Fate of Cd in Soils of Different Occupations in and Around the Cedars Forest Natural Reserve of Tannourine

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***Abstract*—**Trace metals (TM) are naturally present in soils; however, higher amounts of metals are released into the environment by human activities. Soil pollution by TM is therefore a crucial issue. In order to assess the quality of the soils in Tannourine – a village in the North of Lebanon – several surface soils of plots of different occupations were sampled (two apple orchards: one with strictly fertilizers' applications (AF), the other with only pesticides' applications (AP), a grazing field recently occupied by goats and sheep (G), a previously cultivated land (PC) and a soil from the cedars forest nature reserve of Tannourine (F)). The purpose of the sampling was to investigate the presence and level of contamination of cadmium (Cd). Different soil analyzes were performed at the Laboratory of Soil Science of the Holy Spirit University of Kaslik to determine the main physico-chemical characteristics of soil samples: pH, conductivity, particle size distribution and limestone. In addition to these analyzes, a determination of the Cd content in these soils was carried out by the atomic absorption spectroscopy (AAS) method after a total acid digestion of these samples. The transfer of Cd to different compartments (vegetative cover (Rye Grass), soil and infiltrated water) was then studied during laboratory artificial rainfall events. This experimental work consisted on putting the samples under artificial rain events in different conditions: (1) soil covered by Rye Grass; (2) soil covered by Rye Grass with Cd input; (3) bare soil; (4) bare soil with Cd input. These conditions are used to evaluate the rate of Cd found in the soil, Rye Grass and infiltrated rainwater solutions. The dosage of Cd in the soil samples showed no pollution by Cd in comparison with the reference value in the Mediterranean region (0.7 mg/kg); however its presence was noted in all samples except in the sample PA. The results also showed a similarity in the behavior and the transfer of Cd in the three compartments listed for the five samples. Indeed, covered soils after rainfall event with input of Cd, could take up the highest amount of Cd compared to the other two compartments that have captured a small amount of Cd. We can therefore conclude that from one side, in these soils, there are certainly high amounts of chemical components capturing this pollutant such as organic materials and oxides. From the other side, in this study, the Rye Grass was not shown as an adequate Cd bio accumulator since it could not take up a considerable amount of dissolved Cd.

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I. Introduction

THE increase in human population density started at the time of human settlement during the beginning of the Neolithic period characterized by economic, social and technical changes based on agriculture and animal husbandry. Nowadays, men ensure by these two activities, a regular and varied diet for seven billion people living on Earth (El Azzi, 2012). Physical and chemical treatments are used to protect crops against aggressions and guarantee high yields. For the last decades, in all these activities, the soil has always been the support of the majority of human activities and most ecosystems. It acts as an interface with the other compartments of the environment: hydrosphere, atmosphere and biosphere (Zovko & Romić, 2011). Furthermore, it provides a nutrient medium supporting the growth of plants and animals. It is also a habitat and a support protecting wildlife and promoting global nutrient cycling and biomass production. However, industrial, agricultural and urban development is undoubtedly accompanied by pollution problems. Indeed, several chemical substances contaminate the soil *via* human activities and interventions (pesticides, fertilizers, automotive traffic and combustion). Among these chemical pollutants, some are inorganic such as trace metals (TM). These substances occur naturally in rocks and soils. According to Rollin & Quiot (2006), metal consumption has increased by 300% in the last fifty years and anthropogenic salting out of metal elements such as Lead (Pb), Mercury (Hg), Zinc (Zn) , Cadmium (Cd), Copper (Cu) and Chromium (Cr) have tripled since the beginning of the industrial age. Cadmium, one of the toxic TM for living beings (humans, animals and plants) is found naturally in the soils and the terrestrial crust (weathering of rocks, volcanic emissions) at a concentration of 0.1 mg/kg (Li, 2000). It is also provided by anthropogenic activities (inputs and fallouts of industrial and agricultural emissions). Cadmium losses into groundwater are a hundred times less than the inputs (Haluschak, Mills, Eilers, & Grift, 1998), the TM therefore tends to accumulate in the soil. Any soil containing Cd above the world average (0.53 mg/kg) is considered enriched (Kabata-Pendias & Pendias, 1992). In the Mediterranean region, the average is increased to 0.7 mg/kg (Micó, Peris, Recatalá, & Sánchez, 2007). The interest in this element is

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related to its toxicity. In fact, Cd has no biological role in the living organisms, has a high toxicity to organisms even in very small quantities and is often present in pesticides and fertilizers.

