ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2017, *62*(4-5), 373-379

Dedicated to Professor Ionel Haiduc
on the occasion of his 80th anniversary

HEAVY METALS AND AS CONTENT IN SOIL AND IN PLANTS IN THE BAIA MARE MINING AND METALLURGICAL AREA (NW OF ROUMANIA)

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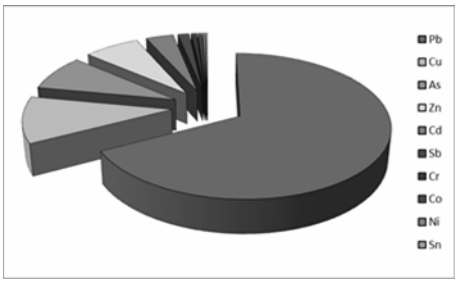
Received December 20, 2016

The paper shows the investigations in the Baia Mare area on the heavy metals and arsenic concentrations in soil (Cu, Zn, Cd, Pb, Ni, Cr, Co, As, Sn, Sb). Statistical analysis was applied to highlight possible correlations. Heavy metals concentrations exceeded in some locations the intervention threshold, according to the Romanian regulations. The highest concentrations of heavy metals in the topsoil were found in samples around the lead smelter Romplumb, where the Pb concentration exceeded 19 times the intervention threshold for insensitive use of soils. The threshold value was also exceeded for Cu, Zn, Cd, As and Sb. Average concentration of Sb is under the threshold value, but higher than the normal value, while the average concentrations of Ni, Cr, Co and Sn are lower than the normal value. Also the pollution indexes were calculated showing the highest values in the Ferneziu area and the highest index was found for Pb.



INTRODUCTION

Environmental protection is of high priority in both national and international levels, as a consequence of the high impact of social and economical activities on the environment. The hazard represented by the high metal concentrations in Baia Mare area, NW Romania, is a consequence of mining and metallurgical activities running for tens and even hundred of years. The heavy metals are generally associated with other elements such as arsenic (As), raising a major environmental and human health problem due to their high toxicity, low biodegradability and cumulative tendency.[1]

Several studies have been lately published about the chemical characterization of the soil in Baia Mare area and the differentiation of the additional contribution of metals and metalloids due to the ongoing human activities. There is available data concerning the nonferrous metals contents in soil in the Baia Mare area which is related to the mining and metallurgical activities[2-7] but only a few works have been investigating the other heavy metals in soil. Baia Mare was and still is a hot spot on the map of soil pollution with non-ferrous metals such as Pb, Cu, Cd, and Zn.[8-9]

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The research has highlighted severe pollution by heavy metals (Pb, Cd, Zn, Cu) in residential, agricultural, and forestry soils in Baia Mare, even at 25-30 km from the major pollution sources, as a consequence of the high emission levels.[10-11] The non-ferrous metallurgical activities have a long history in the area.[12]

The lead factory is working since 1844, and the copper smelter was closed in 2008 after more than 80 years of production. Currently, the metallurgical industry has considerably reduced its activity by closing or diminishing the production capacity. However, Baia Mare is facing the historical soil pollution with heavy metals.[13] The highest concentrations of heavy metals were found in the eastern part and around the industrial zones in Baia Mare. Very high concentrations up to 40375mg/kg Pb and 6122 mg/kg Zn were determined close to the lead smelter, and up to 5823 mg/kg Cu around the copper smelter.[5] Cd contents exceed 10-24 times the intervention threshold value in the investigated area.[14-16] It has to be noticed that the subsoil in Baia Mare area is rich in minerals as native elements (Au, Ag, Cu, As, S), sulphides (pyrite, chalcopyrite, arsenopyrite, sphalerite, galena, stibnite) sulphosalts (tetrahedrite, jamesonite, semseyite, pyrargyrite) and tungstates (wolframite, scheelite), together with quartz, clay minerals, adularia, carbonates, rhodonite and barite as gangue minerals.[17-18]

Historical pollution of the soil is of great concern for experts and local authorities, but at the moment no realistic and feasible means to deal with this challenge are available.

