Global NEST Journal, Vol 9, No 3, pp 201-206, 2007

TOTAL AND BIOAVAILABLE FORMS OF Cu, Zn, Pb and Cr IN AGRICULTURAL SOILS: A STUDY FROM THE HYDROLOGICAL BASIN OF KERITIS, CHANIA, GREECE

A. PAPAFILIPPAKI[1, 2, *]
D. GASPARATOS[1]
C. HAIDOUTI[1]
G. STAVROULAKIS[2]

[1]Laboratory of Soils and Agricultural Chemistry
Agricultural University of Athens, 11855, Athens, Greece
[2]Laboratory of Water & Soil Resources Quality Control
Technological Educational Institute of Crete
73133 Chania, Greece

Received: 16/02/07
Accepted: 02/04/07

*to whom all correspondence should be addressed:
e-mail: npapafilippaki@mail.chania.teicrete.gr

ABSTRACT
The hydrological basin of Keritis in Chania, Greece is mainly an agricultural area where various agrochemicals are used. In topsoils, the total and available forms of Cu, Zn, Pb and Cr were determined after their extraction with boiling Aqua Regia and DTPA respectively. Although the total heavy metal concentrations in Keritis soils were similar to the total concentrations in other agricultural areas, the studied soils can not be described as heavily polluted. The bioavailable concentrations of Cu, Zn, Pb and Cr were low. The relative availability and comparative mobility followed the order of Cu>Pb>Zn>Cr and was closely related to the soil organic matter.

KEYWORDS: Heavy metals, soil, pollution, bioavailability, Keritis basin.

1. INTRODUCTION

Addition of agrochemicals to soils and crops has become common practice in agriculture. The main purposes are the improvement of the nutrient supply in soil (fertilizers), or crop protection and disease control (pesticides). As a result, this may cause chemical degradation of the soil as the contaminants are accumulated (Garcia *et al*., 1995). The fertilizers and the pesticides usually contain significant amounts of heavy metals such as Cu, As, Co, Cr, Mo, Sr, Ti, V, Mn, Fe, Ni, Zn, Cd, Pb, Hg, Ba and Sc (El-Bahi *et al.,* 2004; Abdel-Haleem *et al.,* 2001; Garcia *et al.,* 1995). Some of them (Cu, Zn, Mn, Fe), in low concentrations are nutrient trace elements (Xu and Tao, 2004). Heavy metals are toxic to humans and plants therefore a long-term application of inorganic fertilizers, organic wastes and pesticides to soils, requires a detailed risk assessment of heavy metal accumulation in agricultural lands. The purpose of this study was to estimate the heavy metal pollution due to agrochemical contamination in agricultural soils of the hydrological Basin of Keritis.

2. MATERIALS AND METHODS

2.1 Study Area

The hydrological basin of Keritis is situated in the north part of Chania Prefecture, on the island of Crete, Greece (Figure 1). It covers a total area of 16,036 ha and consists of about 10 villages. The area has a Mediterranean climate with an annual average temperature and rainfall of 19.96°C and 824 mm, respectively. The hydrological basin of Keritis is mainly an agricultural area. The most common cultivations are olive trees, citrus trees, vineyards and vegetables. In the area also, is developed light industry (olive mills, wineries and other agricultural factories) and in the coastal zone there are many touristic units.

