

Experimental Approach for the Study of the Contamination and the Accumulation of Heavy Metals in the Cork Oak and the Stone Pine

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ABSTRACT: *This study aims to evaluate the pollution by Heavy Metals (HMs) of the stone pine (*Pinus pinea* L.) and cork oak (*Quercus suber* L.) in dry- and wet- season, motivated by the road traffic, at the level of the forest of Hafir located in Tlemcen (Algeria). The distribution and the migration of 9 HMs in the green leave and needles and the litter (viz. dead leaves) were studied, viz. Cd, Ni, Co, Cr, Pb, Cu, Zn, Fe, and Ag, in addition to five major elements, i.e. Ca, Mg, K, Na, Mn. The HM -contents are measured by Flame Atomic Absorption Spectroscopy (FAAS) after their dissolution according to several methods. The mineralization of HMs by the strong acids seems to be a good technique by comparing with other techniques, it reported the higher concentrations of metals which is more important for the dosage of the cadmium. This study allowed to understand that the quantities of HMs transported in the atmospheric releases, once deposited on the aerial parts of the leaves and the litter, their futures depend on the accumulative character of the plant, as well as for each metal, there is an adequate chemical extraction with a representative variation.*

KEYWORDS: *Pollution; Heavy metals; Hafir; The mineralization; Chemical extraction.*

INTRODUCTION

Several heavy metals (HMs), such as Cu, Zn, Ni, Co are essential for plants [1] but can be toxic at high concentrations. Other metals, such as Cd, their presence is toxic for the plant [2-3].

Accumulation of metals may differ according to the different genotypes of plants: some plants called "exclusives": a few collect the metals even when they are at high concentrations in the soil. Other called "Accumulators": presents strong accumulations of HMs

even at very low concentrations in the soil. However, when the concentration of metals in the soil raises, their accumulations don't increase, probably because of the competition between metallic ions in the sampling sites. The latest ones called "indicators": the metal concentrations in their tissues reflect the concentration of metal in the soil and increase linearly with it [4].

The concentration of HMs decreases with the development of the plant [5], and detracts also in the tissues

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(the dilution effect). In corn, it appears that the transfer of Cd, Cr, Cu, Mn, Ni, Pb and Zn to the plant, is interrupted at the end of the vegetative cycle [6].

The litter is an essential energy source for the heterotrophic organisms in forest ecosystems, it is the main entryway into the trophic system of many organic elements in the soil. about 90% of the biomass produced by plants penetrates the pool of the organic matter that constitutes the litter [7]. Litter degradation is vital for the performance of the entire ecosystem [8]. In general, the concentration in the leaves increases with age, for example, in the brown leaves (The oldest) of *Armeria maritima* subsp. *halleri*, the concentrations of Cu, Cd, Zn, and Pb are 3 to 8 times higher in comparison with the young leaves [9]. This observation suggests an internal transport from green leaves photosynthetic active, to the leaves which are about to fall. The accumulation of Cd was also observed in trichomes of several species [10]. In some ecosystems, metal concentrations are naturally elevated, which is the case, for example, in the soil evolving on rocks ore carriers (especially Zn, Pb, Ni, Co, Cr, Cu, Mn, Cd, Se, As) or tropical alumino-ferrous acid soils [11].

The plants are exposed to HMs in two ways: by the aerial parts and by the roots. HMs can penetrate through the aerial parts (leaves, stems, and fruits), from particles suspended in the air, gaseous compounds or compounds dissolved in rainwater. HMs can also penetrate through the roots from the ground.

The purpose of this study is to obtain the highest extraction yield to identify the actual rate of pollution, and since for example, the digestion of metals by calcination causes the loss of some volatile elements, such as the lead concentration, we opted for new techniques to compare the results. Our choice is focused on a forest distant from any source of entropic pollution other than that due to road traffic near the forest, or to the natural impact by fires. Two campaigns of sampling are retained: the contribution of rain and the diffusion of pollutants in dry weather, basing on the accumulation capacity of two species dominant in the forest: the stone pine (260 m of the road axis) and the cork oak (600 m from the road).

EXPERIMENTAL SECTION

The study area

The Hafir forest is located in the south-west of the town of Tlemcen (North-west of Algeria) (Fig. 1).