The degree of pollution was assessed for Baia Mare in a previous study that investigated the heavy metal pollution of top soil (0-10 cm) using pollution load index.[19] Soil and plants' level of As and Sb were also analyzed showing high level of these elements especially in Ferneziu area.[20]

In the present paper the levels of heavy metals and arsenic in soil at 10-20 cm depth and in plants in some districts of Baia Mare were examined. The multi-elements pollution that is more hazardous than a single pollutant was especially followed.[21-22]

In this study the concentrations in the soil, at 10-20 cm in depth, were investigated and based on the levels of heavy metals and As content, pollution indexes were calculated due to the complex cumulative pollution with more heavy metals and As. The pollution indexes are useful to estimate the level of contamination. The heavy metal and As tend to accumulate in plants entering the food chain representing a hazard to the environment and human health. Aiming to establish the risk associated to the heavy metal and As presence in soil, the level of these elements in plants was investigated.

EXPERIMENTAL

Zone location

The target areas were three zones with high heavy metals concentration in accordance with previous studies. The high concentrations were caused by the several metallurgical plants located in the area.[4] The target areas were: Ferneziu district where a lead processing plant is located, Sasar district along the Sasar River (along the dominant direction of the wind) and the central area and its surroundings (Fig. 1). Dura, located in the west side of the city in a hilly area, was considered as a reference zone (the hills are protecting this area against plant emissions). Fig. 1 shows the four areas and the sampling location and metallurgical plants location (the stack of each plant is pointed out on the map).

Soil and plants sampling

Ten soil samples were collected from each area except the Ferneziu area, where a total of 19 samples were collected: 8 in 2009 and 11 in 2010. The soil samples had been taken from a depth of 10-20 cm. The soil samples were collected from several locations representing garden soils, residential area soils and industrial area soils. The sampling had been performed during July-September 2009. In the Ferneziu area the sampling was done also in August 2010. The weather was dry during the sampling. A GPS was used to get the location of each sampling point. The samples were conditioned and prepared in a laboratory for the determination of their microelement content. The soil samples were crushed and dried at room temperature for 48 hours, then passed through a 2 mm sieve. Thus, from the processed sample a sub-sample of 100 g was obtained through the method of quarters, being ground to a fine powder in a Fritsch PM100 mill for 3 min and passed through a sieve of 150 microns. From this sub-sample, 2.5000 g of soil were taken and subjected to mineralization with aqua regia according to ISO 11466: 1999. In each sampling points plants from spontaneous flora or cultivated plants were collected. The soil samples were collected from several locations in gardens and squares in the close vicinity of the lead smelter. At the same time, plants growing in the locations from where the soil samples were drawn: onion (Allium Cepa), dill (Anethum graveolens), and plants from spontaneous flora such as bent grass (Agrostis sp) were collected. The plant samples were washed with tap water and then with distilled water to remove the dust and were oven dried. The dried samples were ground and a portion of 1.0 g plant sample was subjected to oxidation of the organic matrix and extraction with hydrogen peroxide and aqua regia following the method from ISO 11466: 1999.

Heavy metals and As analysis

The determination of heavy metals Cu, Zn, Cd, Pb, Ni, Cr, Co and As was done using the inductively coupled plasma atomic emission spectrometer, ICP-AES, with simultaneous detection Optima 5300 DV (Perkin Elmer), with axial and radial dual vision, while for the determination of Sb and Sn the inductively coupled plasma mass spectrometer ELAN DRC II (Perkin Elmer), ICP-MS was used. The quantification limits (in mg /kg of dry soil) in ICP-AES following the aqua regia extraction were: Cu: 0.5, Zn: 0.5, Cd: 0.4, Pb: 0.3, Ni: 0.4, Cr: 0.4, Co: 0.4, As: 0.4, Sn: 0.4, Sb: 0.5.

Fig. 1 – The location of the samples point and of the main pollution sources in the Baia Mare area (google map).

The accuracy of measurements was realized by using check solutions of the analysed elements for each series of measurements. The relative uncertainty of the measurement for P=95% was less than 10%.

