

Evaluation of the Heavy Metals Content in Soil Around a Thermal Station

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In this paper is presented the stage of the soil around a thermal station from Gorj County, Romania charging with heavy metals (cadmium, copper, zinc and lead). The samples were taken on several cardinal points and at the different distances from the thermal station over a period of three years, 2005, 2006 and 2007. The heavy metal concentrations from soil were determined by using inductively coupled plasma atomic spectrometry (ICP - AES). The experimental results showed serious deviations from the valid Romanian law, only in the case of copper and zinc. From the pH point of view the soil is moderately acid.

Keywords: soil pollution; heavy metals; heavy metal content in soil

The current abundance of heavy metals in life environments is the result of two factors. The first factor which contributes with heavy metals in soil is the natural factor and the other is anthropic factor. The anthropic activity represents an important source of heavy metals in soil. If it is taken into consideration that, in fact, the most part of the soils are subjected to these forms of impact, it may be considered that the anthropic factor influences almost totally the general current level of heavy metals in soil [1-3].

In Europe the main sources of soil polluting with metals are: steelworks, antimony and copper smelters, steel mills, mines, chemical industries, oil refineries, cement factories, metal and battery industries, thermal power plants, coal combustion [4-9]. The main countries in which heavy metals soil pollution is due to the thermal power plants activity are: Czech Republic, Germany, Poland, Russian Federation, Slovenia, Turkey, United Kingdom [10, 11].

On the basis of our National Monitoring System it can be estimated that 900 thousands hectare of soil are chemically polluted, from these 200 thousands hectare are excessively polluted, and for this reason they are totally unproductive. Chemical's soil pollution in Romania is due to emissions from chemical industry, iron-and-steel industry, cement factories, metal and battery industries, thermal power plants, coal combustion, refinery, and transportation.

In every year about 138 millions of polluting substances are eliminated in atmosphere, substances which by depositing on soil modify negatively soil properties [12].

The most heavy metals soil polluting factories are: Neferal and Acumulatorul (Bucharest), the smelter from Copsa Mica, mines and copper factories from Zlatna, Baia Mare and Ferneziu (Maramures), metallurgical factory from Hunedoara, fertilizers factory from Valea Calugareasca, Turnu Magurele and Navodari. Also in Romania are many thermal power stations which are working with coal, and they are many sources of soil pollution with heavy metals. At this type of soil pollution is associated acid soil pollution. This unfavourable association leads to an increasing of toxic metal solubility in soil.

In Romania the principal thermal power plants are: Turceni, Rovinari, Mintia, Isalnita, Braila, Brazi, Ludus-Iernut, Borzesti, Bucharest South, Galati, Craiova II, Paroseni. At the end of 2006 they had a total generating capacity of 11.335 MW. The main environmental problem of all these thermal power plants is related to the disposal of fly ash, which in many cases, contains heavy metals. It is known that toxic trace metals may leach when fly ash is in contact with water [12].

The quantitative presence of the heavy metals in the soil is dependent on their concentration in the coal burned in a thermal station, on the coals quality, on the combustion temperature, on the volatilization temperature of the metals and on the climate factors such as wind direction, speed and atmospheric pressure [13-15]. Low quality coals with high ash content cause enormous quantities of both gaseous and solid fly ash emissions.

The variation of concentration of various parameters such as pH value, copper, cadmium, zinc and lead with depth of soil layer has been investigated in this paper to assess the extent of soil pollution near the Rovinari thermal station.

Experimental part

Reagents and stock solutions

All reagents involved in this study (65% HNO₃, 32 % HCl) were of puris p.a. quality. All of them were purchased from Merck Chemistry Co. Ltd. The ICP Multielement Standard Solution IV (1000±10 mg/L element) (Merck) was used to calibrate the ICP spectrometer.

Soil samples collection and digestion method

In order to establish the heavy metals charging degree of the soil around the thermal station, there were taken samples on several cardinal directions and at different distances from the thermal station, being considered a potential pollution source with heavy metals. There were taken samples on two depth profiles: 0 - 10 cm and 10 - 20 cm, on a three years period: 2005, 2006 and 2007.