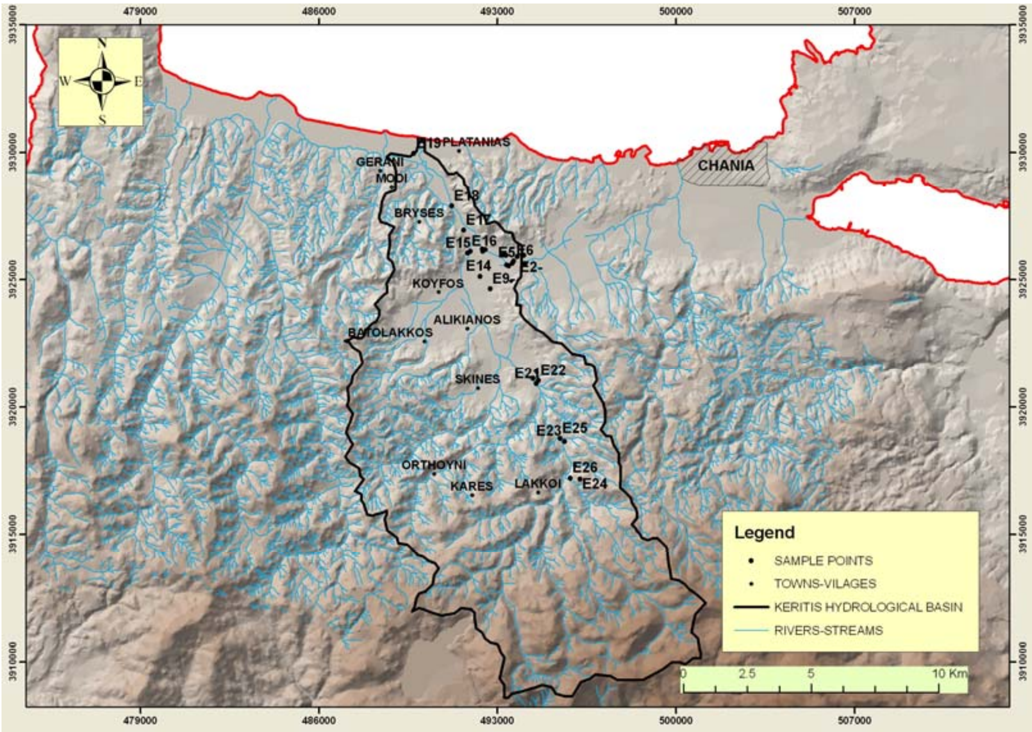

Figure 1. Map of Hydrological basin of Keritis with sample locations

2.2 Soil sampling

Twenty six surface soil samples (0-25 cm), from agricultural soils, were collected in the study area (Figure 1). The soil samples were representative of major agricultural soils in the region. Each soil sample consisted of 7-9 subsamples, were collected using a stainless steel sampling tube. The subsamples were mixed and homogenized. All soil samples were stored in plastic bags.

2.3 Analytical Methods

The collected soil samples were air-dried at room temperature, disaggregated in a ceramic pestle and mortar, and sieved through a 2 mm sieve to remove stones and pebbles. The <2 mm fraction of the soil was used for all soil analyses.

Particle size distribution was determined by the Bouyoucos hydrometer method (Bouyoucos, 1951) and pH was determined by glass and calomel electrodes in 1:1 soil–water ratio (Page, 1982). Calcium carbonate was measured by a volumetric method (Muller and Gatsner, 1971). Organic matter was determined by the Walkley–Black procedure (Nelson and Sommers, 1982).

The total heavy metal content was estimated by refluxing 1 g of soil in 15 ml hot aqua regia for 16 hours (Gasparatos and Haidouti, 2001). The available metal contents were determined by extraction of the soils with 0.005M DTPA (pH=7.3). 20 ml of DTPA solution were added to the 10 g of soil sample placed in polypropylene bottles. The bottles were shaken on a rotating shaker for 2 h and then were centrifuged (Lindsay and Norvell, 1978). The concentrations of total and available metals in the supernatant liquid were measured with a flame Atomic Absorption Spectrometry (Perkin Elmer, AAnalyst 700). All soil samples were treated in duplicate. In all cases, standards (stock standard solution of 1,000 μg ml^{-1} concentration) and blank were treated in the same way as the real samples to minimize matrix interferences during analysis.

3. RESULTS AND DISCUSSION

The texture of the surface soils in the hydrological basin of Keritis was loam, sandy clay loam and clay loam. The soil pH was acidic to slightly alkaline. The free calcium carbonate was generally low and the organic mater ranged from 1.30 - 4.46 % (Table 1).

Table 1. Certain properties of surface soil samples from the Hydrological Basin of Keritis

Property	Mean	Median	Range
pH	6.50	6.70	4.30 - 7.50
$CaCO_3$ (%)	1.39	0.24	0.05 – 10.0
Organic matter (%)	2.35	2.20	1.30 - 4.46

3.1. Total heavy metal concentrations

Table 2 shows the total metal concentrations of the studied surface soils in the hydrological basin of Keritis and, for comparison, their typical concentration ranges and common values in soils (Alloway, 1990).The examined soils can be considered unpolluted, since their concentrations fit in the common values, with the exception of zinc, which seems to have a slightly higher value.

Table 2. Total metal concentrations in studied soils (0-25 cm) of Keritis, typical literature ranges and most common values (mg kg^{-1})

	Hydrological Basin of Keritis				
Element	Mean	Median	Range	Typical range	Common Value
Cu	30.59	25.15	10.28- 68.50	2- 250	20 – 30
Zn	73.2	65.63	39.75 – 139	1 – 900	50
Pb	18.92	18.61	11.48 – 33.55	2 – 300	10 – 30
Cr	100.06	97.02	79.73 – 162.38	5 – 1500	70 - 100

Table 3 shows the total metal concentrations in agricultural soils in various areas of the world. The total concentrations of the studied metals are similar to the total metal concentrations of the investigated soils.