Aqua regia digestion

A volume of 1 mL water was used to turn 2.5000 g sample into a slurry in a reaction flask, then 21 mL of 32% (v/v) HCl followed by 7 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 or sediment. 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. After cooling at room temperature, the sample was transferred in 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.

All reagents used in this study (65% HNO_3, 32% HCl) were purris p.a. quality (Merck). For external calibration, multielemental stock solutions of 1000 $\mu g\ mL^{-1}$ (Merck) were used. All dilutions were made with 2% (v/v) HNO_3. A certified soil CRM (SRM 2709, San Joaquin Soil, NIST) was used to evaluate the accuracy of extraction procedures.

Statistical analysis

An Excell spreadsheet was used for statistical analysis. The mean value, standard deviation and median were calculated for the target heavy metals and As using Excel feautures. Pearson analysis was used to study the correlations between the various heavy metals and As.

RESULTS AND DISCUSSION

Statistical analysis of microelement content of soil samples

The data is summarized in Table 1 (at the bottom of the table the reference values in accordance with Romanian law are indicated).

Heavy metals and As concentrations exceeded in some locations even the intervention threshold, according to the Romanian regulations. The highest concentrations of the analyzed heavy metals in the soil-from 10-20 cm depth were found in samples from the eastern part of the town around the lead smelter Romplumb (in Ferneziu district), where the Pb concentration exceeded 16 times the intervention threshold for insensitive use of soils (16253 mg/kg) and also Cu, Cd, Zn and As registered high values. In Ferneziu district, the threshold value was also exceeded for Cu, Zn, Cd, As and Sb in more sampling points. Expected high values for As, Sb, and Sn were also found in the north-eastern part of the lead factory, due to the dispersion of the dust in stack emissions, in relation with the dominant wind direction and also in Sasar district.

These values define the attribute of high pollution for soils in Baia Mare area. The average concentration of Sb is under the threshold value, but higher than the normal value, while the average concentration of Ni, Cr, Co and Sn is lower than the normal value.

In the reference area the heavy metals and arsenic values are below the alert threshold, but even in the reference area the mean Pb content in soil (48.1 mg/kg) was above normal values of 20 mg/kg.

Pearson correlations

Table 2 shows the Pearson's correlation coefficients for target heavy metals for the whole Baia Mare area. To make the variable normal, before the Pearson's analysis the operator LOG was applied on the data. There are high values for these coefficients for the following pairs of heavy metals: Zn-Cd, Pb-Sb, Ni-Co, Cu-Zn, Cu-Pb, Cu-As, Cu-Pb, Sn-Sb. The values indicate a common source of these heavy metals which is the emissions generated by the metallurgical plants. Pearson's correlation coefficients smaller than 0.5 (as for Cr-Cu, Cr-Zn, Cr-Pb) indicates a secondary soil pollution source. This might be industrial pollution other than metallurgical plants or urban pollution.

Table 1

Statistical analysis of microelement content in the top10 cm soils in the Baia Mare zone in studied areas: Ferneziu, Sasar, Center and Dura as reference area (mg/kg dry soil)

Sampling zone/Element		Cu	Zn	Cd	Pb	Ni	Cr	Co	As	Sn	Sb
Ferneziu district	Mean	621.6	1002	11	3472	8.13	25.	8.2	72.5	3.67	18
	Median	352.5	731	2.5	2100	6	25.7	5.3	64	3.92	15.1
	SD	608.4	766	12.1	3943	8.96	19.9	8.3	59.6	1.44	11.7
Săsar district	Mean	536.9	569	2.4	623.4	4.98	13.8	3.7	80.1	1.72	5.1
	Median	250	548	1.5	495.5	3.73	14.3	2.2	63.8	1.50	2.4
	SD	816.4	288	2.2	366.7	3.73	4.0	4.2	78.8	0.71	5.6
Center area	Mean	185.9	315.8	0.50	272.5	9.4	28.3	4.2	8.3	0.53	0.67
	Median	204,5	313.5	0.43	288.5	7.45	31.2	3.3	5.3	0.53	0.65
	SD	60.2	111.6	0.29	139.9	3.47	11.2	2.8	6.6	0.20	0.42
Dura area	Mean	40.9	82.26	0.04	48.12	9.06	28.0	3.3	0.61	0.2	0.25
	Median	47.8	80.8	0.04	38.70	9.50	28.4	3.7	0.65	0.2	0.25
	SD	18.11	19.4	0.01	15.64	2.27	2.75	2.3	0.16	-	-
Reference values according to the Roumanian legislation for sensitive soils (Order No. 756, 3 Nov 1997)											
Normal concentration		20	100	1	20	20	30	15	5	20	5
Alert threshold sensitive use		100	300	3	50	75	100	30	15	35	12.5
Intervention threshold sensitive use		200	600	5	100	150	300	50	25	50	20