The metals distribution in the top layer of soil is important in relation to the bioavailability for plants and the risk to enter the food chain. This is the reason why for

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the establishing of soil pollution with heavy metals around the thermal station were chosen two depth profiles: 0 – 10 cm and 10 – 20 cm.

Soil samples were first pretreated. They were dried in air at room temperature for one week. After that the samples were crushed, and sieved by using a nylon fiber sieve (2 mm) to remove stones, heated at $105 \pm 5^\circ\text{C}$ for 3 h, grinded then sieved again ($< 90\mu\text{m}$). The resulted powder was stored in plastic bottles until digestion with Lunge mixture was performed.

2.5000 g sample of soil pretreated was moistened with a volume of 1 mL distilled water, and it was transformed into a slurry in a reaction flask. Then 7 mL of 32% HCl followed by 21 mL of 65% HNO_3 were added drop by drop to reduce foaming. A volume of 15 mL 0.5 M HNO_3 was introduced into the absorption vessel connected to the reflux condenser of the reaction flask. The sample was allowed to stand for 16 h at room temperature for low oxidation of the organic matter of soil. Then the temperature of the reaction mixture was slowly risen until reflux conditions and maintained for 2 h. The content of the absorption vessel was added into the reaction vessel through the reflux condenser and both rinsed with 10 mL of 0.5 M HNO_3 [17-19].

After cooling at room temperature, the sample was transferred into a 100 mL graduated flask with 2% (v/v) HNO_3 . The slurry was filtered through a cellulose based membrane filter with medium pores and the filtrate was used to determine the metals by inductively coupled plasma atomic spectrometry (ICP – AES).

Instrumentation

The experimental determinations were carried out in the Laboratory of the Environmental Protection Agency Gorj. Following preparation, samples were analysed ICP – AES, using a Varian Liberty-100 Sequential Spectrometer. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Results and discussions

The pH and the heavy metals content from the soil around the Rovinari thermal station are summarized in table 1.

The interpretation of the obtained results was done according to the valid Romanian law, whose reference values are presented in table 2 [16].

The values of the cadmium concentration from the soil, on the two profiles and on the five cardinal directions, are presented in the chart from figure 1.

The normal cadmium content in soils is of 1 mg/kg, and the alert level for the sensitive usages is of 3 mg/kg whereas the intervention one is of 5 mg/kg.

Analyzing the obtained data for cadmium during the three years of study, it is observed that, in all cases, and cardinal directions and on the two depth profiles, the obtained values are within normal values. The highest value was registered in 2005, on the North direction from the thermal station and at the depth of 0-10 cm (1.0 mg/kg).

On the SE direction from the thermal station and the two sampling depths, the cadmium values determined were under method detection's limit.

Table 1
HEAVY METALS CONTENT IN SOIL NEAR THE THERMAL STATION AREA

Sampling point	2005					2006					2007				
	pH	Cd (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	pH	Cd (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	pH	Cd (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)
2000 m N Thermo 0-10 cm	6.4	1.0	23.8	73.0	12.0	6.2	0.4	31.2	88.8	4.4	6.3	nd	30.0	87.4	10.0
2000 m N Thermo 10-20 cm	6.5	0.2	24.0	73.8	4.4	6.5	0.2	30.8	83.4	6.0	6.2	0.4	133.2	82.2	nd
300 m V Thermo 0-10 cm	6.2	0.2	35.4	112.6	6.4	6.6	0.2	45.0	139.0	6.2	6.5	nd	37.2	47.2	0.4
300 m V Thermo 10-20 cm	6.3	0.2	41.8	91.8	9.4	6.3	0.2	21.2	47.4	2.0	6.6	nd	28.4	158.6	0.2
1000 m SV Thermo 0-10 cm	6.5	0.4	30.0	99.2	28.8	6.2	0.2	49.0	122.8	10.6	6.2	nd	41.0	71.2	nd
1000 m SV Thermo 10-20 cm	6.5	nd	32.0	89.2	2.48	6.1	nd	46.2	115.8	6.2	6.3	0.2	10.0	41.2	1.2
800 m SE Thermo 0-10 cm	6.4	nd	38.0	58.0	3.0	6.5	nd	44.8	43.0	6.2	6.6	nd	19.2	148.2	nd
800 m SE Thermo 10-20 cm	6.4	nd	38.0	55.8	2.4	6.0	nd	21.0	39.8	2.0	6.2	nd	21.4	301.2	0.4
1500 m S Thermo 0-10 cm	6.2	nd	53.4	60.6	5.6	6.1	nd	18.6	35.4	1.6	6.3	0.4	34.0	152.0	3.0
1500 m S Thermo 10-20 cm	6.5	0.6	16.0	44.8	2.0	6.0	0.4	17.8	36.2	nd	6.5	0.8	55.2	232.2	5.6

