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## Selenium levels in Lebanese environment

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#### ABSTRACT

Very limited research has been conducted on selenium (Se) in Lebanese soils and forage crops but no work has been done on Se in water and locally produced vegetables and grains. This research was conducted in order to quantify Se levels and its availability in agricultural soils, vegetables and grains in Lebanon. Sixty-six (66) soil samples were collected from 33 selected sites in Lebanon: the Bekaa Valley, coastal and mountainous regions. Thirteen (13) different plant types (86 samples) were sampled from the same locations. Also, 13 spring water and 10 bottled water samples were collected. Soil samples were analyzed for their physical and chemical properties. Selenium was extracted from soils with: deionized-distilled water (Soluble-Se), KH<sub>2</sub>PO<sub>4</sub>-0.1 M (MKP-Se) and  $concentrated \ (HNO_3 + HCl) \ mixture \ (acid-Se). \ Plant \ Se \ was \ extracted \ by \ acid \ digestion \ on \ a \ hotplate. \ Selenium$ concentrations were measured by the inductively coupled plasma-mass spectrophotometer (ICP-MS). The values of Soluble-Se, MKP-Se and acid-Se ranged between 47 and 142, 147 and 400, and 1749 and 4713 µg/kg, respectively, with average values of 95, 306, and 3118 µg/kg and at a ratio of 1:3:30. Thus, Se extracted with deionized-distilled water is a good indicator for Se availability in the studied soils. The average Se concentration in plants was in the following order: radish>lettuce>cucumber>cabbage>parsley>alfalfa>onion (leaves)> broccoli>tomato>mint>chickpeas> wheat>onion (bulbs). The Se levels in water samples were in the safe range (less than 50 µg/L) and ranged between 2.14 and 17.6 µg/L. The levels of Se in the three soil extractants were positively correlated with each other and with organic matter content, salinity and phosphorus (P). Selenium levels in plant samples were positively correlated at a 0.01 significance level with clay and P content.

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### 1. Introduction

Selenium is an essential element for both humans and animals but it has not been yet recognized as an essential element for plants. It has come to the public's attention because of its role in cancer prevention and in reducing cardiovascular diseases in human beings, which increased the concern of tracing this element all the way from the soil to plants through food chain via animals to human beings. Selenium is widely distributed throughout the environment in rocks, soils, plants, water, and atmosphere, where it originates from volcanic activity, burning of fossil fuels, the weathering of rocks and soils, groundwater transport, precipitation of minerals, adsorption and desorption of elements, chemical or bacterial redox reactions, and metabolic uptake and release by plants and animals (McNeal and Balistrieri, 1989). Selenium concentration in the earth's crust is about 0.05 µg/kg and its concentration in most soils lies between 0.01 and 0.2 µg/kg (Kabata-Pendias and Pendias, 2001). Selenium content in most soils varies from 0.1 to 2 mg/kg, while in seleniferous areas, it is as high as 1200 mg/kg for total Se and 38 mg/kg for soluble Se (Selim and Sparks, 2001; Fordyce, 2005). Tan (1989) defined the Se status for human nutrition according to the concentration of total Se in soils as: deficient <0.125 µg/kg; marginal 0.125–0.175 µg/kg; moderate–high 0.175–3 µg/kg and excessive >3 µg/kg.

Plants differ in their ability to accumulate Se. The great interest in plant Se is mainly due to its importance in human and animal nutrition since Se can act as both a micronutrient and toxin (Kabata-Pendias and Pendias, 2001). The oxidation state of Se is of primary importance in determining its availability to crops (Elrashidi et al., 1987). In addition to that, the accumulation of Se in plants depends on: plant species, environmental factors, age and stage of plant growth, and several soil properties (pH, clay content, mineralogy, organic matter, and the presence of competitive ions) (Mikkelsen et al., 1989).

