in nature in five oxidation states: (-2), (-1), (0), (+4) and (+6). SeO<sub>4</sub><sup>2</sup>- and SeO<sub>3</sub><sup>2</sup>- are soluble oxyanions known respectively, as selenate and selenite (Fernández-Martínez & Charlet, 2009). At the global level there are no mines that extract Se. It is a by-product of the production of other metals such as the refining of Pb and Cu or is recovered from the sludge accumulated in H<sub>2</sub>SO<sub>4</sub> factories (Garousi 2017). It is widely used in metallurgy, manufacturing of glass, chemicals, pigments, electronics, fertilizers, etc. (Khamkhash et al. 2017). Selenium (Se) has dual (beneficial or toxic) effects for humans, animals, and plants. Deficiency of Se in animal diet can be the main cause for growth retardation, impaired bone metabolism, and abnormalities in thyroid function. On the other hand, high levels of Se can imped plant growth, development, and disturb plant ecophysiology (Hasanuzzaman et al. 2020).

Vanadium (V) is a transition metal the fifth most abundant element in the Earth's crust and extensively mined in Russia, South Africa, North America and China (Imtiaz et al. 2015). In the environment, V can occur in various valence states (e.g., -3, -1, 0, +2, +3, +4, and +5), of which V (+5) is widespread (Gan et al. 2020). In small concentrations, V can act as a growth factor in plants (Garcia-Jimenez et al. 2018). In addition, V is a key trace element in the biochemistry of prokaryotic organisms as

an alternative to molybdenum in the molecular structure of nitrogenase, the enzyme of nitrogen fixation (Bellenger et al. 2014). However, at high concentrations, V especially in the pentavalent state can inhibit plant growth and even pose a serious threat to the soil ecosystem (Aihemaiti et al. 2020, Li et al. 2020).

The purpose of this work was to determine the concentrations of Sb, Se and V in the hydrological cycle and soil of a mountain fir stand in the area of Karpenisi, central Greece as well as the assessment of anthropogenic effects on their concentration in their hydrological cycle. As the fir forest under consideration is a remote one, the concentrations values of these elements in waters and soil can serve as a base line to compare other ecosystems.

## **Materials and Methods**

The experimental fir plot is located on the ridges of Timfristos Mountain in Evritania area, central Greece at an altitude of 1170 m. It has an area of 0.27 ha and is included in a catchment area of 147 ha. The average annual rainfall is 1530 mm. The dominant vegetation consists of a stand of Bulgarian fir (Abies borisii-regis Mattf.), about 100 years old with a ground vegetation of bracken fern (Pteridium aquilinum L.), blackberry (Rubus hirtus W. & K.) and herbaceous vegetation (Brahypodium sylvaticum H., Geranium lucidum L.). The soil is deep and classified as a Cambisol (FAO 1988).

## Collection of precipitation, soil solution streamflow and soil

The collection period for all water samples covers the period from October 2012 to December 2014 (with the exception of the 20 cm depth lysimeter). All samples were collected weekly and formed a pooled monthly sample according to the weekly volumes measured.

The bulk deposition was collected in a forest

opening of the experimental plot with two funnels 18 cm in diameter connected to 5-liter containers through a PVC pipe 1.05 m long and 20 cm in diameter. Throughfall was collected with 30 collectors placed randomly similar to those of the total rain. To collect snow during the winter months (November-April), the funnels and containers were replaced with plastic bags about 90 cm long and about 22 to 23 cm in diameter. The volumes of the samples were measured and they were immediately stored in a refrigerator at 4° C. If a storage period of more than two weeks was required, the samples were frozen at -2° C. There was a total of 26 bulk and throughfall deposition samples.

The soil solution was collected at two depths of 20 and 65 cm with zero tension lysimeters. A total of 17 and 26 soil solution samples were taken at 20 and 65 cm, respectively. The reason for this difference in the sample number was the later installation of the 20 cm depth lysimeter.

The streamflow water comes from a catchment of 1470 ha and includes soil water (both capillary and gravitational), groundwater and some surface runoff. It is collected at the hydrometric station of the experimental surface. There were 27 streamflow water samples.