Table 2

Pearson's correlation coefficients (r) of heavy metals and arsenic contents in soil in the Baia Mare area

	Cu	Zn	Cd	Pb	Ni	Cr	Co	As	Sn	Sb
Cu	1.000									
Zn	0.789**	1.000								
Cd	0.847**	0,833**	1.000							
Pb	0.484**	0.368*	0.470**	1.000						
Ni	0.353*	0.245	0.353*	-0.28	1.000					
Cr	0.465*	0.426*	0.500**	-0.060	0.708**	1.000				
Co	0.713**	0.582**	0.727**	0.475*	0.601**	0.674**	1.000			
As	0.515**	0.560**	0.515**	0.439**	0.109	0.026	0.150	1.000		
Sn	0.161	-0.002	-0.006	0.221	-0.187	0.232	0.213	0.238	1.000	
Sb	0.589**	0.700**	0.740**	0.700**	0.280	0.070	0.233	0.529**	0.793**	1.000

* Significant correlation at P<0.05; ** Significant correlation at P<0.01

Table 3

Pearson's correlation coefficients (r) of heavy metals content in soil in the Ferneziu area

	Cu	Zn	Cd	Pb	Ni	Cr	Co	As	Sn	Sb
Cu	1.000									
Zn	0.819**	1.000								
Cd	0.797**	0,972**	1.000							
Pb	0.820**	0.972**	0.971**	1.000						
Ni	0.834**	0.562	0.574	0.522	1.000					
Cr	0.927**	0.768**	0.745*	0.713*	0.954**	1.000				
Co	0.760*	0.602	0.619	0.559	0.866**	0.870**	1.000			
As	0.548	0.830**	0.834**	0.862**	0.151	0.377	0.200	1.000		
Sn	0.665*	0.933**	0.924**	0.936**	0.297	0.531	0.345	0.964**	1.000	
Sb	0.228	0.633*	0.609	0.555	-0.003	0.204	-0.038	0.806**	0.778**	1.000

* Significant correlation at P<0.05; ** Significant correlation at P<0.01

Special attention was paid to the Ferneziu area, the most polluted zone within Baia Mare area as in shown in Table 3. Pearson's correlation coefficients for this area are very high, some of them greater than 0.9. This indicates a strong correlation between pairs of heavy metals because of their common origin. The metallurgical plant (Pb processing plant) located in the area was identified as the main pollutant source. Local pollution was more acute. However some pollution spread over much larger areas affecting almost the whole Baia Mare area.

Pollution index

In order to evaluate the general degree of soil pollution in the studied areas a pollution index was used.[23-24] This index defines the soil contamination with heavy metals based on the sum of the ratios of the actual concentration over the alert threshold as defined by Romanian legislation for the heavy metals considered. Equation (1) shows the formula used to calculate the soil pollution index (SPI). The pollution index was calculated for each location and area based on soil specific pollution indexes (SPI_{sp}). Also, the specific pollution indexes were processed in order to find out useful data (equation 2)

$$SPI = \frac{1}{n}\sum_{i=1}^{n}\frac{C_i}{C_{(PA)_i}}\cdot 100 \qquad (1)$$

where: n is the number of heavy metals considered, C_i is the specific microelement concentration, $C_{(PA)_i}$ is the alert threshold for the specific element in accordance with Roumanian legislation using the sensitive area assumption (residential and agricultural areas).

$$SPI_{Sp} = \frac{1}{m}\sum_{i=1}^{m}\frac{C_i}{C_{(PA)_i}}\cdot 100 \qquad (2)$$

where m is the number of sampling points and C_i and $C_{(PA)_i}$ are defined by equation 1.

