Estimated contamination risk of heavy metals (Ni and Zn) of a soil grown (Cucumis Melo) on industrial activity zone (El-Hadjar - Annaba - Algeria)

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Abstract
Our study, conducted in the industrial area of El-Hadjar (Annaba), aims to assess the impact of heavy metals on an agricultural soil and vegetation (melon) just outside the steel complex. The assessment to cover the total contents, exchangeable and soluble. These metals were measured in the surface soil (0-20 cm) and long (20-40 cm) and the melon sheets. The results obtained confirm the presence of two elements (Zn and Ni) in all samples analyzed (soil and vegetation). The total zinc measured in the soil is in relatively more by contribution to nickel. As for the soluble and exchangeable contents, Ni s is more important than Zn.

Keywords: industrial area (El-Hadjar), heavy metals (Zn, Ni), soil, vegetation (melon)

Introduction
Heavy metals in soils are derived from both natural (geogenic) sources and anthropogenic contamination. The contribution of metals from anthropogenic sources in soils can be much higher than the contribution from natural sources (Nriagu and Pacyna, 1988). There have been a number of studies which reported the deposition of heavy metals in soil, Crops and vegetables grown in the vicinity of industrial areas (Yang and al., 2005, Khan and al., 2008, Zhuang and al., 2013). Among the elements, the most important to consider in terms of food chain contamination are As, Cd, Hg and Pb. Simultaneously, some micronutrient elements (e.g. Cu, Cr, Ni, Zn) may be toxic to both plants and animals at high concentration (Yang and al., 2006).

Heavy metals are ubiquitous in the environment, as a result of both natural and anthropogenic activities, and humans are exposed to them through various pathways (Wilson and Pyatt, 2007). Heavy metal accumulation in soils and plants is of increasing concern because of the potential human health risks. This food chain contamination is one of the important pathways for the entry of these toxic pollutants into the human body. Heavy metal accumulation in plants depends upon plant species, and the efficiency of different plants in absorbing metals is evaluated by either plant uptake or soil-to plant transfer factors of the metals (Rattan and al., 2005).

In Annaba, the problem of pollution by heavy metals has really started to become alarming that from 1986 when the economic crisis has pushed some industrial units especially the steel complex of El Hajar (SNS) and that of phosphate and nitrogen fertilizers (ASMIDAL) to sacrifice "Environment" criterion in favor of the production. And treatment plants have fallen failures, have practically restarted; some filters and other gas cleaning equipment were no longer renewed, sometimes not even maintained. To this is added the aging of some of these industrial units (Louadjani, 1995).

The result of these anomalies has led to air pollution whose impact has resulted in damage to the health of local residents. Numerous studies in the region attest lung problems (asthma and bronchitis) were the most common diseases in the region of El Hajar.

In the context of our work, we tried to evaluate the impact of air pollution on soil and vegetation in the region of Al-Hajar, specifically in an agricultural plot located just dozen meters south of the steel complex. Soils are always neglected, thinking that their auto scrubber will be able to save them from possible contamination. Successful evaluation criteria can be mobilized grades and readily available fraction.

Material and methods
2.1. Presentation of the study area
Covering an area of one hectare, the scope of study is on agricultural land "Beni Yagoub" in the northwest of the town of El-Hadjar (Annaba, Algeria). It is located between longitude: 36° 33' North and latitude and 7° 36' at 7° 44' (topographic map of Annaba /25.000 1). The region is characterized by its agricultural vocation and is in the western extension of the plain of Annaba.

Soils are vertisols; developed on non-calcareous alluvial clay texture, crumb structure to, blackish color. They are based on a clay hydromorphic level appearing at 120 cm deep; it has low salinity 2-4 mS.cm.

The area is drained by a dense network whose flow is the Southwest to the Northeast by the four main wadis (wadi Meboudja; wadi Bou-Athout, wadi Mellah, wadi Rassoul) flowing into Wadi Seybouse then to the final disposal (the sea).