The collection of soil samples was done by systematic sampling according to the instructions of the ICP-Forests program (Cools & De Vos 2020). Specifically, in two imaginary lines that were about 25 m apart from the surface, 12 soil pits were excavated in each line at a distance of 5 m from each other. From each soil pit the horizons L, FH were collected with a frame of 15 x 15 cm. Samples of mineral soil were collected from the depths 0-10 cm, 10-20 cm, 20-40 cm and 40-80 cm. Every 4 soil sections the organic horizons and the inorganic ones (of the same depth) were mixed and formed complex samples. Thus, three samples were formed from each organic horizon and soil depth.

## Sample processing and chemical analysis

Water samples passed through a 0.45 µm filter before analysis. Concentrations of Sb, Se, V and Al in bulk deposition, throughfall, soil solution and streamflow were measured with Inductively Coupled Plasma Argon with Mass Spectrometer (ICP-MS) model Thermo iCAP Qc.

In addition, the concentrations of the anions Cl-, SO<sub>4</sub><sup>2</sup>- and NO<sub>3</sub>- were determined by ion chromatography using chemical suppression (Metrohm Compact IC model).

The L horizon samples (plant material with visible origin, i.e., leaves, twigs etc) were ground in a blade mill. The FH layer (half or fully decomposed plant material) and mineral soil samples passed through a 2 mm diameter sieve and dried at 80°C for 48 hours. All soil samples intended for total analysis were pulverized in a ball mill.

The concentration of Al in all soil layers was measured by X-ray Fluorescence Spectroscopy (XRF) model XEPOS by SPECTRO. To prepare the samples for analysis by the XRF method, 4 g of soil were mixed with SpectroBlend binder (77.1% C, 5.4% O, 12.8% H, 4.7% N) and compressed with 15-ton hydraulic pressure to form a 2 mm thick tablet with a diameter of 32 mm.

For the FH layer and mineral soil samples total analysis 0.20 g of ground soil were digested in a microwave oven with 1 mL aqua regia and 5 mL concentrated HF acid at a temperature range of 160-170°C for 20 min. The digests were diluted to 50 mL with deionized water and the concentrations of Sb, Se, V and Al were measured with the above mentioned ICP instrument.

## Calculations and statistical analysis

Apart from the average values, the coefficients of variation were calculated as the percentages of standard deviations over the average values.

For each element, a comparison was made of its concentrations in the various components of the hydrological cycle with an Analysis of Variance Test (ANOVA). A logarithmic transformation was necessary to conform to the normal distribution requirements.

The effect of the earth's crust on the concentration of the three elements in bulk deposition was calculated as follows: The ratio value (xb / Alb) (xc / Alc) shows the degree of influence of the earth's crust on the composition of rain. Where xb is the concentration (µg L<sup>-1</sup>) of Sb, Se and V in bulk deposition, Alb is the concentration of Al in bulk deposition (µg L-1), xc is the concentration (µg g<sup>-1</sup>) of Sb, Se and V in the earth's crust and Alc the concentration (µg g-1) of Al also in the earth's crust. The higher the ratio the more important is the longrange transport of an element. This relationship has been used by several researchers to find the contribution of the earth's crust to metal concentrations in rain (Poissant et al. 1994, Song & Gao 2009, Zhou et al. 2012). The last mineral soil layer (40-80 cm) was considered to represent the earth crust. This ratio was calculated for all the 26 bulk deposition samples. The comparison of the ratios of the three elements in the 26 samples was carried out with an ANOVA test after a logarithmic transformation. It is the first time that this ratio is applied to a lot of bulk deposition samples and used for statistical comparisons. Usually, it is calculated once taking into account the elemental volume-weighted means. disadvantage is that there is one single value, instead of the 26 values mentioned above. To overcome this problem a statistical test should be applied. If there is no statistical difference between the average elemental concentration in the 26 samples and the single value of the volume-weighted means, the description statistics of the 26 samples can be used. For this reason, a t-test was applied to compare the average values derived from the 26 samples with a single value representing the volume weighted means of each element.

