

GEOCHEMICAL SURVEYS ON THE TOXIC HEAVY METALS Pb, Zn, AND Cd IN AGRICULTURAL SOIL SAMPLES FROM BASHINO VILLAGE–RECHANI AT THE VELES CITY AREA, MACEDONIA

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Abstract. In the agricultural soil samples of the Bashino village–Rechani at the Veles city area were determined polluted surfaces especially by Pb, Zn and Cd of anthropogenic origin (due to the metallurgic activities of Pb-Zn furnace factory), as follows: soil samples with increased Pb contents of cca 100 to 2000 ppm actually represent common contents for the mentioned heavy toxic metal inside the treated region. So, the situation in the investigated area with respect to Pb content is really critical. In some (very rare cases) soil samples were determined even 3000 to 5000 ppm Pb; the Zn contents in the soil samples ranged from cca 600 to 2000 ppm and they are common especially for the agricultural surfaces (extending on the right side of the Vardar river as well as at Lokva, Rechani, Hladnjacha) of the investigated area. The other surfaces (of cca 40-50%) of the investigated area are treated as very weak or yet non-polluted microlocalities with Zn contents below 300 ppm Zn; the surface of the investigated region is nearly cca 90% polluted with Cd contents (ranged from cca 3-7 ppm while at some points were determined extremely high Cd contents of cca 30-70 ppm Cd).

Keywords: geochemical assessment, heavy metals pollution, agricultural soil samples.

AIMS AND BACKGROUND

The investigated area from Bashino village to Rechani microlocality (with total surface of cca 3-3.5 km²) in the frame of the Veles city region, is very well known¹⁻³ for its early vegetable products widely distributed on the markets in Macedonia. The Pb-Zn furnace factory (35 years ago) was located in the close vicinity of the investigated region (for cca 300-500m westward).

The geological-petrologic characteristics of the soil in the Veles city and the whole region belong to the so-called 'Veles series' composed of different schists (quartz-sericite-chlorite, graphitic schists, etc.), serpentinites, ultramafic rocks, limestone, marbles, etc. of Paleozoic age and characterised with very low Pb, Zn and Cd backgrounds. So, the primary geological-petrologic composition of the soil of the Veles city and its surroundings is not responsible for the very high levels of Pb, Zn and Cd contents in the agricultural soils of the region.

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EXPERIMENTAL

Sampling method, preparation. The investigated area was treated inside one detailed sampling grid on cca 100×200 m (Fig. 1) with total 148 agricultural soil samples. Every soil sample actually represents an average sample, obtained by means of 5 soil samples according to one sampling scheme (Fig. 2), performed from the surface to a depth of cca 10-20 cm (Ref. 4).

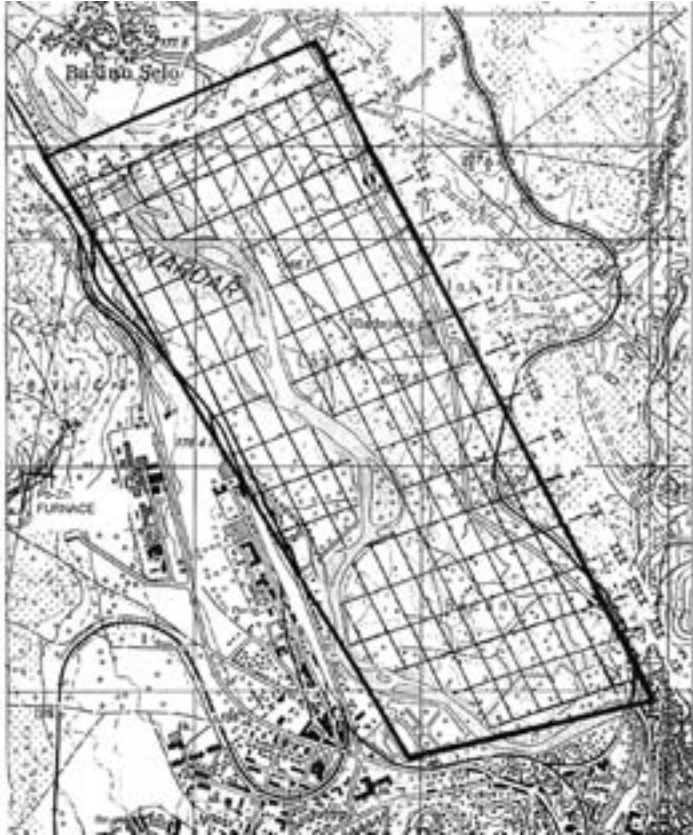


Fig. 1. Sampling map of the investigated area Bashino village–Rechani, the Veles city

