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Arsenic and Cadmium in the Hydrological Cycle and Soil in a Maquis Broadleaved Evergreen Forest Stand in Greece. Sources of Some Uncertainties

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Abstract: The concentrations and fluxes of arsenic (As) and cadmium (Cd) were examined in the hydrological cycle (bulk, throughfall deposition and percolation water), litterfall and soils in a maquis broadleaved evergreen forest stand in western Greece. It was found that the enrichment of As in the atmosphere was both due to suspended geogenic material and long range transfer, whereas for Cd the long range transfer was the predominant way for deposition in the ecosystem. Three models were assessed to find the volumes of percolation water and therefore the fluxes of As and Cd in the water that leave the ecosystem permanently. When calculating the total amounts of the heavy metals in soils, the statistical uncertainty derived from every soil layer has to be taken into account.

Keywords: arsenic; cadmium; hydrological cycle; soil; fluxes; litterfall

1. Introduction

Cadmium a heavy metal together with As, a metalloid, are of great interest in bioavailability studies (due to their toxicity), as listed by the U.S. Environmental Protection Agency (EPA)[1]. The World Health Organization (WHO) provisional guideline value for As and Cd concentrations in drinking water are 10 and 3 μg L^{-1}, respectively [2].

The anthropogenic sources of As include the use of arsenical pesticides, application of fertilizers, burning of fossil fuels, mining of As containing ores and disposal of industrial wastes [3]. The major anthropogenic sources of Cd are electroplating, mining, stabilizing plastics, alloy, cement, pigment, manufacturing batteries, fossil fuel combustion, high phosphate fertilizers, and municipal and sewage sludge incineration [4].

Both elements can be toxic to plants. The As species having V and III oxidation numbers can affect plant metabolism. AsV is a chemical analog of phosphate that can disrupt at least some phosphate-dependent aspects of metabolism[5]. The effects of Cd on plants are growth retardation, alteration of photosynthesis, interferences with enzymatic activities, mineral uptake, protein metabolism and membrane functioning[6] .

The fact that remote forests can be affected by the deposition of heavy metals prompted scientists to study their status and cycling in forest ecosystems not near industrial and/or urban areas [7-9] . The reason for this deposition is the long-range transfer of some elements above forests and their subsequent deposition on forests.

The aim of this work was twofold; to study the cycling of As and Cd in an evergreen broadleaves forest stand and underline some uncertainties inherent to the studies of heavy metals. The study involves the hydrological cycle of the two elements, their fluxes in litterfall and their concentration as well as their stocks in soils.

2. Materials and Methods

2.1. Study area

The experimental plot is in the area of the city of Amfilochia in western Greece. It has an altitude of 332 m, a northeast aspect and the slope is moderately steep (14.4 %). It has an area of 0.274 ha and the average annual rainfall is 1123 mm derived from 20 years of observation (1996-2016). The age of the stand has a range of 60-100 years and its canopy closure is about 1.2 as there is overlapping of canopies of the various species. The vegetation consists of the evergreen species holm oak (*Quercus ilex* L.), strawberry tree (*Arbutus unedo* L.), Kermes oak (*Quercus coccifera* L.), tree heaths (*Erica arborea,* L.), march heath (*Erica verticillata* L.) and green olive tree (*Phillirea latifolia* L.)

The soil was developed on sandy flysch, it is deep, well drained and classified as Eutric Cambisol [10].

2.2. Deposition sampling

Sampling of bulk and throughfall deposition was done on a weekly basis and a composite sample was formed every month according to weekly volumes. Bulk deposition was collected in a nearby forest opening with two polyethylene funnels, whereas throughfall was collected with 20 collectors, identical to those for bulk precipitation, placed randomly in the plot. The volume of water samples was measured, and all samples were stored in a fridge at 4 °C. Sampling started at the start of October and ended approximately the same month of the next year. These periods are usually the hydrological years in Greece. Three hydrological years were sampled for this work, i.e., 2012-2013, 2013-2014 and 2014-2015.