The effect of dry deposition and/or leaching on throughfall deposition was calculated as the ratio of the concentrations of the elements in throughfall to those in bulk deposition. This ratio is called throughfall enrichment. If it is statistically higher than one, this means an increase in concentrations in throughfall. The statistical comparison (to the value one) was made with the Student's T-test (one tailed). There were 26 and 25 cases for V and Sb, respectively. In addition, all the throughfall enrichments of the three elements were compared with an ANOVA test. No logarithmic transformation was necessary in this case.

The correlation of the three elements with other ions (SO<sub>4</sub><sup>2</sup>, NO<sub>3</sub>, Cl<sup>-</sup> and Al) in bulk deposition as well with themselves was done with the Spearman coefficients.

### Results

The concentrations of the three elements and Al in bulk deposition, throughfall, soil solution and streamflow are shown in Table 1. It contains the averages of monthly weighted means for the four elements from October 2012 to December 2014. The statistical comparison was not made for Al. The concentration of Al in the bulk deposition was used to calculate the contribution of the earth's crust on the concentration in bulk deposition. The statistical comparison for each element in the hydrological cycle did not show relevant statistical differences. The low concentrations of Sb and Se in the streamflow water can be observed. Among the three elements, V had by far the highest concentrations in all the components of the hydrological cycle.

Table 2 shows the concentrations of the three trace elements and Al in soils. It is interesting that Se presents the highest variability. In terms of absolute concentration values, Al was the first and V, the second.

The t-test showed that the ratios of Sb, Se and V concentrations in throughfall over the bulk deposition (throughfall enrichment) were statistically higher than one (p< 0.05). This means enrichment with dry deposits and/or leaching. Among the three trace elements, there was no significant difference for the throughfall enrichment ratios (Table 3).

Table 1 Average values of Sb, Se, V and Al concentrations (μg L<sup>-1</sup>), in the hydrological cycle, i.e. bulk deposition, throughfall (Thr), soil solution at 20 cm (L20) and 60 cm (L60) depth, and streamflow (SF).

	Bulk	Thr	L20	L60	SF
Sb	0.058 <b>ac</b> (67)* 0.02-0.202**	(147)	(49)	(45)	
Se	0.079 <b>a</b> (45) 0.015-0.159	0.124 <b>ab</b> (45) 0.06-0.215	(45)	(65)	0.093 <b>a</b> (68) 0.019-0.294
V	0.301 <b>a</b> (58) 0.03-0.84		0.405 <b>a</b> (47) 0.04-0.820	0.422 <b>a</b> (90) 0.120-1.74	
Al	15.9 (57) 2.19-43.0	67.8 (71) 17.1-253	67.8 (71) 17.1-253	212 (124) 4.70-1119	69.9 (200) 3.28-714

Notes: \*Coefficient of variation, \*\* Range. Within the same row, different letters denote significant difference for at least 0.05-probability level.

**Table 2** Concentrations of Sb, Se, V and Al in the soil of the forest stand. Sb, Se and V are expressed in mg kg<sup>-1</sup> and Al in g kg<sup>-1</sup>.

Layer	Sb	Se	V	Al
	0.048	0.161	2.50	1.74
L	(18)*	(96)	(35)	(12.5)
	0.042-0.054**	0.051-0.27	1.88-3.13	1.52-1.95
	0.717	0.52	66.0	29.8
FH	(2.8)	(77)	(16)	(14)
	0.70-0.74	0.09-0.89	59-78	26.9-34.4
	0.655	0.456	108	58.9
0-10 cm	7.4	(78)	(4.5)	(5.2)
	0.60-0.69	0.109-0.822	102-112	55.4-60.9
	0.628	0.423	117	64.8
10-20 cm	(5.4)	(61)	(0.77)	(3.1)
	0.61-0.67	0.135-0.633	116-118	62.6-66.6
	0.670	0.672	122	68.3
20-40 cm	(20)	(48)	(3.7)	(3.0)
	0.54-0.82	0.371-1.01	118-128	66.5-70.6
	0.694	0.497	131	69.6
40-80 cm	(16)	(55)	(5.2)	(1.4)
	0.62-0.82	0.224-0.769	124-138	68.5-70.4