¹Thermo – thermal station; ²N, S, SE, SV – sampling directions; ³nd – not detected

Table 2
NORMAL VALUES ALERT LEVEL AND INTERVENTION LEVEL FOR SOIL [16]

Metal	Normal value (mg/kg)	Alert level (mg/kg)		Intervention level (mg/kg)	
		Sensitive area ¹	Less sensitive area ²	Sensitive area ¹	Less sensitive area ²
Cu	20	100	250	200	500
Pb	20	50	250	100	1000
Zn	100	300	700	600	1500
Cd	1	3	5	5	10

¹Sensitive area: residential and agricultural

²Less sensitive area: commercial and industrial

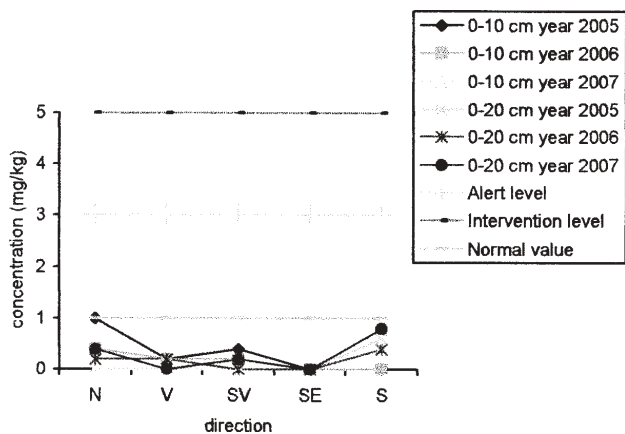


Fig. 1. Cd content in soil around the Rovinari thermal station

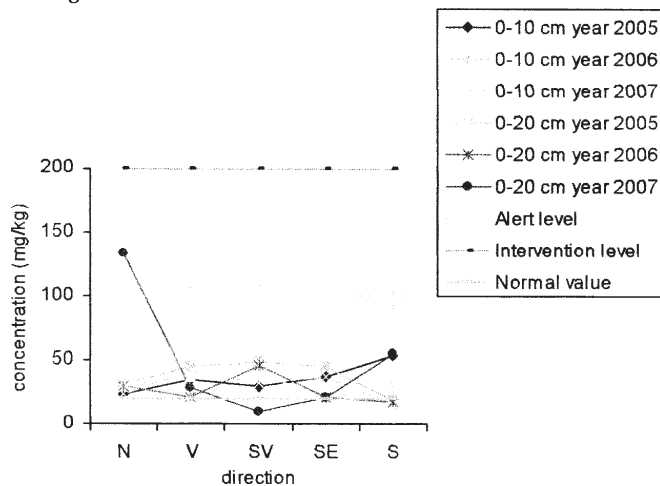


Fig. 2. Cu content in soil around the Rovinari thermal station

The values of the copper concentrations from the soil, on the two depth profiles and the five cardinal directions, are presented in figure 2.

On the N direction, during 2005 and 2006, the normal content in the soil was exceeded on both sampling depths. In 2007, on the depth profile 0-10 cm the normal content was exceeded, and on the 10-20 cm profile both the normal value and the alert level were exceeded. This means an excess of 6.6 times from the normal content and of 1.5 times the alert level.

On the W direction there were registered excesses of normal values in all cases on the two depth profiles. The highest values was registered in 2006 (45.0 mg/kg) on the 0-10 cm depth profile, which represents a 2.2 times excess from the normal value, and the lowest value registered in 2006, on the 10-20 cm depth profile (21.2 mg/kg), was close to normal.

On the SW direction, on the 0-10 cm depth profile, during the three years of study, there were registered excesses of the normal copper content, the highest value being in 2006 (49.0 mg/kg). This represents an excess of 2.45 times from the normal level. The lowest value was in 2007 (10 mg/kg) on the depth of 10-20 cm.