2.3. Litterfall collection

For litterfall collection, 10 littertraps (cylindrical plastic buckets), having a collecting area of 0.242 m2 each, were placed systematically along a line in both plots, approximately 0.50 m above ground at a distance of 10 m from each other. The bottom of each trap was drilled so that rainwater could drain out. A plastic net was put at the bottom of the litter traps to keep small material in the trap. Collection of litterfall was carried out approximately every three or four months and not in a shorter time space to have enough material for chemical analysis. Initial and final samplings were done the same dates as in deposition. A pooled sample from all traps was formed and transported to the laboratory for analysis. For each collection, the leaves formed one sample, whereas for the other fractions we had a composite sample per year. Accordingly, we had three or four leaves samples per year and one sample from the other fractions. All litterfall fractions were dried at 80 °C, ground in a special stainless mill and stored for analysis.

2.4. Collection of soil samples

Soil collection was done by systematic sampling in the summer of 2007. The layers from which samples were collected were the L, the FH from the organic horizons and from the mineral soil layers the depths were the 0–10 cm, 10–20 cm, 20–40 cm and 40–80 cm. Three replicates per layer in space were formed.

The L and FH layers were weighed. The bulk density of mineral soils in all layers was assessed by a cylinder having a volume of 129 cm^3. The samples of the FH and mineral layers passed through a 2 mm sieve.

Subsamples of the L, FH and mineral soils were pulverized in a ball mill for total elemental analysis.

2.5. Chemical analysis

Litterfall samples were digested in a mixture of HNO3-HClO4. Exchangeable Ca^{2+}, Mg^{2+} and K^{+} in the FH and mineral soil layers were extracted with a 0.1 M unbuffered $BaCl_2$ solution and their concentrations were determined with an atomic absorption spectrophotometer (Perkin Elmer 3110). The texture of soils was assessed by the hydrometer method. Cation exchange capacity (C.E.C.) of the samples was determined by the Na-acetate method [11]. Organic C was determined with the potassium dichromate method ($K_2Cr_2O_7$), while organic plus ammonium N was extracted with concentrated sulfuric acid (H_2SO_4) and its concentration was measured by the Kjeldahl distillation method [12]. For the total As and Cd assessment in soils, the samples were digested in a microwave oven with HF and aqua regia at a temperature range of 160–170 °C for 20 min. Concentrations of As and Cd in the digests of soils, litterfall as well as waters were measured with an ICP-MS instrument (Thermo iCAP Qc). Total Al in soils was determined with the Energy Dispersive X-Ray Fluorescence method (XEROS model of the TURBOQUANT Company).

2.6. Calculation and statistics

The influence of the earth's crust, or the enrichment factor, on the concentrations of the metals (M) in bulk deposition were assessed according to the following: The ratio values (Mb / Alb) over (Mc / Alc) stand for the degree of the effect of the earth's crust on the composition of rain. In the equation, Mb stand for the concentrations ($\mu g\ L^{-1}$) of M in bulk deposition, Alb is the concentration (μg L-1) of Al in bulk deposition; Mc are the concentrations (μg g-1) of the two M in the earth's crust and Alc the concentration (μg g-1) of Al in the earth's crust. The higher the ratio, the higher the impact of the long-range transport of an element, [13,14]. The last mineral soil layer (40─80 cm) was considered to represent the content of both As, Cd and Al in the earth crust for each plot. Those calculation were based on the measured data (Table 4). When that data is not available, the average values found in literature are used. In this case, the average concentration of Al is 8.8%, that of As 1.5 $mg\ kg^{-1}$ and that of Cd 0.1 $mg\ kg^{-1}$ [15]. Both methods were used and compared through an ANOVA test. For this comparison, all values in the three hydrological years were used (25 in total). The data had to be transformed into logarithms to conform to the criterion of normality.

Fluxes of As and Cd in bulk, throughfall deposition, percolation water and litterfall were calculated by multiplying the concentrations of metals in litterfall with the respective amount of water and masses in the hydrological cycle and litterfall, respectively. Litterfall was analyzed for two hydrological years, i.e., 2012-2013 and 2013-2014 and not for three, as there was no data for the third year.

Percolation monthly water (mm) derived from a depth 40-80 cm was calculated and compared with the simulated values estimated from two different hydrological models (WBS3 and Brook90). For the calculation of deep percolation rates in the study area [16] we applied the following procedure: Soil physical characteristics (soil texture, hydraulic conductivity and bulk density) were determined in the laboratory from 12 mineral soil samples, the same samples collected for the As and Cd assessment. The values from the physical parameters were used as input data points in RETC model the [17] for the extrapolation and estimation of pF curves which disclose the relationships between pressure head (h) and hydraulic conductivity (K) with soil moisture (θ). Afterwards, deep percolation was calculated (in mm) from the daily mean soil moisture and the respective K for the time of 24 h.