Notes: \*Coefficient of variation, \*\* Range

The effect of the earth's crust on the concentration of the three elements in bulk deposition was calculated based on the information in Tables 1 and 2 regarding the concentrations of Sb, SE V and Al in bulk deposition and soil. There was no significant difference between the elemental volume weighted means (Table 1) and the means of the 26 samples in the bulk deposition and therefore the 26 values were used to calculate means and other statistical parameters. The ratio values were 13.2 for V, 928 for Se and 502 for Sb (Table 3). In contrast to the throughfall enrichment

ratios, the crustal enrichment ratios differed significantly.

Table 4 contains the Spearman correlation matrix for the three trace elements. This piece of information helps to explain the origin of the enrichment in throughfall as it will be discussed in the following section.

Table 3 Throughfall and crustal enrichment.

Throughfall Enrichment				
Sb	Se	V		
1.55 a	1.62 <b>a</b>	1.44 <b>a</b>		
(44)*	(42)	(31)		
0.01-3.54**	0.62-2.92	0.76-2.48		
Crustal Enrichment				
Sb	Se	V		
502 a	928 <b>b</b>	13.2 <b>c</b>		
(95)	(70)	(72)		
104-2350	235-2858	0.668-46.3		

Notes: \*Coefficient of variation, \*\*Range.

Values in the same row followed by different letters differ for at least 0.05-probability level.

**Table 4** Spearman correlation coefficients for the three trace elements.

	Sb	Se	V
SO <sub>4</sub> <sup>2-</sup>	0.599**	0.441*	0.542**
NO <sub>3</sub> -	0.575*	0.358	0.432*
Cl-	0.794	-0.087	0.404*
Al	0.416*	0.507*	0.487*
Sb	1	0.541**	0.189
Se	0.541**	1	0.149
V	0.367	0.149	1

Notes: \*, \*\* mean significance for 0.05 and 0.01 probability levels.

 $\begin{array}{lll} \textbf{Table} & \textbf{5} & \text{Quality assurance and quality control of} \\ & \text{some parameters in water. Target values and} \\ & \text{Quantification limits are expressed in mg L-1} \\ & \text{for SO}_4^{\ 2^{-}} - \text{S, NO}_3^{\ -} - \text{N and Cl-, whereas Al, Sb,} \\ & \text{Se and V in } \mu \text{g L}^{-1} \\ \end{array}$ 

	Target value	CV (%)	Quantification limit
$\overline{SO_4^{2-}-S}$	1.67	1.98	0.21
NO <sub>3</sub> -N	0.180	3.4	0.65
Cl-	3.00	3.03	1.37
Al	34.4	2.44	0.79
Sb	3.36	1.26	0.15
Se	3.42	1.44	0.97
V	7.03	2.17	0.53

## Discussion Hydrological cycle

The concentrations of Se in bulk deposition in the fir stand are somewhat high taking into account that Suzuki et al. (1981) found an average Se concentration of 0.079 µg L<sup>-1</sup> (exactly equal with the value found in the bulk deposition in our work) in the rain over the city of Tokyo. At two high altitude sites in Swiss Alps the Se concentration in rain ranged from 0.016 to 0.051 µg L-1 (Suess et al. 2019). In contrast, the concentrations of Sb and V in the bulk deposition and throughfall are not high when compared to recent or older works. A few decades ago, V concentrations were much higher than today even compared to modern industrial areas. Galloway et al. (1982) found 42 µg L-1 in urban areas and 9 ug L-1 in rural areas of America. Schlesinger et al. (2017) cited by Gustafsson (2019), using a large number of data, found that in remote areas, the volume weighted V concentration in precipitation ranged from 0.0005 to 0.2 µg L-1. The volume weighted mean obtained in the present study is higher than the upper limit of the range, but close to it.