The pollution index was calculated for each of the four analyzed areas. The data is shown in Fig. 2. The specific soil pollution indexes for each studied element are shown in Fig. 3.

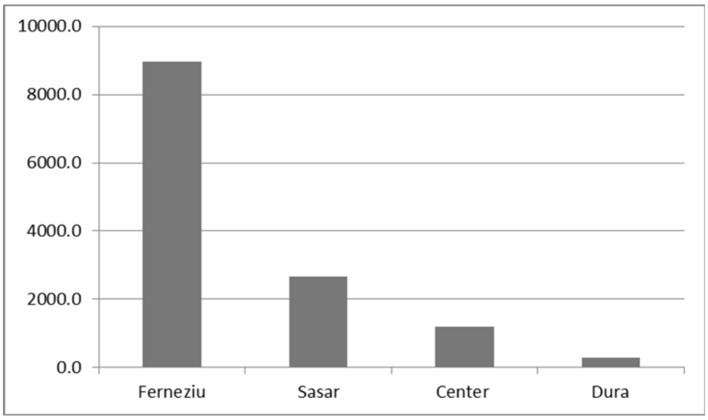

Fig. 2 – Soil pollution index (all areas).

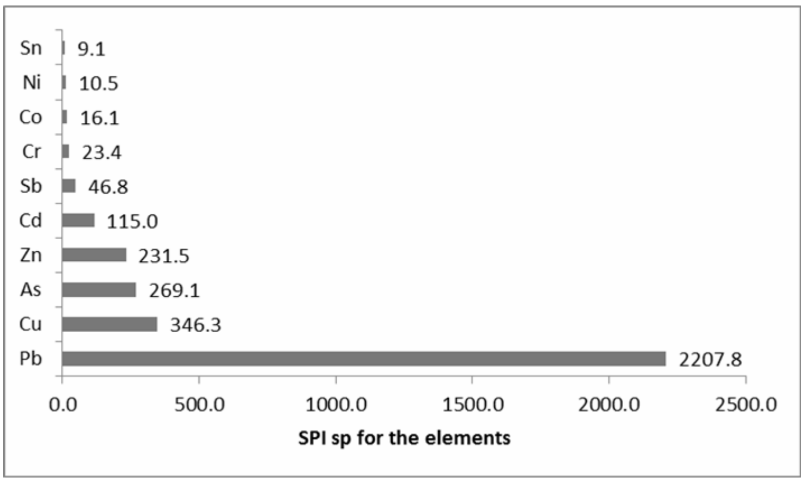

Fig. 3 – Specific soil pollution indexes for the heavy metals considered for Baia Mare area.

The data shows that the Ferneziu area is the most polluted area within Baia Mare area (the soil pollution index is about 30 times higher than the soil pollution index for reference zone Dura). Pb is the main contributor to Ferneziu pollution (70% of the soil pollution index of Baia Mare area) followed by Cu, As, Zn and Cd. The small contributors are: Sb, Sn, Ni, Co and Cr.

Significant contributors to soil pollution index are Zn < Cd < As < Cu.

These results show a good correlation with the history and location of polluters in the lead processing plant in Ferneziu and copper processing plant in Baia Mare. Even if in the present the metallurgical plants are closed, the heavy metals and arsenic pollution of the soil have a high persistence.

In the previous study[19] made in the same area but for the top soil (0-10 cm), pollution load indexes were calculated as the n^{th} root of the product of the n CF, where n is the number of samples and CF is the contamination factor expressed as the ratio obtained by dividing the concentration of each metal in the soil by the background values (from reference area) [25]. The results also showed the main pollutant elements in the Baia Mare area to be the same elements: Cd, Pb, Cu and Zn. In this case, the most pollutant element was found to be Cd due to the low concentration of the reference area.

Concentrations of heavy metals and As in plant samples in the studied areas are presented in Fig. 4 and 5. The highest metals content in plants was found for Zn in the districts Săsar and Ferneziu. The highest contamination of plants with Pb was established for the Ferneziu area due to the lead smelter located in this district. Also in the Ferneziu area elevated concentrations of Cd and As were found in plants.