The most important species that inhabit this forest are the cork oak (*Quercus suber* L.), green oak (*Quercus ilex*) and the zeen oak (*Quercus canariensis*). The Hafir pinewood is a low perch of reforestation that has supplanted the field of the green oak, the substrate being fersialitic more or less deep. The forest of Hafir is constituted essentially from an old forest cork oak (200 to 250 yr), with some young coppice. The majority of stands (2,300 ha) are pure, while the others are mixed with the other hardwood species, such as the green oak, the zeen oak and in lesser degrees the barbary thuya (*Tetraclinis articulata*) and the berried-cedar (*Juniperus oxycedrus*).

The massif suffered several successive fires, the most important was registered in 1892 with 1783 ha. This fire was the origin of the release of the degradation processes in this forest [12]. Over a reference period of 44 yr (1961-2005), the passage of fire varies from one year to another, the annual average is estimated to 98 ha [13]. This repeated passage of fires is the main factor of degradation of these stands and the structure becomes very simple [14].

The study station is located near a road axis (low car traffic). The most dominant winds in the region are those from the northwest. The region belongs to a sub-humid climate, which is characterized by a cool winter and a dry summer. The Hafir forest is located between the following geographical coordinates:

$$\begin{array}{ll} X_1 : 118 & Y_1 : 172.7 \\ X_2 : 124 & Y_2 : 177.3 \end{array}$$

Sampling method

Four sampling compartments were defined: stone pine needles, stone pine needles superficial litter, cork oak leaves, cork oak superficial litter. In the present study, two sampling campaigns have been carried out: the first at the beginning of the winter season (dry season) and the second in wet-weather (after rainfall leaching) (rainy - season):

Pine needles and superficial litter

The sampling of the stone pine needles and superficial litter is carried out at the pinewood level of the forest (plot 1) (Fig. 2), at a distance of 260 m from the road, at the following points:

- Average altitude: 1270 m
- Geographic location :
Latitude: 34°46'43,82'' N; Longitude: 1°26'1,06'' W

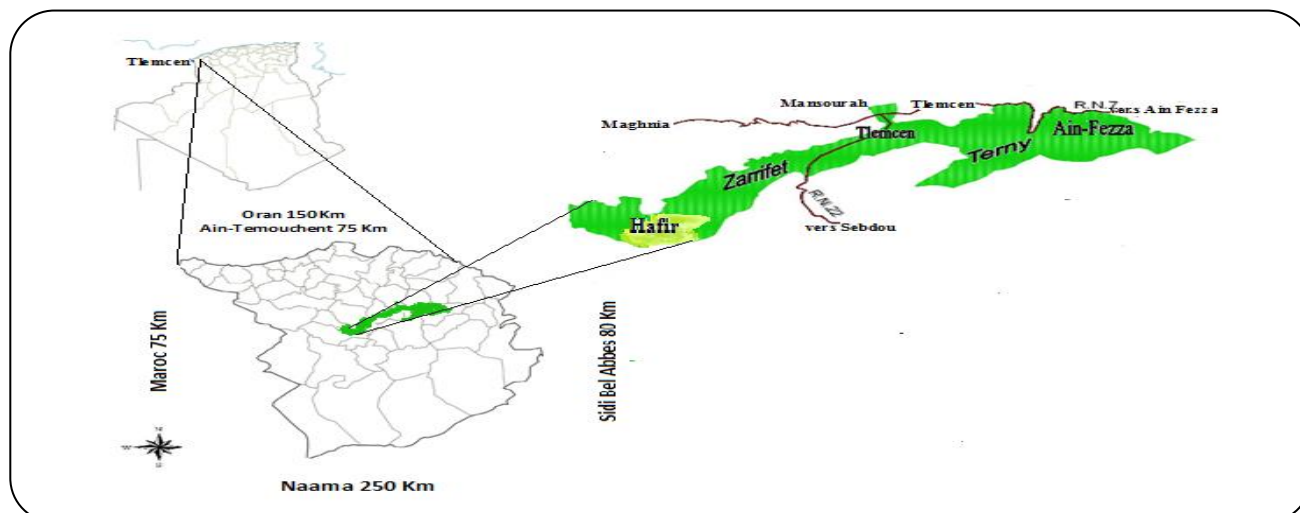


Fig. 1: Location of the Hafir forest.



Fig. 2: Stone pine plot.