In the Mediterranean zone of Turkey, 20 km west of the city of Antalya, the concentration of Sb (0.19 µg L<sup>-1</sup>) reached the maximum limit in our work (A1-Momani & Aygun 1998). Song and Gao (2009) found 0.28 and 0.36 μg L<sup>-1</sup> for V and Sb, respectively, in the east coast of the Americas. They attributed the highest concentrations of Sb to anthropogenic influence, while for V the natural emissions also played a role. Zhou et al. (2012) measured 1.08 µg L-1 V in bulk deposition in a mountainous area in China near industrial sources of pollutants. Honório et al. (2010) found high concentrations of V in rain (1.78 μg L<sup>-1</sup>) and throughfall rain (2.60 μg L<sup>-1</sup>) in the Amazon rainforest in Brazil. They attributed it to the aerosols enriched by deforestation, the burning of vegetation as well as the use of fossil fuels in large cities.

In the present work, the enrichment values of throughfall for Sb, Se and V were 1.55 1.62 and 1.44, respectively and were statistically significant > 1 for at least 0.05 significance level. The enrichment for Sb found by Gandois et al. (2010) in 6 forest types in France (three *Picea abies*, two *Abies alba* and one *Fagus sylvatica*) was very large, about 64 (0.018 μg L<sup>-1</sup> in rain and 1.16 μg L<sup>-1</sup> in throughfall).

## The effect of the earth's crust on the concentration of the two elements in the rain

The concentration of Al (69.6 g kg<sup>-1</sup>) in Table 2 used in the equation to find the effect of the earth's crust on the concentration of Sb and V in the rain is close to that found by Gao et al. (1998) (75.1 g kg<sup>-1</sup>) in soils of the China region. According to Poissant et al. (1994), ratios between 1 and 10 imply a large effect of the earth's crust on the composition of the elements in the rain, while values between 10 and 500 a moderate effect of the crust and the rest is complemented by anthropogenic influences. According to Table 3, high values were found for Sb (502) and Se (928), whereas V had a low value (13.2). This means that anthropogenic emissions for Sb and Se play an important role in its concentration in the rain even in remote forests. Gandois et al. (2010) found a good correlation in rainfall between Cd and Sb, which indicates a common origin or possibly their long-distance transport.

The correlation coefficients among the elemental concentrations in the bulk deposition (Table 4) showed some interesting relations. The three elements were correlated positively with sulfates. The latter are usually found in the form of dry deposition in tree canopies (Lindberg et al. 1986). The NO<sub>3</sub> ions were also related positively with the Sb and V. The reason for this enrichment is probably the dry deposition of HNO<sub>3</sub> in vapor form. This form of HNO<sub>3</sub> acid is easily trapped by tree

canopies (Lovett et al. 1993). Both sulfates and nitrates probably come from long distances. The Al correlates positively with the three elements. Al is an element of geogenic origin. It can be concluded that the three elements are deposited in dry deposition derived both from long and short distances. The positive relation of Cl<sup>-1</sup>, a marine derived ion, with V is rather unexpected. One would expect such relation from Se, as aerosols derived from marine sources could also play an important role for long-range transport (Suess et al. 2019).

The significant relation between Sb and Se shows that both elements have a similar behavior, probably the long-range transport.

### Soil solution and streamflow

The concentrations of the three elements did not differ significantly in the soil solution in both depths (Table 1). The concentrations in streamflow water are relatively low apart that of V for which however, as we will see below, there is not any problem with regard to drinking water. In any case, the variability for all elements was high but lower than that of Al in streamflow, which reached a coefficient variability of 200%.

The concentrations of Sb in the solution and streamflow of the fir stand were much lower than those in soils with a history of pollution. In areas with As-Sb mining activities in Northern Macedonia, Alderton et al. (2014) found Sb concentrations 2.1 and 0.60 µg L<sup>-1</sup> in surface and groundwater, respectively. High concentrations of Sb in water extracts (22-159  $\mu$ g L<sup>-1</sup>) and leaching (30–70  $\mu$ g L<sup>-1</sup>) from soils from shooting areas have been found and considered serious Sb contamination (Okkenhaug et al. 2013). According to the World Health Organization (WHO 2017) the Sb concentration limit for drinking water is 20 μg L-1. Streamflow is often the drinking water of an area. Fortunately, the Sb concentrations in this component of the hydrological cycle in the fir stand in our work are much lower (at least 500 times the concentration limit).