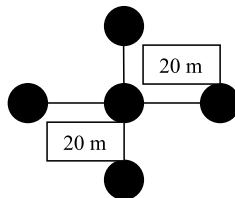


Fig. 2. Sampling scheme for each soil sample

The soil samples were air dried for four weeks, after that gently crushed and then passed through a sieve below 0.063 mm.

The obtained soil samples, according to the mentioned preparation procedure, were further subjected to emission spectral analyses (ESA) as well as to control ICPS analyses.

Chemical analysis. ESA was applied for all 148 agricultural soil samples, according to an analytical and technical procedure as follows:

- PGS-2, Zeis, Jena equipment;
- The Hilger projector;
- Direct electric arc obtained at 220 V and 2-10 A.

ICPS and RF-analysis were applied as control analyses, especially for certain samples, characterised by very high Pb, Zn and Cd contents.

RESULTS AND DISCUSSION

PB DISTRIBUTION IN THE AGRICULTURAL SOIL SAMPLES FROM THE INVESTIGATED AREA OF THE VELES CITY

The obtained data on the Pb contents (by ESA) in the examined agricultural soil samples (from Bashino village–Rechani at the Veles city) are summarised in Table 1.

Table 1. Pb distribution in soil samples of the investigated region, the Veles city

Pb content (ppm)	<i>f</i>
Below 99	48
100-300	74
301-600	11
601-5000	15
Total	148

On the basis of the data in Table 1, a polygon of frequency (Fig. 3.) for Pb distribution in the examined soil samples was constructed.

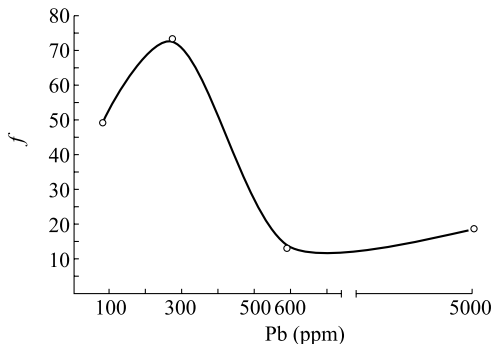


Fig. 3. Polygon of frequency of Pb distribution in agricultural soil samples from the investigated area, the Veles city

Table 2. Statistical data on Pb distribution in the examined soil samples, the Veles city

Total number of examined soil samples	148
Minimum (ppm)	20
Maximum (ppm)	5000
Median (ppm)	200
Detection limit (ppm)	2
Arithmetic mean	305
Maximum allowed Pb content in soil samples ⁵	100
Standard deviation (σ by log. method)	6.71
The Clarke content of Pb in soils	30

The data obtained for Pb contents in the soil samples studied allow to make the following conclusions:

- about 33% of the total number of the examined soil samples have Pb contents to 90 ppm;
- about 50% of the total number of the examined soil samples show Pb contents (91-300 ppm) nearly three times higher than the maximum allowed Pb contents in soil samples;
- nearly 17% of the total number of examined soil samples are estimated as extremely polluted points, and have Pb contents ranging within 301-5000 ppm.

Drawing of eco-geochemical map of Pb distribution in soil samples, the Veles city.

The drawing of the eco-geochemical map of Pb distribution in the soil samples of the examined area of the Veles city (Fig. 4), was performed on the basis of the following criteria:

- All soil samples with Pb contents up to 99 ppm are connected by the interpolation processes in light-grayish or non coloured surfaces of yet non-polluted areas at Bashino village, Hladnjacha, Rechani microlocality, etc.
- Agricultural soil samples with Pb contents, varying within 100-300 ppm, actually represent the first Pb polluted zone of minor importance at Lokva microlocality (grayish coloured surface).
- The contoured surfaces (at Rechani, Lokva, near Bashino village localities as well as the right beach of the Vardar river) with Pb contents from 301 to 600 ppm, actually represent the second and more Pb polluted zone (dark grayish coloured surface).
- The extremely Pb polluted zone is the zone with Pb contents in the range from 601 to 5000 ppm, marked in the map with the most darkened halos, at the microlocalities Lokva, near the main road to the Bashino village–Rechani, on the right beach of the Vardar river, just vis-à-vis the Pb-Zn furnace factory.