In this context, our present work is structured around two main objectives:

- Identify and evaluate the content of Cd in five soils of different occupations in Tannourine: (1) apple orchard whose only inputs are chemical fertilizers; (2) grazing land recently occupied by goats and sheep; (3) land formerly cultivated; (4) apple orchard whose only inputs are pesticides and (5) soil of the cedars forest natural reserve of Tannourine. The contamination rate is estimated by comparing the rate of Cd in soils to that of the bedrock.
- Monitor the behavior and the transfer of Cd in these soils during an artificial rainfall event under different conditions: (1) bare soil with "uncontaminated" artificial rain; (2) bare soil with artificial rain contaminated with Cd; (3) covered soil with "uncontaminated" artificial rain and (4) covered soil with artificial rain contaminated with Cd.

II. Material And Methods

A. Site Description

Tannourine is located in Northern Lebanon and belongs to Batroun Caza. Its altitudinal gradient rises from 800 to 2600 m above sea level, with an area of 74 km^2, including a cedars' nature reserve (Fig. 1). It has a temperate climate with hot and cold seasons. Tannourine is known for its natural reserve of cedars forest inducing tourism, it is also known for its agricultural lands; from one side its apple orchards and from the other, its lands suitable for cattle grazing during spring and summer. Tannourine was chosen to investigate the soils' quality and assess their toxicity levels of Cd.

Fig. 1 Geographical Map of Lebanon Locating Tannourine

B. Sampling

Sampling was performed during the month of July 2013 and was carried out using augers. Soil samples were taken from the surface layer to depth of about 15 to 30 cm and were stacked in nylon bags. The choice of the soil samples taken is mainly based on their function and use. A sample of bedrock and five different soils (three samples per soil) were taken. The parcels sampled were as follows: one apple orchard with only fertilizers' applications (AF), one apple orchard with only pesticides' applications (AP), a grazing field recently occupied by goats and sheep (G), a previously cultivated land (PC), and a soil from the cedars forest nature reserve of Tannourine (F). These samples were brought to the laboratories of the Holy Spirit University of Kaslik. A drying process of the samples for three days in the open air is needed in order to facilitate subsequent work and to ensure a better preservation. A sieving process (at 2 mm) for the samples is a preliminary step to remove the coarse stones (> 2mm) and dispose of the fine matter (< 2mm) for the successive analysis. The storage of these samples throughout the duration of work was at room temperature in well closed nylon bags; all placed in a closed box, away from light.

C. Soil Analyses

Several experiments were made in order to evaluate the properties of the soils taken from Tannourine. In total, five analyses were performed: pH measurement (pH-water and pH-KCl), electrical conductivity, particle size analysis, determination of the total limestone and the dosage of Cd content in the soils. In order to realize the dosage of Cd with the atomic absorption spectrometry (AAS), a total acid digestion of the soils was needed. The microwave method provides the acid digestion of the soil samples in a closed container device produced by ETHOS lab named "Milestone ETHOS lab station with easy WAVE" through a microwave heating under controlled temperature. The process is to introduce 9 ml of hydrochloric acid (37%) and 3 ml of nitric acid (65%) with 0.5 g of the soil sample. At the end, the samples are kept in a cold room at a temperature of about 3°C. The AAS is an analytical technique that measures the concentrations of certain chemical elements, usually TM. The AAS device called contrAA 600 is connected to a computer which registers the obtained Cd concentrations in µg/l converted afterwards into mg/kg. In order to use AAS to estimate the concentration of Cd in the samples, three different solutions are prepared:

- A stock solution of nitric acid (0.5%) used for the dilution done by the device during the dosage process.
- A stock solution of Cd used as a reference (100 µg/l).
- A digested soil solution diluted.