A quantity of 500g of pine needles was collected at the height of 2m of 4 ventilated trees and located on the diagonal of the plot. As for the superficial pine litter specimens, the dead and green needles (fig. 3) are collected avoiding sampling the soil. Pine needles and litter samples are stored separately in a labeled polystyrene bag, for the level/concentration of the metals assay.

Cork oak leaves and surface litter

Samples of cork oak leaves and surface litter were gathered at the leafy level of the forest (plot 2) (Fig. 4) at a distance of 600 m from the road, and of rugged mountainous relief at the following point:

- Average altitude: 1227 m

- Geographic location :

Latitude: 34°47'6,77 N ; Longitude: 1°25'54,36'' W

As for the sampling of cork oak leaves, they were collected at the height of 2m of 4 ventilated trees and located on the diagonal of the plot. On the other hand, samples of the superficial cork oak litter were taken, by collecting dead leaves at 2 cm depth and avoiding the surface layer of the soil (Fig. 5). The samples having a mass of approx.500 g, were then stored in a labeled polystyrene bag, at 4 ° C. and protected from light.

Analysis method

The plants were dried at 40°C until constant weight. The water -content was determined on a fraction



Fig. 3: The superficial litter of stone pine.

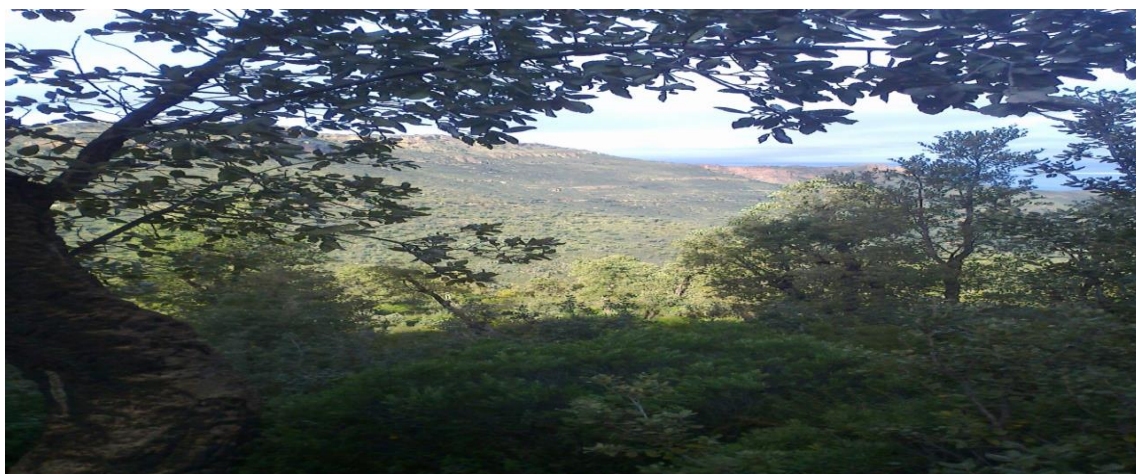


Fig. 4: Cork oak plot.



Fig. 5: Illustrating picture of the sampling of cork oak superficial litter.

of the sample at a temperature of 103 ± 2 ° C. The samples were dried and crushed to a fraction <500 μm [15]. The dissolution of the metallic elements was carried out on a ground sample (1 g sample). The samples were dissolved according to five techniques for comparison purposes:

The first protocol was the dissolution of the metallic trace elements by etching with hydrochloric and nitric acids (commonly known as aqua regia) of the solid phases, this method leads to obtaining a concentration intended for assays by AAS. The second protocol was the mineralization with a mixture of strong acids of which 1 g of sample was weighed in an Erlenmeyer of 250 mL with 7 mL of HNO_3 + 21 mL HCl and carried under a heating plate until total evaporation of the solvent, then 10 mL of HCl and 20 mL HClO_4 was added, go to white fumes, cool and add 50 mL H_2O , proceed until boiling temperature then after a hot filtration, gauge. The sample was stored at 4 ° C for the FAAS dosage.

The other three protocols used for the dissolution were inspired by the IIC (Inter-Institutes committee of analytical techniques) methods:

Use of two different mineralizations [15]:

1- Dry process

2- Dry process with silica removal

The last one was the dry process with silica removal modified: a dry procedure with silica removal was added to the table by replacing the hydrofluoric acid (HF) by HNO_3 after the calcination for comparison (Table 1).

The samples thus dissolved were assayed by FAAS. All the analyses were carried out by FAAS (Aurora AI1200).