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The climate of the region is the Mediterranean which is characterized by irregular rainfall and a long period of summer drought. The study area is located in the bioclimatic sub-humid which is characterized by a wet period extending from September to May (seven out of twelve months) and a long period of summer drought. The region receives a water column of 659.8 mm which 40.60% fall in the winter months and 4.84% in the summer season. This irregularity affects the water regime of the soil and therefore on vegetation.

A melon field, a parcel located between faba bean and wheat plot, originally intended for a tomato crop. For reasons specific to the operator, the culture of tomato was replaced by a culture of melon.

2.2. Methodology

For each station two soil samples were prepared at two depths (0-20 and 20-40 cm). 2 (soil samples) x 2 (depth) x 10 (stations) = 40 soil samples for analysis.

An average sample of the plant studied (melon: Cucumis Melo), consisting solely of the aerial part (leaves), is taken from each station. The choice of the aerial parts was made for the following reasons: according to most authors, the greatest amount of heavy metal accumulates in the leaves (Bonte and De Cormis, 1979; Coullery, 1996; Zhuang and al., 2010). The potential hazard can be transmitted through these anatomical parts of the plant: the leaves.

In the laboratory each sample melon sheets is divided into two lots:

- A batch has been cleaned with distilled water to remove any impurities deposited on the surface of the sheets, and then drying in an oven at a temperature of 65 ° C for 72 h. After drying, the leaves are finely ground and the powder thus obtained is stored until the time of analysis.
- A second unwashed lot, but subject to the same treatment that the lot washed Thus, we can compare the results of two lots and highlight the presence of any atmospheric deposition.

After extraction, heavy metals in soil (easily removable, exchangeable and total) and vegetation were assayed using a flame atomic absorption spectrometer (SAAF-100AA) with a BGCD2 Correction.

3. Results and Discussion

The physicochemical results show that the plot " Melon " is characterized by clay texture (51.25% to 57.5%) (Table 1). The projection of percentages sands, silts and clays on the textural triangle American (USDA) defines the clay class in all samples of surface soils studied. According to the standards issued by the French Ministry of Cooperation (MFC, 1974), the pH of our soils change very little (CV = 2%), neutral to slightly alkaline; a high CEC (between 25 and 40), and the presence of total limestone is low; average organic matter content in depth and low on surface.

| Stations | pH | OM% | CaCO₂ % | CEC (meq/100g) | Clay% | Silt% | Silica% |
|----------|----|-----|---------|----------------|-------|-------|--------|
| 1        | 7.25 | 1.5 | 4.4 | 27 | 53.5 | 28 | 9.35 |
| 2        | 7.3 | 1.72 | 5.4 | 27.5 | 53.25 | 28 | 10.75 |
| 3        | 7.19 | 1.76 | 2.6 | 30.25 | 57.5 | 30.5 | 7.5 |
| 4        | 6.91 | 1.17 | 2.2 | 28.75 | 53.5 | 27.75 | 11 |
| 5        | 7.26 | 1.53 | 2.7 | 29 | 55 | 29.75 | 9.35 |
| 6        | 7.2 | 1.43 | 6 | 26.75 | 51.75 | 27 | 10.51 |
| 7        | 7.39 | 1.4 | 4.8 | 30 | 56.75 | 31.5 | 9 |
| 8        | 7.15 | 1.37 | 3.65 | 30.5 | 56.75 | 29.75 | 9.25 |
| 9        | 7.48 | 1.24 | 4.6 | 26.5 | 51.25 | 27.5 | 11.85 |
| 10       | 7.34 | 1.23 | 4.4 | 29.25 | 55.5 | 31.25 | 9 |
| average  | 7.24 ±0.15 | 1.43 ±0.19 | 4.07± 1.25 | 28.55± 1.5 | 54.47±2.16 | 29.1± 1.64 | 9.75 ±1.26 |
| Median   | 7.25 | 1.41 | 4.4 | 28.87 | 54.25 | 28.87 | 9.35 |
| Min-Max | 6.91-7.48 | 1.17-1.76 | 2.2 - 6 | 26.5- 30.5 | 51.25- 57.5 | 27- 31.5 | 7.5- 11.85 |
| % CV     | 2 | 13.28 | 30.71 | 5.25 | 3.96 | 5.63 | 12.92 |