D. Experimental Section: Study of the Cd Transfer During Artificial Rainfall Events

In this experimental section, we are working on the soil samples, noting that the three samples of each type of soil are mixed together to form a single representative sample of the plot. There will be in total, the following samples: AF; AP; G; PC and F. The purpose of this study is to submit these samples coming from different occupation soils to many conditions: (1) bare soil with "clean" artificial rain; (2) bare soil with Cd contaminated artificial rain; (3) covered soil with "clean" artificial rain and (4) covered soil with Cd contaminated artificial rain, in order to assess the transfer of Cd to the three compartments: (1) soil; (2) vegetation cover (Rye Grass) and (3) collected solution after rainfall event.

A culture of Rye Grass (Lolium perenne) was used to assess the phyto-availability of Cd in pots under controlled conditions. Rye Grass was previously used for the study of phyto-availability of several pollutants since its roots seem to cause increased interception of soil pollutants (Hinsinger & Gilkes, 1996); (Sterckeman, Duquène, Perriguey, & Morel, 2005). Indeed, previous studies have shown that the root system of the Rye Grass improves the purifying capacity of the soil and enables the remediation of the elements leaching (Gray & McLaren, 2005).

A preparation of the equipment needed to run the experiment is to take 20 g of the samples fine fraction of each type of soil and place them in a polypropylene funnel over a bunch of sterile cotton and a filter paper. These funnels are placed on plastic pillboxes. Each case is made in duplicate to minimize errors. For a repeat, there are four sets, each containing the previously mentioned five samples with one blank by series. Each series is subject to various activities. It should also be noted that throughout this manipulation, the samples were exposed to natural outdoor light. All the material used (funnel and pillbox) was soaked in nitric acid (1%) for 24 h to remove any residue or contamination.

The water used as artificial rain water during the experiment is distilled water with a pH set at about 6.5, similar to natural rain water in the region. The amount poured to each rainfall event is equivalent to two thirds of the water holding capacity of each soil. The rain mixed with Cd in the series 1 and 2, had a concentration of 2.5 mg/l; the choice of this concentration comes from the fact that the best adsorption of Cd to the particles is 10 µg/l to 1g/l of total suspended solids (TSS) or more commonly of the soil (El Azzi, 2012). Furthermore, pure nitric acid was added to the water samples collected (9 drops of HNO3 / 125 ml of the sample volume) for the storage of the samples in a cold room before analysis.

The four series with the different conditions are shown in the Fig. 2.