RESULTS AND DISCUSSION

The quantities of HMs transported in atmospheric discharges deposited at the level of the aerial parts of the needles, present concentrations which allow the use of the calcination extraction, followed by the acid mineralization. The results of the assay of metals in stone pine needle, cork oak leaves, as well as litters for both seasons (dry/wet), are presented in Tables (2a-5b), where:

M₁: mineralization by aqua regia

M₂: mineralization by the mixture of strong acids

M₃: Dry process mineralization

M₄: Dry process with silica removal (by HNO_3) mineralization

M₅: Dry process with silica removal (by HF) mineralization

The total analyzes evaluate the total metal stock given in (mg/kg).

There are significant differences in heavy metal contents ranging from pine needles to litter or from cork oak leaves to litter during the two sampling campaigns. In the study area, which is exposed to atmospheric pollution of natural sources (fires) and anthropogenic, where the only likely source is the road traffic, the atmospheric depositions of HMs occur on the aerial parts of plants, by rains or dust. A part of this contamination can be removed by simple washing with water, which shows that it remains on the surface of the aerial parts in a superficial deposition. Another part may remain trapped in the leaves. A third part of the HMs can likely be transported in the plant, but its importance is controversial [16]. However, the extent of the area subject to HM deposits is specific to the site: it varies mainly according to three major factors: traffic flow, prevailing wind patterns, the topography of the road and the site.

In fact, for this study, natural and accidental pollution are the main factors affecting the deposition of metals on cork oak leaves, tree 20 m high, evergreen trunk with thick cork bark and largely cracked, with leaves (3-7 cm long), ovate, elongated, shiny, sinuous, or slightly toothed. The oak is resistant to fire, due to the thickness of its bark. After crossing the atmosphere and a stable layer of air near the vegetation cover called the boundary layer, the pollutants reach the leaves [17].

The dust, containing the micropollutants, accumulates on the aerial parts, particularly the leaves, by the interception-deposition process. This leaf surface deposition can be described as latent pollution because the cuticle is considered as an impermeable barrier that prevents penetration into the leaves. The deposit may, however, possibly penetrate into the plant, after its dissolution, which will depend on the intensity of the wet episodes and their acidity.

Among the factors that influenced the sensitivity of cork oak, wind and climate; when the wind speed increases, the thickness of the boundary layer around the leaf decreases and the resistance to the diffusion of pollutants becomes lower. Pollutants can be absorbed by stomata more easily. It should be noted, however, that wind also tends to cause stomatal closure to limit water loss, which helps to reduce pollutant absorption [17].

Table 1: Analytical techniques for the mineralization of stone pine needles, cork oak leaves and the litter.

Dry process	Dry process with silica removal
Calcined at 420 ° C for 4 hr (heating program), added 5 mL HNO ₃ to ashes evaporation	
Addition of 10 mL of HNO ₃ 50% Filtration Gauging to 100 mL	Addition of 5 mL of HNO ₃ 50% Filtration Filter calcination at 520 ° C (heating program) Return of the ashes by 5 mL of HF Evaporation addition of 5 mL of HNO ₃ Evaporation addition of 5 mL of HNO ₃ 50% Filtration Gauging to 100 mL

In the wet season, vegetation is more sensitive to pollutants than in the dry season, partly because moisture allows surface deposits to dissolve and penetrate through the cuticle and, secondly, because it increases the degree of opening of the stomata.

While for the superficial litter, when the leaves grow old, the effectiveness of this barrier is impaired, it appears micro-cracks and pollutants that normally remain on the surface can easily penetrate. At the sampling site, less than 20% of the leaves fell; it is obvious that the conditions associated with fires are responsible for this effect, of which growth reductions are often observed;

Otherwise, the leaves with a large surface have an absorption capacity more important than needles because their surface is smaller for the same exposure rate [18, 19, 20].

The pine exhibition to motor vehicle emissions accelerates the corrosion and fusion of epicuticular waxes in the form of needle tubules [21]. This acceleration of the degradation of the waxes cause occlusion of the stomata responsible for early senescence of the needles (on healthy trees, the phenomenon is natural: the degradation of the cuticular waxes increases with the age of the needles). Stomatal obstruction inhibits transpiration and photosynthesis, which has side effects on the plants.