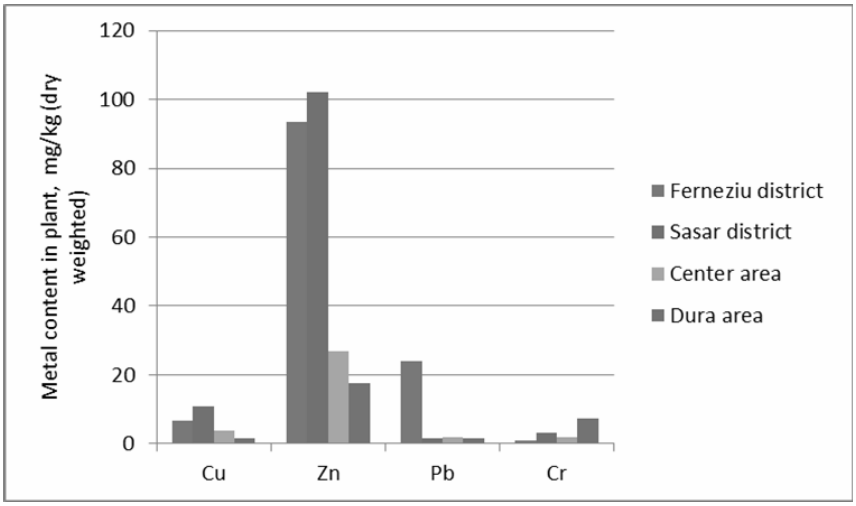

Fig. 4 – Variation of mean values of Cu, Zn, Pb and Cr content in plants from different areas in Baia Mare.

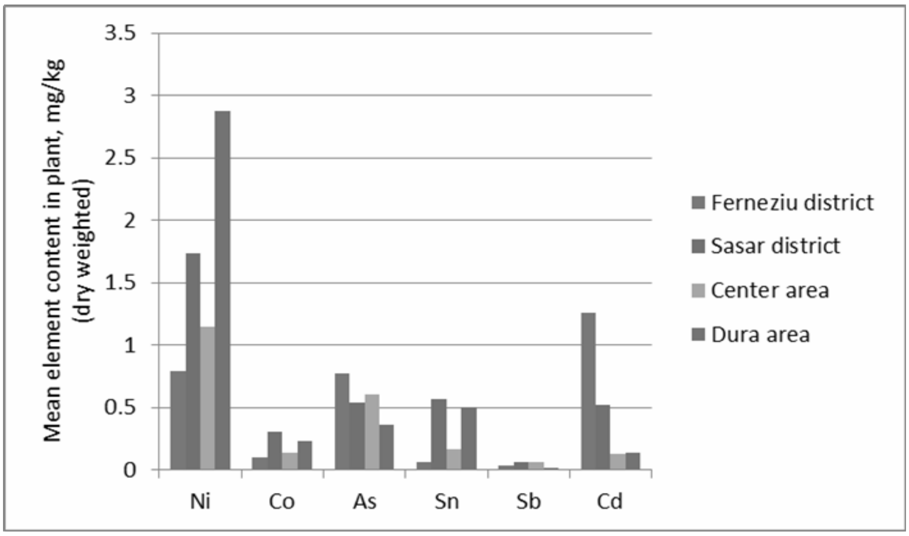

Fig. 5 – Variation of mean values of Ni, Co, As, Sn, Sb and Cd content in plants from different areas in Baia Mare.

CONCLUSIONS

The study indicates soil pollution with Pb as the main pollutant and also with Cu, As, Cd and Zn as significant contributors. Cr, Ni, Sn, Sb and Co are bellow the alert threshold.

Pearson correlation analysis indicates strong correlations between some pairs of heavy metals like Pb, Cu, Zn and As.

Ferneziu district is the most polluted area, followed by Săsar and in a small extent by the Center. Dura area can be considered an unpolluted area. Also the heavy metals' and As contents of plants were higher in the Ferneziu area representing a hazard to the health of residents.

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