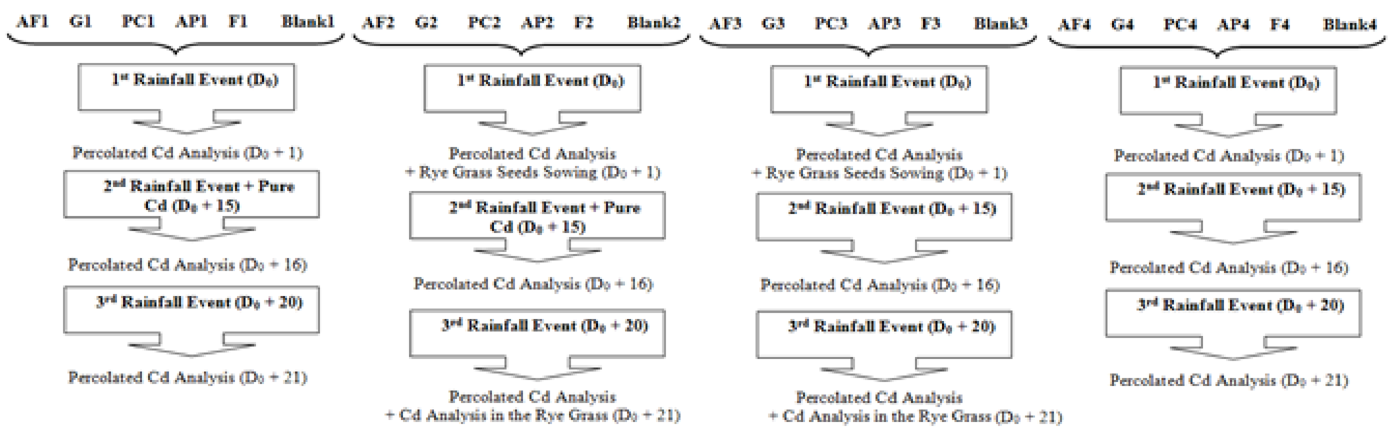

Fig. 2 Detailed experimental activities showing the four series under different conditions

III. Results and Discussion

A. Soil Analyses

Table I shows the results of the pH-water, pH-KCl, conductivity and total limestone for the different soil samples. Regarding the results of the particle size, it was revealed that the AF soil has a "sandy loam" texture whereas G, PC, AP and F soils are "loamy sand". Table II shows the different concentrations of Cd for each soil type.

TABLE I
RESULTS OF PH-WATER, PH-KCL, CONDUCTIVITY AND TOTAL LIMESTONE OF THE SAMPLES

Sample	AF	G	PC	AP	F
pH-water	7,41 ± 0,12	7,18 ± 0,15	6,14 ± 0,06	7,04 ± 0,33	6,88 ± 20
pH-KCl	6,55 ± 0,41	6,55 ± 0,38	5,32 ± 0,14	6,32 ± 0,19	6,03 ± ,21
Conductivity (µS/cm)	433 ± 32,31	1011,67 ± 291,77	293 ± 163,41	437,75 ± 103,05	307,5 ± 91,78
Total limestone(%)	4,88 ± 5,18	0,00	0,61 ± 0,11	0,84 ± 0,50	0,33 ± 0,002

TABLE II
Cd Concentration of the samples

Sample	Cd Concentration (mg/kgs soil)
AF	0,0069 ± 0,01
G	0,0000
PC	0,4058 ± 0,63
AP	0,0480 ± 0,08
F	0,0380 ± 0,07
Bedrock	0,0114 ± 0,01

By comparing the values obtained with the reference value in the Mediterranean region (0.7 mg / kg) (Micó, Peris, Recatalá, & Sánchez, 2007), we note that none of these soils is significantly contaminated with Cd. By doing the same comparison with the work of (Pérez, Martínez, Vidal, & Navarro, 2002), we note that the rate of Cd in the AC ground is at the upper limit of the reference value (0.4 mg/kg).

However, we can present some conclusions in relation with these values. First, we note that in both apple fields, the Cd concentration is higher in the one following cultural practices based on pesticides inputs than in the one following cultural practices based on fertilizers inputs; this is confirmed by some previous studies (Llewellyn, 1994). Second, the Cd content found in the soil of the natural reserve of Tannourine is relatively high compared to a soil receiving no anthropogenic input and relatively to the Cd content of the bedrock (0.0114 ± 0.01 mg/kg). This accumulation can be explained by several mechanisms; either by atmospheric deposition from the Lebanese coast where industries are concentrated (Nakhlé, 2003) and / or by erosion of the bedrock releasing the Cd (Tuchschmid, et al., 1995) in the soil, and / or even by erosion of cultivated soils above the reserve since it is located in the heart of a valley. Third, it should be noted that the rate of Cd in the PC soil is relatively high compared to other soils. Since it is a soil that was formerly cultivated, we can hypothesize that agricultural practices that had been applied in that time were probably more random, perhaps using organochlorine or organophosphate persistent pesticides that were widely used in years 1940 to 1970 or even phosphate fertilizer; forming all together, Cd sources to the environment (El Azzi, 2012).