The results of the analysis of metallic trace elements in plants and superficial litters show that for:

Ni, Pb, and Co

In dry-season, Ni is present in the stone pine litter, but at a value corresponding to the lower limit of the toxicity threshold relative to these elements, and the

mineralization by a strong acid mixture is favored for the four samples, followed by the mineralization by aqua regia which gives values close to the previous mineralization, as well as the nickel contents decrease after the rainy weather, which is explained by washing the leaves as well as the infiltration of the metals via the litter to the ground.

On the other hand, the cork oak accumulates the Pb in the leaves. The measured lead levels remain in the standard. Pb concentrations are higher in wet weather (after runoff), which corresponds to the literature where the lead content is significantly higher wet season than dry; especially during snowfall [21]; on the other hand, the lead deposit is superior when the prevailing wind blows perpendicularly on the road and when the temperature rises [22]. Arvik and Zimdahl (1974) [23] have shown that very fine lead particles can enter into the stomata, but this process can only be responsible for a small part of lead contamination of the leaves, but it does not have effects on plant growth [24].

The lead concentration in the litter can be explained by the degradation of the epidermal layers that allow access to lead to an internal level [25]. The dosage that raised the highest contents is the mineralization by the aqua regia for the dry season and in the rainy season it is the mineralization by the aqua regia for both of the stone pine needles and the pine surface litter, and the calcination followed by recovery with HNO₃ for cork oak leaves and oak litter.

The cobalt contents are low and in the standards, and these values decrease after the rain for all samples, in the wet season it is the mineralization by the mixture of strong acids which gave the highest concentrations and in dry

Table 2a: Pollutant contents of the stone pine needle samples in mg/kg.

Mineralization	Ni	Pb	Co	Cu	Fe	Mn	Zn
M ₁	5.4 / 7.6	44 / 51	34 / 6.4	11 / 17	330 / 412	22 / 29	260 / 96
M ₂	40 / 6.6	- / 5.4	- / 14	5.8 / 13	546 / 859	38 / 37	378 / 105
M ₃	9.4 / 4.3	6.6 / 3.8	6.9 / 0.6	4.7 / 8.1	256 / 563	27 / 27	174 / 88
M ₄	6.1 / -	9.3 / -	5.5 / 5.2	6.5 / 26	180 / -	48 / 5.1	510 / 29
M ₅	3.3 / -	15 / 17	14 / 0.4	7 / 12	129 / 9.2	0.4 / 9	198 / 265
Toxicity value [5]	10-100	12-300	15-50	20-50	1000	300-500	100-400

Table 2b: Pollutant contents of the stone pine needle samples in mg/kg.

Mineralization	Cd	Cr	Na	Mg	K	Ca	Ag
M ₁	0.4/-	17/2.7	370/140	1700/2763	820/1774	6020/2177	- / 17
M ₂	4.8/ -	16/9.2	704/573	1440/3070	1020/2347	6560/3420	6/5.3
M ₃	3.9/-	-/1.1	450/434	1970/2904	120/4351	5310/3000	-/-
M ₄	1.6/-	28/45	133/92	149/104	124/42	606/-	3.7/-
M ₅	0.2/-	16/3	247/258	212/176	424/164	145/250	-/-
Toxicity value [5]	5	3	-	-	-	-	-

Table 3a: Pollutant contents of the stone pine litter samples in mg/kg.

Mineralization	Ni	Pb	Co	Cu	Fe	Mn	Zn
M ₁	12/7	14/30	28/0.1	14/7.7	880/1477	34/40	390/74
M ₂	26/6.5	-/-	2.6/13	6.2/16	1284/2660	46/57	482/151
M ₃	17/3.7	0.1/-	11/0.7	6.3/22	866/2258	38/52	236/108
M ₄	12/-	4.9/42	12/6.2	6.6/27	183/516	14/8	400/255
M ₅	15/0	24/-	4.4/2.6	5.5/7.9	557/710	10/8.8	222/81
Toxicity value [5]	10-100	12-300	15-50	20-50	1000	300-500	100-400

Table 3b: Pollutant contents of the stone pine litter samples in mg/kg.