WBS3 [18] is a daily deterministic forest-hydrological model. For the calculation of deep percolation from the application of WBS3 model, we followed the previous procedure by converting the infiltration water (output variable) into soil moisture above the available water content (output variable) and applying the estimated K(θ) relationship.

Brook90 [19] is a physically based 1D semi-distributed soil-plant-atmosphere model. Its simulation calculates directly the daily vertical flow rate between layers and deep percolation rates by applying a subroutine following the Darcy’s Law and using a gravity unit gradient which is proportional to the hydraulic conductivity of the bottom layer corrected for the stone fraction [20]. The actual percolated water (mm) was compared with the other two models through a pair t-test. In order to avoid negative values and zeroes, a logarithm transformation was applied (data +2).

The stocks of total As and Cd in mineral soil layers up to 80 m depth were calculated by multiplying the measured metal concentrations in each soil layer with layer depth and bulk density of the fine earth (<2 mm). The volume of large stones, assessed by visual observation, was subtracted from the soil volume used for calculations in order to have a real picture of the soil mass. The metal pools in the L and FH horizon were calculated by multiplying the soil mass by the metal concentrations.

The standard deviations of the average amounts of metals in each soil layer were taken into account to calculate the standard deviation of the total amounts of HM. The next step was to calculate the confidence interval of the total stock of HM for 0.05 probability level [21].

The coefficients of variation for all parameters were calculated as the percentages of the standard variations over the means.

The residence time of the metals in the forest floor was found by dividing the amounts of metals in the forest floor (sum of the L and FH amounts) with the fluxes of As and Cd in litterfall and throughfall

3. Results

Table 1 shows the concentrations of As and Cd in the hydrological cycle and Table 2 the fluxes of the two metals in the hydrological cycle and litterfall. The variability of Cd concentration is far higher than that of As. Interestingly enough, it drops down in the percolation water. The fluxes of the two metals in litterfall are lower than those in bulk deposition and throughfall.

Table 1. Average concentrations (μg L^{-1}), coefficients of variations and ranges of the weighted means of As and Cd in the three hydrological years in throughfall, bulk deposition and percolation water.

	Throughfall	Bulk	Percolation water
		As	
Average	0.121	0.076	0.306
CV	(25)	(40)	(18)
Range	0.088-0.146	0.042-0.101	0.266-0.369
		Cd	
Average	0.043	0.040	0.050
CV	(67)	(87)	(12)
Range	0.016-0.074	0.011-0.078	0.043-0.054

Table 2. Average fluxes (g ha^{-1} yr^{-1}), coefficients of variations and ranges of the As and Cd fluxes in the three hydrological years in throughfall, bulk deposition, percolating water (three models) and litterfall.

	Throughfall	Bulk	Percolation water (profile method)	Percolation water (WBS3)	Percolation water (Brook90)	Litterfall
			As			
Average	1.071	1.704	0.349	0.352	0.229	0.746
CV	(21)	(5.3)	(26)	(37)	(53)	(4.3)
Range	0.819-1.232	1.633-1.806	0.277-0.451	0.209-0.464	0.141-0.368	0.723-0.760
			Cd			
Average	0.728	0.787	0.054	0.052	0.014	0.579
CV	(53)	(102)	(28)	(54)	(45)	21
Range	0.363-1.696	0.174-1.137	0.037-0.066	0.020-0.061	0.014-0.039	0.493-0.664

With regard to the percolation volumes, the lumped model of WBS3 yielded better results for the two hydrological years (2013-2013 and 2013-2014). It overestimated percolation volumes by 11,1% and 13,7% respectively, while in the 2014-2015 hydrological year the percolation flow was overestimated by 62,2%. In contrast, the BROOK90 overestimated percolation volumes, in the hydrological year 2014-2015 only for 10,5%, while in the rest investigated hydrological years (2012-2013 and 2013-2014) showed a low performance, underestimating the percolation volumes by 47,8% and 46,2%, respectively. The monthly values assessed by the models gave statistical differences. The actual (profile method) and WBS3 models of percolation water did not differ in a paired t-test. Both of them differ statistically from the Brook90 model. The profile method and the WBS3 gave close results with regard to the metals fluxes in percolation water (Table 2).