Table 3. Total metal concentrations in agricultural soils in the world (mg kg^{-1})

	Cu	Zn	Pb	Cr
England[a]				
Mean	23.1	97.1	74	41.2
Median	18.1	82	40	39.3
USA[a]				
Mean	29.6	56.5	12.3	-
Median	18.5	53	11	-
China[b]				
Mean	33.0	84.7	40	71.4
Median	27.3	83.6	33.5	67.8
Range	4.1 - 189	11.1 – 284	10.1 -180	14.8 - 317
Italy[c]				
Mean	30	94	215	162

a: Alloway, 1995, b: Wong *et al.*, 2002, c: Abollino *et al.*, 2002.

3.2. Available heavy metal concentrations

The bioavailable concentrations of the studied heavy metals in soils of the hydrological basin of keritis were low (Table 4).

Table 4. Bioavailable heavy metals concentrations in the studied soils (mg kg^{-1})

Element	Mean	Median	Range
Cu	4.86	3.19	1.55 – 15.93
Zn	2.09	1.82	1.31 – 3.26
Pb	2.28	2.36	0.97 – 3.98
Cr	2.11	1.93	1.39 – 3.12

The correlations between the total concentrations and the DTPA extractable fractions, were studied and were found significant. Figure 2 shows the linear relationships between the total and bioavailable forms of Cu, Zn, Pb and Cr in the investigated soils of Keritis. Andreu and Garcia (1999), observed similar correlation coefficients for Cu, Zn and Pb in agricultural soils.

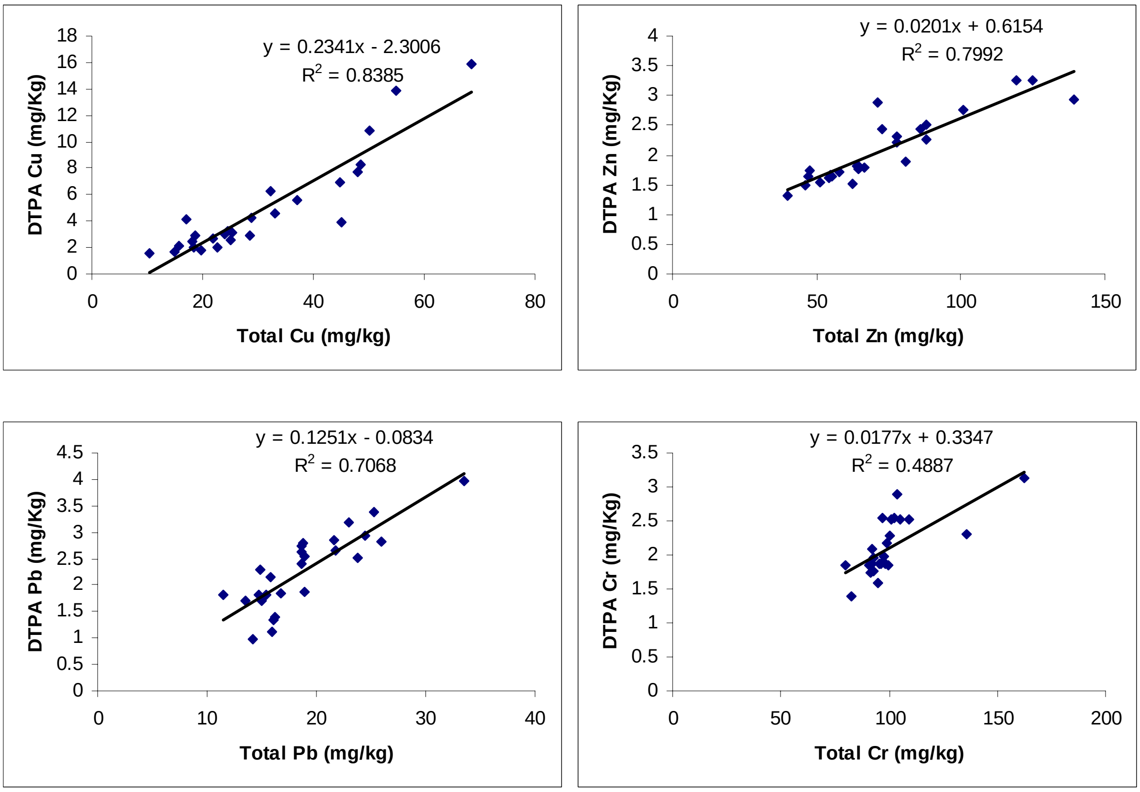

Figure 2. Linear relationships between total – DTPA Cu, Zn, Pb and Cr in soils of the Hydrological basin of Keritis

The percentages of the total Cu, Zn, Pb and Cr extracted with DTPA (Table 5) could be a good indicator of the quantity of metal available for plants and could reflect their comparative mobility (He and Singh, 1993).