The average concentration of Se for surface waters is 0.20 μg L<sup>-1</sup> (Lemly 2004). However far higher concentrations (140-1400 μg L<sup>-1</sup>) were found in agricultural drainage water (Yan & Zhang 2006) and mining wastewater (3-12 μg L<sup>-1</sup>) (Wasewar et al. 2009). For Se the World Health Organization has given guidelines for 40 μg L<sup>-1</sup> to be the highest concentration in drinking water. In our work, the Se concentration found in streamflow was 0.093 μg L<sup>-1</sup> much lower than the above-mentioned concentrations.

Vanadium concentrations in proportion of EU surface waters have a concentration range 0.05 μg L<sup>-1</sup> to 19.5 μg L-1; median 0.46 µg L-1). However, many surface waters exceed this median (Watt et al. 2018). The dissolved concentration of V in river water is about 0.7 μg L-1, according to Schlesinger et al. (2017). For V there is no limit to the concentration recommended by the World Health Organization. The Italian Ministry of Health has set a limit of 140 µg L-1 (Russo et al. 2014). The Dutch Government set much lower limits (Smit 2012), proposing standards for water quality concentrations for dissolved V of 1.2 and 3.0 µg L-1 for long-term and short-term exposure, respectively. In both cases the concentrations V in the rain, in the soil solutions but also in the streamflow water (0.301 µg L-1) of the fir stand (Table 1) are lower than the safety limits.

#### Soils

Although the focus of this work is the hydrological cycle, the soil content of the three trace elements (Table 2) is of importance to compare contaminated sites either forested or agricultural ones. Average values reported are 0.900 mg kg<sup>-1</sup> for Sb (Kabata-Pendias & Pendias 2001), 0.40 mg kg<sup>-1</sup> for Se (Fernández-Martínez & Charlet 2009) and 150 mg kg<sup>-1</sup> for V (Roychoudhury 2020) and. The maximum

concentrations of these two elements in the soil of the fir plot were and 0.694 mg kg<sup>-1</sup> for Sb, 0.672 mg kg<sup>-1</sup> for Se and 131 for V mg kg<sup>-1</sup>, respectively. The Se concentration is somewhat higher than the average, whereas the others are a little lower.

High concentrations of these elements have been found around the world. Takeda et al. (2004) found a concentration range of 39-540 mg kg<sup>-1</sup> for V and 0.10-1.70 mg kg<sup>-1</sup> for Sb in Cambisol soils of Japan. Particularly high concentrations of Sb are derived from mining and shooting-related activities. Concentrations of 15 g kg<sup>-1</sup> were found in an area in southern Tuscany in Italy where Sb ores had been mined (Barroni et al. 2000). The soils of shooting areas had a high Sb load due to its high percentage (2-8%) in projectiles (Lewis et al. 2010). Johnson et al. (2005) found 13.8 g kg<sup>-1</sup> Sb in the topsoil in Switzerland in a shooting area. Concentrations of V as high as 0.738 g kg<sup>-1</sup> (Teng et al. 2009) and 3.51 g kg<sup>-1</sup> (Panichev et al. 2006) have been reported in metal mining areas.

The average Se content in most soils ranges from 0.01 to 2 mg kg<sup>-1</sup>. Dhillon and Dhillon (2003) proposed a range of 0.1 mg kg-1 for the limit in concentration under which soils are considered deficient in selenium and 0.5 mg kg-1 of selenium for a soil to be seleniferous. However, much higher concentrations (1200 mg kg-1) have been reported for soils with high organic matter content in Ireland (Fernández-Martínez & Charlet 2009). The soils in our work are considered to have a normal concentration.

## **Conclusions**

The enrichment of the three elements in throughfall deposition is derived from dry deposition either transported or regional. Antimony and selenium have probably similar origins related with long-range transport. Further research is needed to verify if vanadium can be transported from marine sources. The concentrations in soils and waters are characteristics of a non-contaminated forest ecosystem.

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