B. Results of the Experimental Section – Collected Rain Solutions

First of all, we notice that the Cd contents of the recovered solutions are limited (within the scale of ng/kg). This amounts to the fact that the first rainfall event had only distilled water for the four series. These traces of Cd in the recovered water are a result of the water passing through the soil and washing away traces of mobilized dissolved Cd.

After application of Cd with the rain in series 1 and 2, we note that the concentration of Cd in the recuperated solutions from these series is relatively high compared to the other two series (3 and 4) receiving no input of Cd (Fig. 3). Moreover, we also note that the concentration of Cd is higher for all collected solutions from series 1 than from series 2. We conclude that for a covered soil, in our case the one cultivated by Rye Grass (series 2), there is less leaching loss, in fact, it is the canopy that has absorbed some of the Cd added amount. This specification allows us to discuss the soil management at the natural reserve of Tannourine. Given that it is located in a valley, we can thus suggest to install around the border of the reserve, at the top of slopes, adequate grass strips having the role to extract pollutants from soil, among others, the TM, since during the determination of Cd rate in the soil of the reserve, we identified the presence of this metal. These grass strips, not only promote the extraction of pollutants, but also the protection of groundwater, the risk reduction of erosion and the improvement of the soil structures.

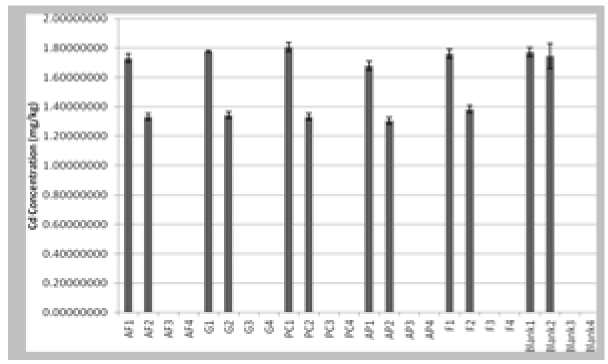

Fig. 3 Cd concentration in the Recovered Solutions (after 2nd rainfall)

For the third solutions' recuperation after the last rainfall event (without added Cd) for four series, we note that in series 1 and 2, the concentration of Cd is higher than that of the first solutions recovered, despite the use of the same rain (without adding Cd) for the four series (Fig. 4). We assume that it is the rest of Cd in the aqueous phase still present in the pores of the soil. In addition, the Cd concentration in solutions of the series 1 is greater than those of series 2; we can then evoke the same conclusion made previously: the Rye Grass grown has certainly captured some of the Cd added. Thus, covered soils leach fewer pollutants in the subsoil

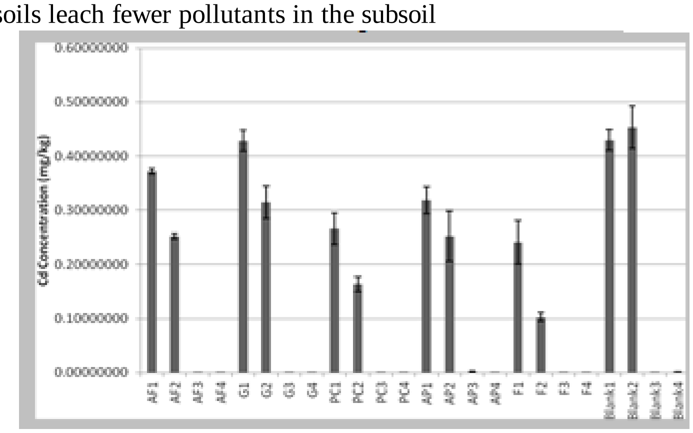

Fig. 4 Cd concentration in the Recovered Solutions (after 3rd rainfall)

C. Results of the Experimental Section – The Soils

According to the Fig. 5, we can reveal the following remarks:

- For the series 3 and 4, the Cd contents obtained are very similar to that of the samples initially. What we can infer is that even after fertigation without inputs of Cd, content is stable and does not change much.