Fig. 4. Eco-geochemical map of Pb distribution in the examined soil samples, the Veles city

Zn DISTRIBUTION IN THE AGRICULTURAL SOIL SAMPLES FROM THE INVESTIGATED AREA, THE VELES CITY

The distribution of Zn in the examined soil samples at the Veles city area is quite well visible and evident from the following table (Table 3).

Table 3. Distribution of Zn in the agricultural soil samples from the investigated area, the Veles city

Zn content (ppm)	<i>f</i>
Below 299	84
300-600	47
601-1000	11
1500-2000	6
Total	148

On the basis of the data of Table 3, a polygon of frequency of Zn distribution in the examined soil samples was constructed (Fig. 5).

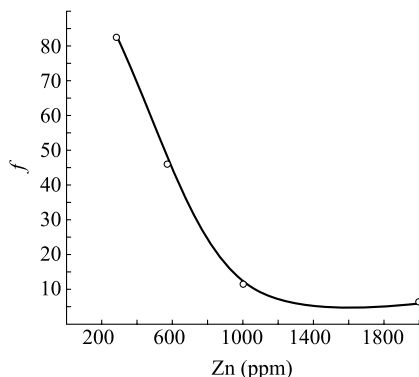


Fig. 5. Polygon of frequency of Zn distribution in the agricultural soil samples from the the investigated area, the Veles city

Table 4. Statistical data on Zn distribution in the examined soil samples, the Veles city area

Total number of examined soil samples	148
Minimum (ppm)	50
Maximum (ppm)	2000
Median (ppm)	200
Detection limit (ppm)	50
Arithmetic mean	320
Maximum allowed Zn content in soil samples ⁵	299
Standard deviation (σ by log. method)	4.9
The Clarke content of Zn in soils	90

Due to very intensive metallurgical activity (more than 35 years) in the Veles city area, the Zn contents in the examined agricultural soil samples increased as follows:

- arithmetic mean, for Zn (320 ppm) in the examined soil samples is about 3.6 times higher than the Clarke value (90 ppm) for the same element;
- from the total number (148) of examined soil samples, in 64 samples were determined Zn contents higher than 300 ppm, which in the limits between 300-2000 ppm, and representing cca 43% of the mentioned total number.

Drawing of eco-geochemical map of Zn distribution in soil samples, the Veles city. The distribution of Zn in the examined soil samples from the Veles city area is presented on a eco-geochemical map (Fig. 6) based on the following criteria:

- All points of soil samples with Zn contents to 299 ppm are enclosed and contoured (by the interpolation processes) in yet non-polluted areas (for example

one bigger surface at Rechani, Hladnjacha, Bashino village microlocalities) representing cca 2-2.5 km² of the total 3.5 km² (white marked surfaces).

- The examined soil samples I with Zn contents ranging within 300-600 ppm comprises the first (I) Zn-polluted zone (marked by light-grayish colour).

- More intensively Zn polluted areas (contouring surfaces with Zn contents in the limit of 601-1000 ppm) were determined at some surfaces at the microlocalities of Rechani, Lokva, Hladnjacha and on the right beach of the Vardar river just eastward and north-eastward of the Pb-Zn furnace factory (grayish coloured).

- The most intensively polluted areas (with Zn contents within 1500-2000 ppm) were determined just eastward from the Pb-Zn furnace factory for cca 300 to 1000 m (the most darkened halos).

- The most intensively polluted areas were determined also at the main road from Hladnjacha to the Bashino village as well as in smaller surfaces at Rechani microlocality.



Fig. 6. Eco-geochemical map of Zn distribution in the examined soil samples, the Veles city

Cd DISTRIBUTION IN THE AGRICULTURAL SOIL SAMPLES FROM THE INVESTIGATED AREA, THE VELES CITY

In the investigated area of agricultural surfaces at the Veles city were determined very interesting results on Cd contents from eco-geochemical point of view (Table 5).