Mineralization	Cd	Cr	Na	Mg	K	Ca	Ag
M ₁	1.4/-	30/0.7	140/132	1700/2154	192/509	12100/3775	8/-
M ₂	3/-	30/0.8	346/398	1500/2781	240/945	8140/5537	10/-
M ₃	2.7 / -	- / 1.2	151/254	1280/2533	110/1163	8000/5801	0.9/-
M ₄	1.1/-	8.2/5.4	197/105	255/311	110/186	743/-	2.9/-
M ₅	1.1/-	30/5.2	168/345	261/306	606/632	3.5/22	-/-
Toxicity value [5]	5	3	-	-	-	-	-

Table 4a: Pollutant contents of the cork oak leaves samples in mg/kg.

Mineralization	Ni	Pb	Co	Cu	Fe	Mn	Zn
M ₁	17/4.6	72/43	0.4/2	16/13	540/307	140/188	240/69
M ₂	12.4/4.7	-/75	3.9/9.5	9.6/17	780/869	194/202	230/105
M ₃	5.3/2.3	14/-	16/0.3	5.7/27	214/569	53/125	95/78
M ₄	8.9/2.2	-/97	-/7.1	4.1/27	282/-	7.1/32	214/43
M ₅	9.3/-	-/35	3.7/3.2	1.9/10	133/40	23/72	98/84
Toxicity value [5]	10-100	12-300	15-50	20-50	1000	300-500	100-400

Table 4b: Pollutant contents of the cork oak leaves samples in mg/kg.

Mineralization	Cd	Cr	Na	Mg	K	Ca	Ag
M ₁	-/-	22/5.3	140/135	2040/2607	150/1632	12700/4124	4/-
M ₂	4/3.4	23/0.9	384/402	2540/3175	2120/2243	5620/5955	-/-
M ₃	1.2/-	-/3.1	80/257	900/3055	1210/3770	6070/6562	0.3/-
M ₄	-/-	0.5/4.7	149/89	92/179	65/521	296/-	2.3/-
M ₅	0.2/-	23/7	211/202	212/180	473/174	579/153	-/-
Toxicity value [5]	5	3	-	-	-	-	-

Table 5a: Pollutant contents of samples of the cork oak litter in mg/kg.

Mineralization	Ni	Pb	Co	Cu	Fe	Mn	Zn
M ₁	9/6.2	42/-	17.2/2.5	12/13	3746/4043	150/186	320/99
M ₂	22/12	-/92	7.2/14	17.8/22	3920/4340	206/249	2062/105
M ₃	4/5.7	13/82	1.7/35	17/30	1487/3462	102/167	1300/3434
M ₄	0.5/5.4	-/84	9/-	3.9/38	284/1843	8.5/29	340/581
M ₅	21/-	-/25	14/7.3	5.7/14	1134/1738	20/18	204/256
Toxicity value [5]	10-100	12-300	15-50	20-50	1000	300-500	100-400

Table 5b: Pollutant contents of samples of the cork oak litter in mg/kg.

Mineralization	Cd	Cr	Na	Mg	K	Ca	Ag
M ₁	3/-	30/5.3	210/138	2160/2569	420/758	10300/4430	4/-
M ₂	7.2/14	40/3.5	446/318	3900/3270	560/1628	11960/7086	22/-
M ₃	1.6/-	-/3.6	138/223	1040/2295	580/1059	20200/-	0.2/-
M ₄	2.4/4.8	5.9/2.5	80/229	270/1187	67/176	1280/2733	2/-
M ₅	-/-	40/8.5	110/868	2360/278	1330/2328	26/30	-/-
Toxicity value [5]	5	3	-	-	-	-	-

season it is the mineralization by the aqua regia except for the oak leaf where the calcination by the dry process is favored.

Cu, Fe, and Mn

The cuticle can leave pass elements such as cobalt, copper or manganese [26]. When the leaves get older, the effectiveness of this barrier is impaired, it appears a micro-cracks and the pollutants that normally remain on the surface can easily penetrate.

Cu, Fe, and Mn -contents increase after the rain, but generally remain in the standards for pine needles, as well as for cork oak leaves, except for litter at the two plots, where Fe exceeds the norm with a value between 1284 and 4340 mg/kg, which can be explained by the leaching of the soil.

For the dry period, the mineralization by aqua regia is favored except for the cork oak litter where the mineralization by the mineralization with the mixture of strong acids is favored while for the wet period the calcination followed by recovery with HNO₃ recorded the highest levels for the four samples. While for iron and manganese for both seasons the technique for the four samples is favored by the mineralization by the mixture of strong acids.