- The soil samples of the series 1 all have the highest Cd content whereas those of the series 2 have a relatively high content of Cd with respect to the initial content but are still lower than that of the samples from series 1. We deduce that during an intake of Cd by fertigation on bare soil (series 1), there will be a certain amount to be retained by the soil before the leaching phenomenon. The same amount retained by a covered soil (series 2) will be divided between the soil and the vegetation cover. This is what explains the reduced amount of Cd in the soils of the series 2.

- We note that in both series 1 and 2, subjected to inputs of Cd during artificial rainfall event, the evolution of the increase in the concentration of Cd is proportional to the initial rate of Cd for each sample, that is to say that if we take the example of PC soil with the highest initial Cd concentration of all the samples (0.4058 mg/kg), with Cd inputs during the experiment, the final Cd concentration is also the highest in the series 1 (43.14 mg/kg) and 2 (31.50 mg/kg). This allows us to conclude that the evolution and transfer of Cd was almost similar in all the samples despite their distinct occupation.

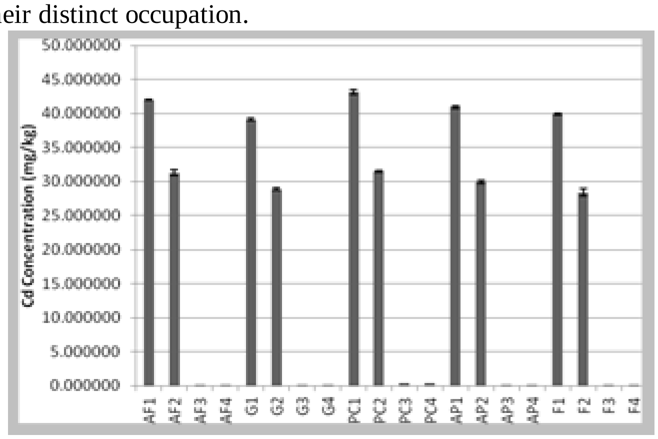

Fig. 5 Cd concentration in the Soil Samples after the Experiment

D. Results of the Experimental Section – Rye Grass

The Cd concentrations in the Rye Grass from the series 2 and 3 are resumed in the Fig. 6.

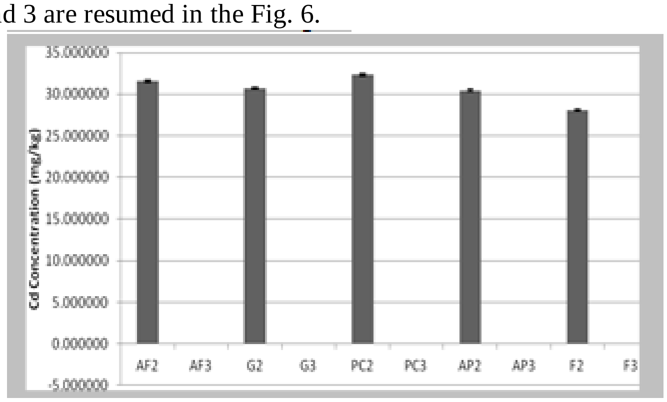

Fig. 6 Cd Concentration in the Rye Grass

According to this graph, we see that in series 2 (rain with input of Cd), the concentrations of Cd in the Rye Grass are relatively high, while in Series 3 (rain without input of Cd) levels are almost zero. As a first conclusion, we deduce that the Rye Grass is a Cd bio accumulator. This has already been demonstrated in the literature (Hinsinger & Gilkes, 1996) (Gray & McLaren, 2005) (Sterckeman, Duquène, Perriguey, & Morel, 2005). Second, despite the high initial Cd concentration in the PC soil, we do not observe a distinctly broader content in the Rye Grass grown in this soil compared to the other concentrations in the other samples. To go further, this can be explained by two hypotheses:

- The Cd in the soil can be mobile (available), moderately mobile (limited availability) or very stable (not available). It is possible that in this formerly cultivated soil, the Cd has undergone a process of stabilization known as the "aging" process, and is now strongly linked to soil particles that its excess was not transmitted in the recuperated solutions nor in the cultivated Rye Grass.