Table 5. Bioavailable content as a percentage of the total metal content in Keritis soils (%)

Element	Mean	Median	Range
Cu	14.10	13.60	2.30 – 25.30
Zn	2.92	2.85	2.35 – 4.06
Pb	12.04	12.25	6.80 – 15.90
Cr	2.11	2.04	1.68 – 2.78

The bioavailable content as a percentage of the total metal content was generally low. The relative availability and consequently the comparative mobility of the studied metals followed the order Cu > Pb > Zn > Cr. The same order of relative availability of Cu, Pb and Zn was observed by Andreu and Garcia, (1999) in agricultural soils and by Gasparatos *et al.,* (2001b), in urban- industrial soils in Athens, Greece. Maiz *et al.,* (1997), showed that Cr had the lowest availability compared to Cu, Pb and Zn.

Organic matter plays a significant role in the availability and mobility of the heavy metals in soils. The humified organic matter is involved in the formation of soluble complexes especially with Cu and Zn (Vega *et al.,* 2004). On the other hand the presence of organic matter retards the mobility of Cr due to the reduction of the mobile Cr(VI) to the relatively immobile Cr(III) (Banks *et al.,* 2006).

The extractable forms of these metals are strongly related to the organic matter concentration. Figure 3 shows the linear relationships between organic matter and bioavailable forms of Cu, Zn, Pb and Cr in the investigated soils of Keritis.

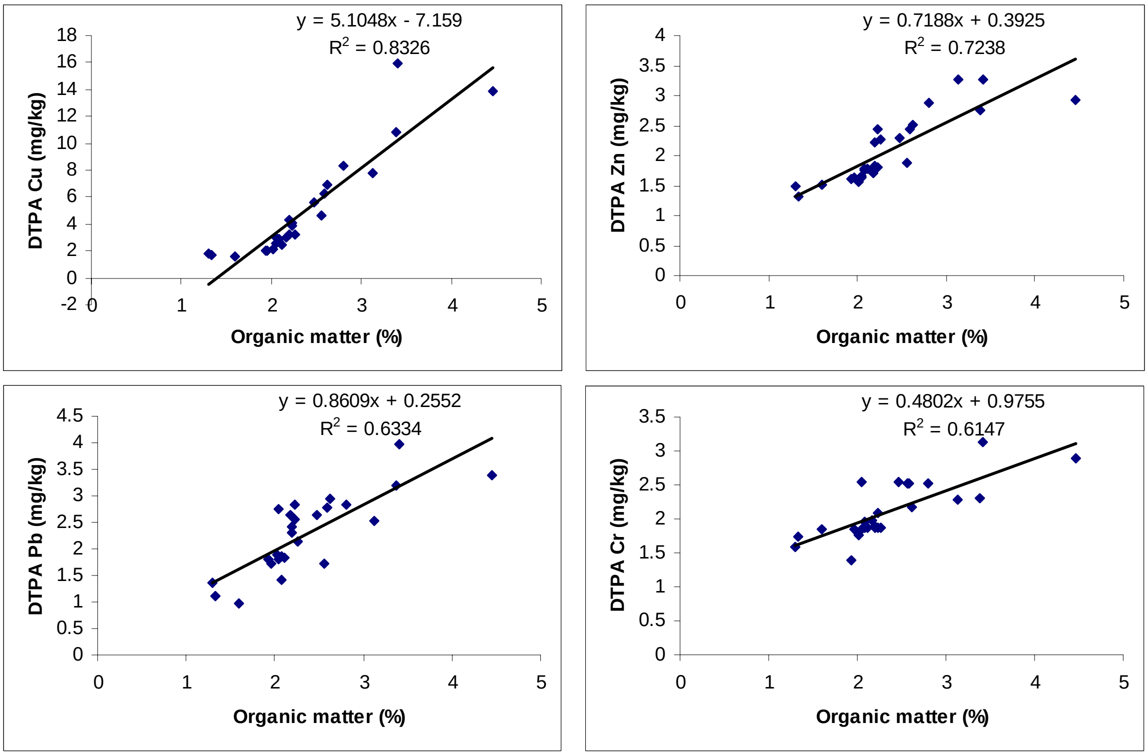

Figure 3. Linear relationships between organic matter – DTPA Cu, Zn, Pb and Cr in soils of the hydrological basin of Keritis.

4. CONCLUSIONS

This study investigated the pollution of Cu, Zn, Pb and Cr in agricultural soils of Keritis Hydrological basin. The examined soils can be considered unpolluted since their total and bioavailable concentrations were generally low. The relative availability and comparative mobility followed the order Cu>Pb>Zn>Cr. Soil organic matter showed a strong relationship with this order due to the formation of soluble and insoluble complexes with the metals.

ACKNOWLEDGMENT

Financial support for this project was provided from the Operational Program for Education and Initial Vocational Training of the Ministry of Education of Greece and the European Union in the framework of the project Archimedes II: "Support of Research Teams of Technological Educational Institute of Crete", entitled Multiparametric identification system development for the origin of water resources in karstic basins: Application in the Keritis river basin (Natura 2000-Chania)

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