Zn

Zinc, despite relatively low solubility, the lowest of the metals, is significantly the most absorbed by the vegetation, which explain the high rate and which exceeds the norm especially for cork oak litter 2062 mg/kg in dry weather and (3434 mg/g) in rainy weather, his plot that is present on a slope, therefore, has undergone the effect of runoff and it has experienced several fires. Conversely, cork oak leaves have a low accumulation of zinc.

Zn -content (510 mg/kg) in pine needles, in dry weather, exceeds the toxicity threshold, therefore stone pine strongly accumulates zinc in the needles as well as in the litter. It appears that the inputs of the Zn by atmospheric road way originate from the brakes, the tires and it also comes from the lubricants.

For pine needles, in dry weather, it is the calcination followed by a recovery with HNO₃ which gave us the highest content and the mineralization by the mixture of strong acids for the other three samples, whereas for the second sampling campaign

mineralization by the mixture of strong acids seems to be favored for cork oak leaves and pine litter whereas for the cork oak litter where the concentration is too high, the proper chemical extraction is the dry calcinations, and wet calcination followed by HF mineralization is favored for pine needles.

Cd

Cd -content in the plots of stone pine and the cork oak in dry weather remains below the toxicity threshold (5 mg/kg). It is absent in wet weather in needles as well as pine litter and it decreases for the leaves, this can be explained by the leaching, by the rain, of the small quantities existing on the surface, by cons for the cork oak litter, the cadmium presents a risk with a concentration that exceeds the toxicity threshold and which doubles after rainwater runoff, which requires monitoring of the cork oak plot that accumulates cadmium over time. For both periods the mineralization by the mixture of strong acids is the proper cadmium dosage technique where the contents are the highest compared to the rest of the other techniques.

Cr

For all samples the chromium contents far exceed the threshold of toxicity of the plants. Stone pine needles and cork oak leaves strongly accumulate the chromium. The chromium content is higher for pine needles in wet weather, whereas it decreases for the rest of the samples after rain. Chromium may originate from dust emitted by the catalytic converters of brake linings, clutch discs, automatic transmissions.

The technique adopted for the dosage of the chromium in the leaves of cork oak and the stone pine litter is the mineralization by the aqua regia in dry weather, and the mineralization with the mixture of strong acids for the cork oak litter, and the calcination followed by recovery with HNO₃ for the pine needles for both periods while the calcination followed by a recovery with HF is adequate for the other three samples in wet weather.

Na, Mg, K and Ca

Na-contents increase after the rain except for pine needles where it decreased, for both periods, it is the mineralization by the mixture of strong acids which

is favored for all the samples except for the oak litter where the calcination followed by recovery with HF has reported the highest content in the wet season.

The Mg-contents increase after the rain, except for the cork oak litter where it has decreased after the runoff, and for cork oak plot it is the mineralization by the mixture of strong acids for both periods which is favored then that for the stone pine plot in the wet period it is the mineralization by the mixture of strong acids whereas, for the dry period, it is the dry calcination for the needles and mineralization by aqua regia for the litter of the pine.

The calcium contents decrease after the rain for all samples, during the dry periods for cork oak leaves and pine litter it's the mineralization by aqua regia which is favored whereas for the oak litter it's the dry process, and for the stone, pine needles are the mineralization by the mixture of strong acids.

For the potassium, for all samples, the contents increase after the rain and the mineralization with the mixture of strong acids and the dry process calcinations raise the highest concentrations.

Ag

Silver is present in trace amounts in plants (pine and leaves) as well as for both of the litters.

CONCLUSIONS

Forest ecosystems are privileged areas for the deposition of pollutants carried by the atmosphere, where the plant contamination is susceptible to intervene either by atmospheric deposition or by root absorption. The stone pin has no major problems at present, but the effect of the pollution by Cr, Zn, and Pb HMs is observable in plants, which is inhibition of growth. This is often accompanied by many other indications of dysfunction: leaf chlorosis, major necrotic lesions, progressive yellowing, folding or drying of the foliage. The results obtained have shown that in terms of the total content, the recorded values are in the most lower than standards taken into consideration, except for the Cr and Zn, which originate from the deposits of atmospheric pollution, due to the road, where the contents for the set of samples have largely exceeded the standard. The mineralization of Metallic Trace Elements (MTE) by strong acids seems to be a good technique which gives the highest concentrations in comparison with the rest of the mineralization processes.

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