On the SE direction, from the six measured values for copper, the highest concentration was registered in 2006 (44.8 mg/kg), on the depth 0-10 cm, representing an increase of 2.24 times from the normal value. In 2007, on the depth 10-20 cm, the obtained value was 19.2 mg/kg, under the normal content, and for the rest of the samples, the usual concentrations for copper exceeded the normal values.

On the S direction, three of the samples had values under the normal content (16.0 mg/kg in 2005, on the depth 10-20 cm and 18.6 mg/kg and 17.8 mg/kg, in 2006).

For the rest of the cases, the values exceeded the normal quantity of copper from the soil.

Besides, on this direction there were met the most cases of soil charging with copper, under the normal values.

The alert level for sensitive usages of zinc is 300 mg/kg, and the intervention level of zinc for sensitive usages is 600 mg/kg.

The values obtained for zinc, on the five cardinal directions and two depth profiles are presented in the chart from figure 3.

On the N direction, all values determined for zinc are under the normal content in the soil. The highest value was registered in 2006, on the depth 0-10 cm (88.8 mg/kg), with 11.2% under the normal value. The lowest value was registered in 2005, on the depth 10-20 cm (73 mg/kg), this representing 27% less than the normal content.

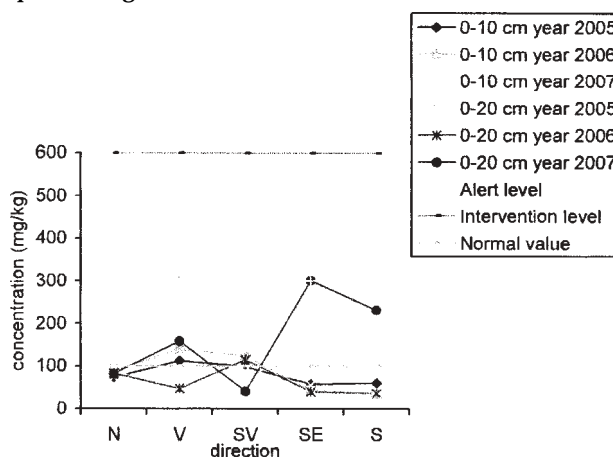


Fig. 3. Zn content in soil around the Rovinari thermal station

On the W direction there were registered excesses of the normal zinc content from the soil, but also values under the normal level.

Thus, in 2005 and 2006 there were registered excesses on the depth profile 0-10 cm (112.6 mg/kg, 139 mg/kg respectively), and in 2007 - 158.6 mg/kg, on the depth profile 10-20 cm.

In the other cases, the obtained values were under the normal level, the lowest concentrations being registered in 2006, on the profile 10-20 cm and in 2007 on the profile 0-10 cm (47.4 mg/kg, 47.2 mg/kg respectively).

The largest excess from the normal content of Zn in the soil was registered in 2007, on the depth 10-20 cm (158.6 mg/kg), 58.6% increase.

On the SW direction, in 2005 the obtained values were under the normal content, on the two depth profiles (99.2 mg/kg and 89.2 mg/kg). In 2006, on both depth profiles there were registered excesses of the normal content (122.8, 115.8 mg/kg respectively).

For 2007 there were determined values under the normal level on both depths (71.2 mg/kg and 41.2 mg/kg).

On SE direction, during 2005 and 2006 there were no records of excesses of the zinc content from the soil as compared to normal values. The highest value was registered in 2005, on the depth 0-10 cm (58 mg/kg), and the lowest in 2006, on the depth 10-20 cm (39.8 mg/kg). During 2007, on the depth 0-10 cm, the obtained value for zinc exceeded the normal content with 48.2% (148.2 mg/kg), and on the depth 10-20 cm there was exceeded both the normal content, as well as the alert level (301.2 mg/kg).

Besides, this was the only case when the alert level for zinc was exceeded for sensitive usage fields. On the S direction, during 2005 and 2006, there weren't registered any excesses as compared to normal values, on neither of

the depth profiles. Higher values were measured in 2005 as compared to 2006. In 2007 there were registered excesses as compared to the normal zinc level from the soil on both depths, the higher value being registered on the depth 10-20 cm (232.2 mg/kg), as compared to 152 mg/kg, the value on the depth 0-10 cm.