Table 5. Distribution of Cd in the agricultural soil samples from the investigated area, the Veles city

Cd content (ppm)	<i>f</i>
Below 1	39
3-7	87
8-20	21
21-70	1
Total	148

On the basis of the aforementioned data was constructed the polygon of frequency of Cd distribution in examined soil samples (Fig. 7).

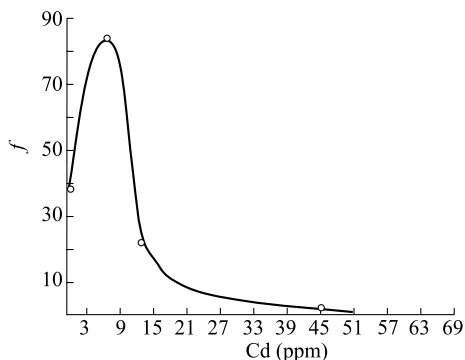


Fig.7. Polygon of frequency of Cd distribution in the agricultural soil samples from the investigated area, the Veles city

Table 6. Statistical data for Cd distribution in the examined soil samples, the Veles city area

Total number of examined soil samples	148
Minimum (ppm)	3
Maximum (ppm)	70
Median (ppm)	5
Detection limit (ppm)	1
Arithmetic mean	7
The Clarke content of Cd in soils (ppm)	0.35
Median for Cd in soils from Slovenia (ppm)	0.5
Median for Cd in soils from Ljubljana (ppm)	0.6
Standard deviation (σ by log. method)	1.44

According to the presented geochemical data concerning the Cd distribution in the soil samples under study (Tables 5 and 6) may be concluded that they are characterised by peculiar (unusual high) and remarkably anomalous Cd values in comparison, for example, with Slovenian–Ljubljana and world averages.

Drawing of eco-geochemical map of Cd distribution in soil samples, the Veles city area. The geochemical map of Cd distribution (Fig. 8) in the examined soil samples for the studied area was constructed based on the following criteria:

- All soil samples with Cd contents below the detection limit (1 ppm) for this micro-element are enclosed by the interpolation processes in yet non-polluted surfaces of minor importance at some smaller microlocalities of Rechani, Hladnjacha, Bashino village (Fig. 7) (marked light grayish).

- The examined soil samples with Cd contents ranging within 3-7 ppm, comprise the first (I) Cd-polluted zone which is the most widespread through all microlocalities (Rechani, Hladnjacha, Bashino village, the right part of the Vardar beach) of the investigated area (marked grayish).



Fig. 8. Eco-geochemical map of Cd distribution in the examined soil samples, the Veles city

- The second (II) more intensive polluted area encloses smaller surfaces of the aforementioned microlocalities with Cd contents in the limit of 8-20 ppm (marked dark grayish).

- The third (III) as well as the most intensive polluted zone characterised by Cd contents in the range of 21-70 ppm actually is presented in strictly and very small surfaces about 500-700 m eastward of the Pb-Zn furnace factory on the right beach of the Vardar river (the most darkened halos).

CONCLUSIONS

In the frame of the aforementioned examinations may be concluded the following:

- The polluted points with 301-600 ppm Pb actually represent usual Pb content, while polluted points with 700, 1000 and 2000 ppm Pb are not so rare in the mentioned microlocality. At one point was determined even extremely high Pb content of 5000 ppm. So, in the examined surface at the Bashino village in Rechani area, the polluted points are characterised with 2, 3, 6, 10, even 20-30 times increased Pb contents in comparison with the tolerant 100 ppm of the same microelement according to the world values.

- The examined area is also polluted with Zn. In comparison with the tolerant 300 ppm Zn, in the examined area were determined even 2-3 times higher contents of the same microelement.

- The pollution with Cd in the examined area was estimated also at one level of alarming category, because at certain points were determined from cca 3-7 ppm Cd to extremely 20-30 or even 70 ppm Cd. These Cd contents are cca 3-7 to cca 20-30 times higher than the world values (0.5-1 ppm).

- Thus, it may be underlined that the agricultural soil samples at the Bashino village–Rechani, the Veles city area, are actually highly polluted to one alarming ratio with the heavy toxic metals Pb, Zn and Cd.

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