Selenium occurs as a minor constituent in drinking water at a concentration ranging from 0.1 to  $100 \,\mu\text{g/L}$  (NAS-NRC, 1983) and appears in water as a result of weathering of rocks and minerals, and dissolution of soluble salts in soils. In 2006, the Environmental Protection Agency (EPA) set the maximum contaminant level in drinking water (MCL) at  $50 \,\mu\text{g}$  Se/L.

Since the soil Se is the primary source for human food and animals feed, this study was conducted to improve our understanding of Se availability in Lebanese products. This study deals with the geographical distribution of Se in the soils of three major geographical areas in Lebanon: mountainous, coastal and central valley of Bekaa. It also evaluates the association between three Se fractions (water soluble, KH<sub>2</sub>PO<sub>4</sub>-Se and acid extractable-Se) in soils and some locally produced vegetables and cereals.

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#### 2. Materials and methods

#### 2.1. Sample collection

Sixty-six soil samples (33 surface (0–15 cm) and 33 subsurface (15–30 cm)) were collected from major agricultural regions in Lebanon (16 sampling points from Bekaa Valley, 5 coastal and 12 mountainous). Global Positioning System (GPS) was used to locate the sampling sites (Fig. 1). Eighty-six plant samples were collected from the same sites, as well as 23 drinking water samples (13 spring samples and 10 bottled samples).

#### 2.2. Sample analyses

#### 2.2.1. Soil samples

The soil samples were analyzed for their textural class (sand, silt and clay contents) and chemical properties (pH, electrical conductivity (EC 1:2.5 ratio), organic matter, CaCO<sub>3</sub>, NaHCO<sub>3</sub>-P, NH<sub>4</sub>OAC extractable —

(Ca, Mg, K, and Na) and DTPA extractable — (Fe, Zn, Cu, and Mn) as outlined by Bashour and Sayegh (2007)).

The three fractions of Se were extracted from the soil samples as follows:

- Soluble fraction: was extracted with distilled–deionized water which predominantly extracts the soluble and plant available selenate fractions. 10 g soil, and 30 ml distilled–deionized water, shaken for 1 h and filtered twice, first by Whatman® No.42 filter paper, followed by syringe regenerated Alltech® cellulose filters of pore size less than 0.45 µm.
- MKP extractable fraction: this extractant was reported to extract both soluble selenates (SeO<sub>3</sub><sup>2</sup>) and specifically adsorbed selenites (SeO<sub>3</sub><sup>2</sup>) on clay and oxide minerals. 10 g soil, and 30 ml 1 M–KH<sub>2</sub>PO<sub>4</sub> solution, shaken for 1 h and filtered twice, first by Whatman® No.42 filter paper followed by syringe regenerated Alltech® cellulose filters of pore size less than 0.45 µm (Chao and Sanzolone, 1989).
- Acid extractable fraction: obtained from the digestion of soil samples with a mixture of concentrated nitric and perchloric acids

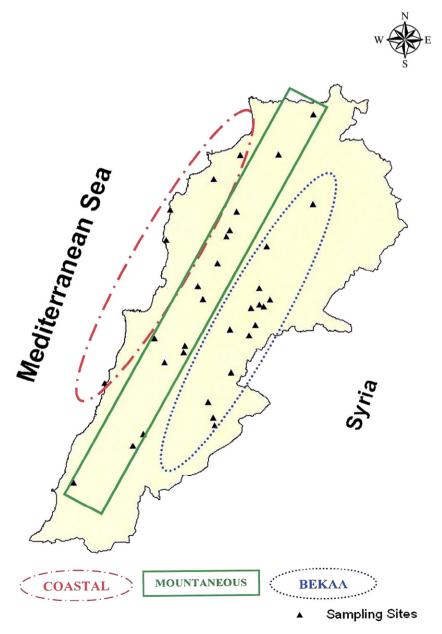


Fig. 1. Map of Lebanon showing the location of soil and plant sampling sites in three geographical regions.

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