Lead has a normal content in the soil of 20 mg/kg, an alert level of 50 mg/kg, and an intervention level of 100 mg/kg for sensitive usages.

During the three years of study, on the N direction, the values obtained for lead are under-normal on the two sampling depths. The highest value was registered in 2005, at the depth of 0-10 cm (12 mg/kg), 1.6 times smaller than normal. In 2006 and 2007, on the sampling depth 10-20 cm, the obtained values for lead were under the method's detection limit.

On the W direction, all values obtained for lead during the three years and on both depths were under the normal level from the soil. The highest value was registered in 2005, on the depth 10-20 cm (9.4 mg/kg), and the lowest in 2007 on the same depth (0.2 mg/kg).

The values obtained for lead, on the five cardinal directions and two depth profiles are presented in the chart from figure 4.

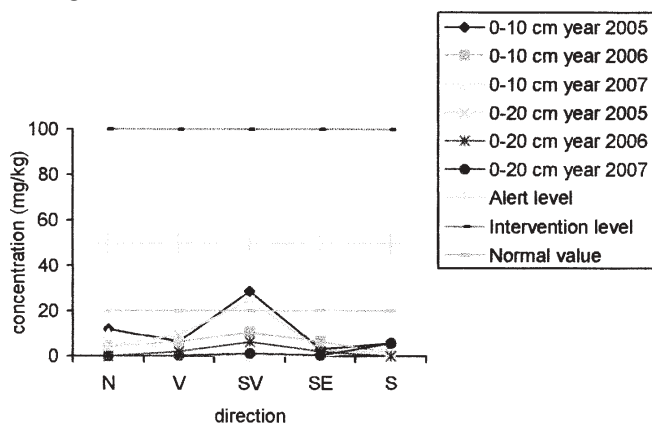


Fig. 4. Pb content in soil around the Rovinari thermal station

On the SW direction there were registered the highest lead values in the case of the soils used for agricultural purposes. Thus, during 2005, on the two sampling depths, the values obtained for lead exceeded the normal content (28.8 mg/kg and, respectively, 24.8 mg/kg), which represents an excess of 1.44 times from the normal value. In 2007, on the depth 0-10 cm, the obtained value for lead was under the method's limit detection.

On SE direction, the values obtained for lead during the three years of study on the two sampling depths were under the normal level of 20 mg/kg. The maximum value was registered in 2006 and was of 6.2 mg/kg, and the minimum value in the year 2007, this being under method detection's limit.

The same situation was met on the S direction, the measured values for lead, during the three years and on the two depths, being under the normal level. The maximum was registered in 2005 and 2007 (5.6 mg/kg), on the depth 0-10 cm and, respectively, 10-20 cm. In 2006, on the depth 10-20 cm, the value of lead was under method detection's limit.

The measurements performed in order to determine the soil's pH in the influence area of the Rovinari thermal station, makes them part of the moderately acid soil category. The values obtained for pH had values between 6.0 and 6.6 and are presented in figure 5.

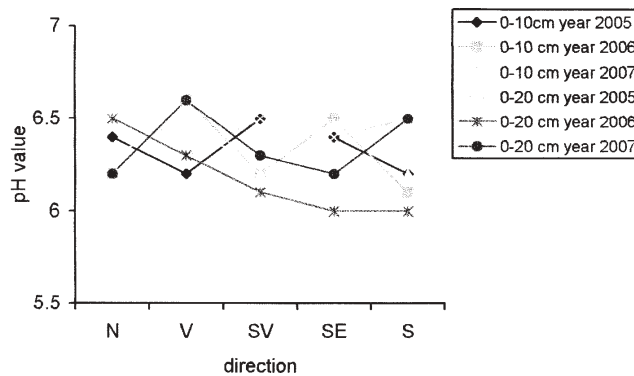


Fig. 5. The soil pH variation around the Rovinari thermal station during the 2005-2007

Conclusions

The measurements regarding the stage of heavy metals charging of the soil close to the thermal station from Gorj County, Romania, emphasized the following:

- for cadmium, in all cases the obtained values are within the normal limits, there is no record of exceeding the alert or intervention levels. On the SE direction, on both depths, the measurements evidenced the absence of cadmium in the soil;

- in case of copper, from the total of 30 measurements made during the three years, 25 had values exceeding the normal level, which represents 83.3%, only one exceeded the alert level, representing 3.3%, and the exceeding of the intervention level was not registered for any sample;

- for zinc, from the total of 30 measurements, 9 had values exceeding the normal level, representing 30%, and only one exceeded the alert level;

- lead recorded values are above the normal content in 2 cases from the 30 measurements, representing 6.6%. There are no records of excesses of the alert or intervention levels for the sensitive usages type;

- the values obtained for pH of the soil from the area showed that around a thermal station from Gorj County the soil is moderately acid;

- the data obtained shown that in case of copper and zinc in samples from soil around the Rovinari thermal station were recorded excesses of normal values, and for cadmium and lead were recorded excesses of normal values only in one or two cases in one direction (N for cadmium and SV for lead). These results emphasized that the soil around the Rovinari thermal station is polluted with copper and zinc probably because of the metals concentration in the coal burned, and the directions were registered the highest values of the metal concentration in soil are due to the wind direction and wind speed.

References

1. NEAG, G., The de-pollution of the soils and underground waters, Casa Cartii de Stiinta Publishing House, Cluj-Napoca, 1997
2. NEAG, G., CULIC, G., VERRAES, A., Soils and polluting waters, Depollution techniques, Dacia Publishing House, Cluj-Napoca, 2001
3. RAUTA, C., CARSTEA, S., The prevention and the combating of the soil pollution, Ceres Publishing House, Bucharest, 1983
4. BABA, A., GURDAL, G., SENGUNALP, F., OZAY, O., Environ. Monit. Asses., **139**, nr. 1-3, 2008, p. 287
5. BABAAND, A., KAYA, A., J. Environ. Manag., **73**, nr. 3, 2004, p. 199
6. CICEKAND, A., KOPARAL, A.S., Chemosphere, **57**, nr. 8, 2004, p. 1031
7. PATEL, C.B., PANDEY, G.S., Sci. Total Environ., **57**, 1986, p. 67
8. ÈEBURNIS, D., ŠAKALYS, J., ARMOLAITIS, K., VALIULIS, D., KVIETKUS, K., Atmospheric Environ., **36**, nr. 9, 2002, p. 1465
9. CALANDRA, R., LECCESE, A., PINNOLA, I.M., TORTORETO, G., Annali della Facoltà di Agraria - Università di Perugia, **54**, 2002, p.25

10. MARKERT, B., HERPIN, U., SIEWERS, U., BERLEKAMP, J., LIETH, H., *Sci. Total Environ.*, **182**, nr. 1-3, 1996, p. 159
11. HERPIN, U., BERLEKAMP, J., MARKERT, B., WOLTERBEEK, B., GRODZINSKA, K., SIEWERS, U., LIETH, H., WECKERT, V., *Sci. Total Environ.*, **187**, nr. 3, p. 185
12. MACOVEANU, M., MACOVEANU, M., PALEU M., *Impactul compu^oilor macromoleculari asupra solului*, Editura MATRIX ROM, Bucure^oti, 1998
13. DOBRA, M., VIMAN, V., *Rev. Chim. (Bucure^oti)*, **57**, 2006, p. 1283
14. FRENTIU, T., PONTA, M., DARVASI, E., REIZ, B., SENILA, M., CORDOS, E., *Studia Univ. Babeş - Bolyai, Chemia LI*, 2005, p. 183
15. CORDOS, E., ROMAN, C., PONTA, M., FRENTIU, T., RATIUM, R., *Rev. Chim. (Bucure^oti)*, **58**, no. 5, 2007, p. 470
16. MONITORUL OFICIAL No. 303 bis/06.11.1997, Romanian Ministry of the Forests, Waters and Environment, Order No. 756/1997
17. *** EN 13657:2003, Characterization of waste - Digestion for subsequent determination of aqua regia soluble portion of elements;
18. *** ISO 11466:1995: Soil quality - Extraction of trace elements soluble in aqua regia.
19. *** US EPA 3050B: Acid digestion of sediments, sludges, and soil

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