The total cation of Zinc is relatively dominant in the ground, surface and depth (Table 2). Average total contents assayed surface are 47.55 and 35.26ppm respectively for zinc and nickel. In depth, they are 53.94 ppm for zinc against 46.71ppm for nickel. The distribution of the two components varies little in surface of sites (Zhuang and al., 2009). This variability seems slightly noticed either for Ni with a coefficient of variation of 20.03% or Zn with CV = 11.32% in depth. The total contents assayed for zinc varied between 34.39 and 72.28 ppm in surface. At depth, they range from 42.85 to 62.92 ppm.

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For nickel, the levels found evolve the 29.47 to 43.5 ppm on the surface and 34.84 to 61.25 ppm in depth. A statistical analysis (ANOVA) showed that there was a highly significant difference between the levels of total Ni surface and those dosed at depth (F = 11.47, α = 0.003). The statistical study shows that the total zinc in depth and surface is not related to any parameter of the ground, despite the richness of the clay substrate \((r = 0.95 ***)\); unlike the total nickel, which seems related to the clay fraction of the soil surface, as we observe a significant relationship with \(r = 0.77 **) which confirms the same origin.

Finally, if one refers to standards adopted (Oso, 1986), we can conclude that terms of total contents, zinc is below the indicative standard of 200 ppm; by cons we observe, for nickel, the standard used (50 ppm) is exceeded in about 40% of the stations. Nickel appears to have a relatively greater risk if e can be transferred to plants, not to mention the biggest danger to groundwater. It is especially the exchangeable and soluble contents which can cause health problems or damage to the environment.

Zn is present in soluble form particularly on the surface in all the stations, in contrast to soluble Ni which is present in large quantities in depth where it is dosed in 90% of the stations. Zn contents range from 0.4 to 13.63 ppm at the surface and 0.27 to 7.16 ppm in depth. For Ni, they vary from 3.28 to 15.65 ppm on surface to 28.01 ppm in depth.

Unlike total contents, where zinc is the dominant cation, the soluble content is exchangeable and nickel which is the dominant cation. Soluble Zn is not represented in depth and it usually accumulates in the upper horizon where it is mobilized mainly as organic complexes (Parmentier et al., 1997). In short, zinc is mainly CaCO3 complexes to the surface, its correlation with the latter because it is not represented in depth and that the leaching processes have no significant effect on mobility. For its persistence against surface probably creates an ion imbalance that would cause leaching of nickel increasing the content of the latter in depth whether in exchangeable form \((r = 0.69 *)\) or total form \((r = 0.83 **)\); it is the same for Ni, an increase in the total fraction depth result in an increase of the soluble content of Zn \((r = 0.69 \ast\)\), an increase in Ni soluble surface lead to a leaching of the latter increasing the total contents of depth \((r = 0.72 \ast\)\) and in turn the exchangeable contents \((r = 0.55 \ast)\).

Table 2. Exchangeable and total soluble Average levels of Zn and Ni (ppm) on the surface and in depth (cm)