- It is possible that the Rye Grass has a Cd content/absorption limit. In this case, this plant is unable to extract a larger amount from the solution that contains the available Cd or to mobilize the Cd present in the soil in high quantities.

We can clearly notice that there is a very uneven distribution of the amount of Cd between the soil and the Ray Grass in all cases considered in the series 2. On the one hand, contrary to the results of research by Sauvé, Hendershot, & Allen (2000), indicating that Cd is highly mobile and does not accumulate much in soils and is transported with the soil solution, our results showed that the amount of the highest Cd was found in the compartment 'soil' for all samples and not in the compartment "recuperated solution" after the second rainfall event. On the other hand, since the Rye Grass is considered as a good Cd hyper accumulator therefore a purifier agent to the soil (Gray & McLaren, 2005), the results showed the opposite. This could be explained according to various assumptions:

- As already mentioned, the Rye Grass may have a Cd absorption threshold; it is unable to extract a large amount of Cd dissolved in the soil solution;

- Soils may contain high amounts of particulate organic matter (POM), oxides (iron or manganese) or clay, known for their high complexation with the Cd (Gonzales, 1999)

IV. Conclusion

This study was conducted primarily to assess the degree of contamination by Cd of the surface soil layers of different occupations in Tannourine region. A second part of the work was to study the transfer of this element during artificial rainfall event on both bare and cultivated soils.

The results of soil analysis obtained show a similarity between Tannourine soil characteristics despite their various occupations. In addition, the content results of Cd in these samples show that there is no soil contamination by that pollutant: the levels of Cd are below the reference value in the Mediterranean region (0.7 mg / kg) (Micó, Peris, Recatalá, & Sánchez, 2007), however these soils still contain Cd concentrations ranging from 0.006 mg/kg to 0.5 mg/kg except for the soil G with no Cd at all.

Finally, the soil has adsorbed the greatest amount when comparing the Cd quantity partitioned between the soil, the collected solution, and the Rye Grass for the series 2. In terms of quantities, the Cd captured by the Rye Grass is very small that its consideration as a Cd hyper accumulator is not appropriate in this work. It is also the same for the very small amount found in the recuperated solution right after the rain accompanied with Cd input.

In perspectives, further in-depth studies are needed:

- A soil characterization in terms of presence and quantification of certain soil components, such as POM, iron or manganese oxides, and clays could help to understand better the behavior and transfer of Cd in these soils.

- Chemical fractionation would allow detecting the fraction to which the Cd is linked to evaluate its mobility and its bioavailability in soils.

- A study on the same soil but throughout the whole profile thus including the deeper layers would also be interesting to assess the risk of contamination in subsoil and groundwater especially that in this region there is a water production on the local country level.

- Finally, the Cd content may increase and become more and more bio available even in a region that is supposed to be "uncontaminated" as in the case of the natural reserve of Tannourine, and this is due to the continuing agricultural activities including tree crops and applications of chemical contaminants (fertilizers and pesticides). On the one hand, limiting agricultural applications causing this Cd contamination or their substitution by non harmful products to the environment and living beings would be a simple and sustainable solution. On the other hand, it would be interesting to conduct a phyto purification or phyto remediation by cultivating the edge of the natural reserve with grass strips that have the ability to accumulate and integrate this pollutant and to focus it in the aerial parts or roots. Thlaspi caerulescens J. Presl & C. Presl (Brassicaceae), naturally present in Tannourine, is distinguished for its Cd tolerance and could be the best choice to apply the phyto-remediation (Diallo, 2003). Studies by (Brown, Chaney, Angle, & Baker, 1994) have shown that this plant is able to accumulate Cd concentration ranging up to 1020 mg/kg.

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