The comparison of the enrichment factors derived from literature and measurements for As and Cd (Table 3) showed that there were significant results for the enrichment factor with regard to As ($p<0.05$) but not for Cd. The values of Cd were found far higher than those of As.

Table 3. Values of crustal enrichment factors of As and Cd derived from (a) literature and (b) values measured in the area of the experimental plot. Values in the same row with different letters differ significantly for at least 0.05 probability level.

	Literature	**Measured**
	As	
Average	1042 **a**	165 **b**
Range	100-5,380	16-849
	Cd	
Average	298,875 **a**	217,461 **a**
Range	15,766-873,791	11,471-635,741

Table 4 contains the concentrations of soil properties, As, Cd, total Al and the coefficients of variations of all the parameters. The highest variability can be observed in the values of total Cd.

Table 4. Averages and coefficients of variations (in parentheses) of selected soil properties in the soil layers of the maquis plot. Clay and organic C are expressed in percentages (%), CEC in cmolc kg^{-1}, total As and Cd in mg kg^{-1}, total Al in mg g^{-1}.

Layer	pH	Clay	CEC	C	Total As	Total Cd	Total Al
L				49.4 (2.8)	0.216 (80)	0.088 (34)	1.59 (56)
FH	6.60 (3.7)		71.6 (8.1)	26.0 (7.1)	3.44 (9.3)	0.421 (18)	24.4 (7.9)
0-10 cm	6.26 (2.0)	23.6 (6.2)	24.5 (12)	5.0 (14)	6.34 (1.9)	0.257 (37)	58.5 (0.26)
10-20 cm	6.18 (6.6)	24.2 (14)	15.8 (20)	2.73 (17)	6.72 (1.4)	0.188 (34)	62.7 (0.82)
20-40	6.12 (2.3)	26.0 (19)	12.8 (11)	1.44 (17)	6.77 (3.9)	0.104 (24)	64.1 (1.2)
40-80	6.53 (5.7)	29.3 (15)	13.7 (13)	0.86 (14)	7.19 (3.0)	0.104 (14)	66.6 (0.81)

The amounts of As and Cd together with standard deviation of the sum of amounts are in Table 5. From Table 5 the confidence interval for the total amounts of metals can be calculated for 0.05 probability level and 6 soil layers:

- For As in kg ha^{-1}: 26.5 <average of As amounts < 27.3 (1)
- For Cd in g ha^{-1}: 532 < average of Cd amounts < 677 (2)

The residence times of As was higher than that of Cd almost 6 times as high (Table 6). That finding to do with the mobility of Cd as discussed below.

Table 5. Stocks of As kg ha^{-1} and Cd g ha^{-1} in the soil layers the maquis plot. The values in the parentheses are the standard deviations of the total sums of the two elements.

Layer	As	Cd
L	0.00263	1.072
FH	0.0633	7.357
0-10 cm	4.476	181
10-20 cm	5.601	156
20-40	11.57	177
40-80	5.281	76.3
Total	27.0 (0.496)	600 (96.8)

Table 6. Pools of As and Cd (g ha^{-1}) in forest floor and fluxes (g ha^{-1} yr^{-1}) in litterfall and throughfall as well as residence time (years) of the two heavy metals in the forest floor of the maquis plot.

	As	Cd
Forest floor	65.9	8.43
Litterfall	0.746	0.579
Throughfall	1.071	0.728
Residence time of As and Cd in the forest floor		
	As	**Cd**
Years	36.3	6.4

4. Discussion

4.1. Hydrological cycle

The variability of Cd is much higher than that of As in the hydrological cycle. The reason for this is the mobility of Cd in soils. The mobility is manifested not only by the high coefficients of variation but also by the short residence time of Cd in the forest floor when the throughfall deposition is taken into account. Citeau et al [22] argued that Cd moves in an ionic form in soil solution and for this reason it is more mobile than As which forms organic complexes. In any case, both metals, in the whole hydrological cycle, have much lower concentrations than the limits set by the WHO. The hydrological fluxes of metals (bulk – percolation) are positive. This stands true for all models of percolating water. This means that both metals are withheld by soils. Of course, if the last finding was not true, things would be alarming.