| Station | Soluble fraction | Exchangeable fraction | Total fraction | Soluble fraction | Exchangeable fraction | Total fraction |
|---------|------------------|----------------------|---------------|------------------|----------------------|---------------|
| 1       | 1.81             | <Ld                  | 72.28         | 5.05             | 1.64                 | 12.01         |
| 2       | 2.57             | <Ld                  | 52.32         | 3.28             | 8.61                 | 32.84         |
| 3       | 2.63             | <Ld                  | 52.63         | 6.81             | 13.78                | 38.51         |
| 4       | 7.16             | <Ld                  | 47.77         | 13.88            | 0                    | 7.16          |
| 5       | 9.43             | <Ld                  | 34.48         | 13.88            | 28.01                | 47.77         |
| 6       | 1.74             | <Ld                  | 34.39         | 10.35            | 6.81                 | 31.44         |
| 7       | 0.8              | <Ld                  | 34.39         | 15.65            | 26.25                | 38.24         |
| 8       | 2.95             | <Ld                  | 54.33         | 6.81             | 20.95                | 41.75         |
| 9       | 0.27             | <Ld                  | 34.64         | 5.05             | 17.42                | 31.22         |
| 10      | 0.47             | <Ld                  | 49.29         | 6.82             | 6.82                 | 34.73         |
| Moy±σ   | 3.91±2.11        | 4.20                 | 47.55±11.73   | 8.75±3.46        | 10.06±2.42           | 35.26±4.96    |
| Median  | 2.44             | 0                    | 48.53         | 6.81             | 10.24                | 33.87         |
| Min     | 0.4              | 13.6                 | 34.3          | 3.28             | 13.78                | 29.47         |
| %CV     | 107.41           | 103.31               | 24.66         | 49.82            | 88.22                | 14.06         |

Despite its relatively high solubility in surface and deep, nickel is absent (not detectable) in the washed vegetation. In unwashed leaves, it was metered into three samples (2, 4 and 6) only. The difference between levels of unwashed and washed leaves confirms that it is external deposits were observed firsthand, insitu during the sampling periods (Table 3). It should be emphasized that in our case, we focused only on levels of heavy metals in the aerial part (leaves) of the plant. The element Zn, despite its low relative solubility (8.2 and 0.54%), it is respectively found on surface and in depth, and it is better absorbed in the leaves (relative to nickel) with values ranging from 15.45 to 30.1 mg Zn / kg (DM) in the washed leaf (and 26.06 to 38.18 mg Zn kg (DM) in unwashed. The difference between the washed and unwashed leaves confirms the existence of deposits on the leaves and the latter has been withdrawn after washing. The importance of the evidence, visible to the naked eye at the time of sampling is increased by the prevailing winds in that period and blowing in the direction of the plot. The surplus "washed", may

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represent up to 50% of the content in the leaves. These results confirm the obvious Zn accumulation in the leaves is produced either by either depositing dust (industrial waste), or according to Kabata Pendias and Pendias (1986), zinc is easily leachable because it easily penetrates in the leaves; either through the root, or by both channels simultaneously.

Table 3. Contents of Zn and Ni (ppm) in the washed (WL) and unwashed leaves (UWL) of melon

| Stations | Zn (WL) | Ni (WL) |
|----------------|--------|--------|
|              | (UWL)  | (UWL)  |
| 1            | 24.54  | 33.63  |
| 2            | 22.02  | 31.61  |
| 3            | 30.1   | 26.06  |
| 4            | 20     | 38.18  |
| 5            | 28.58  | 27.57  |
| 6            | 25.05  | 28.58  |
| 7            | 30.1   | 31.61  |
| 8            | 24.04  | 34.64  |
| 9            | 23.53  | 26.06  |
| 10           | 15.45  | 30.6   |

| Moy ± σ | Médiane | Min-Max | %CV | %RA |
|---------|---------|---------|-----|-----|
| 24.34±4.58 | 24.29 | 15.45-30.1 | 18.81 | 48.25 |
| 30.85 ± 3.92 | 31.10 | 26.06-38.18 | 12.70 | 61.16 |
| 0 | 0 | 0-0 | 0 | 0 |
| 4.67 ± 7.58 | 0 | 0-0 | 0 | 0 |

Conclusion

In conclusion, we can say that if nickel, compared to zinc is more available in the soil solution, its ability to be absorbed is less. Or, zinc is a trace element, and its nutritional and physiological needs of the plant regulates the passage of elements it needs it most. Our results confirm the obvious Zn accumulation in the leaves is produced either by dust deposits (industrial waste). This study allowed us to understand that regardless of the amounts of heavy metals carried in air emissions, once deposited on the ground level, their fate is governed by the physicochemical properties of soil, biological activity and vegetation type. Thus, the plot "Melon" is contaminated by two elements: Ni and Zn (exchangeable). And limestone and to a lesser degree the pH are the two determining factors in the dynamics of metals.

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