4.1.1. Bulk deposition enrichment factors

The enrichment factors of bulk deposition in the atmosphere of the two metals are completely different in terms of magnitude. According to Steiness and Friedland [23], very high enrichment factors are the values exceeding the number 1000 threshold. This stands true for Cd in both methods (calculations from literature and measured). With regard to As, however, the methods gave results that differed significantly. The real measurements showed that the earth crust had a higher influence than previously thought. Among the 25 values, more than half (14) were lower than 100. These 14 values are considered to have a medium (and not high) influence of long-range transfer of aerosols [23]. Of course, it is not always possible to carry out chemical analyses of all the parameters per area. There are elements where information on literature suffices such as the case of Cd for which the aerosols play a predominant role beyond doubt. It can be suggested that in areas, which have monitoring data of chemical hydrology, to combine the results found with soil chemical analysis to draw conclusions on the effect of earth crust on the formation of aerosols.

4.1.2. Percolation water modelling

The monthly differences in percolation volumes estimated with the application of a hydrological model could lead to errors to the metals fluxes. Our results showed that the less complex model (WBS3) performed better which means that added complexity did not necessarily improve the hydrological model performance, which might vary greatly depending on the simulated variable [24]. In this work, monthly percolation volumes, derived for the actual method and the WBS3 model, used the percolation theory without taking into account the hydrophobic particle. These particles are generally affected by the interactions of matric potential and contact angle effects [25]. BROOK90 uses a subroutine in which the preferential flow is simulated along with the stone fraction. That means that the model takes into account the fast water vertical transport created by the macropores. These different approaches may lead to several uncertainties, which can affect the accuracy and reliability of the predictions [26]. Only the model structure uncertainty may contribute up to 30% of the total predictive uncertainty [27]. So, depending on the variable to be simulated, the user should be very careful on the selection of the proper model.

4.2. Soils

The properties of soils show that all properties are higher than any deficiency limit [28]. The concentrations of As in soils are generally of the order of 5–10 mg kg^{-1} [29] but higher values have been found in mineral uncontaminated soils (10-24 mg kg^{-1}) of forests [8]. In our work, the As concentration ranged from 0.22 mg kg^{-1} in the L horizon to 7.19 mg kg^{-1} in the 40-80 cm mineral layer. Cd occurs at concentrations of 0.01 to 1 mg kg^{-1} in soils [30]. In the maquis plot the Cd concentration ranged from 0.088 to 0.421 mg kg^{-1} in the FH horizon. In the FH layer of a beech forest Michopoulos et al. (2022) found 1.07 mg kg^{-1}. This concentration is rather high and can be attributed to the deposition of Cd aerosols from a long distance. Indeed, that beech forest has received aerosols at least in the past [31]. Therefore, it can be inferred that the highest value of As concentrations appears in mineral soils, whereas that of Cd in the organic horizons probably due to the long range transfer of Cd in the atmosphere. The other conclusion is that the soil in this maquis plot is not contaminated with either As or Cd.

Sometimes it is interesting (and useful) to find not only the concentrations of an element in soils but also its amounts per depth and furthermore the total sum of amounts. These cases deal with element limits above which there can be toxic effects. As mentioned in the Materials and Methods section a common standard deviation has to be found of the sums of amounts of an element (to the depth we are interested in) and then the confidence interval for a given probability level. In our work, the confidence interval for the total sum of stocks of As up to 80 cm depth is small, whereas that of Cd is large [equations (1) and (2)]. These findings and their implications, for example, toxicity ranges should be taken into account. Future research directions such as analyzing more replicates to decrease the confidence intervals may be necessary.

5. Conclusions

The As in bulk deposition is probably enriched by geogenic material to a higher degree than previously expected. In contrast, the long-range transfer of Cd enriches the organic FH layer of soils. The volume of percolation waters varies according to the model chosen. In turn, this volume affects the fluxes of the metals. The total sum of the metals amounts in soils differs according to the chosen

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statistical confidence interval. It should be taken into account when dealing with stocks of nutrients or toxic metals.

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