

Group Composition Forms of Heavy Metals in the Anthropogenically Transformed Soils in the South of West Siberia

T I Siromlya

Institute of Soil Science and Agrochemistry, Siberian Branch of Russian Academy of Sciences Novosibirsk, Russia

E-mail: tatiana@issa.nsc.ru

Abstract. The contents and ratios of strongly and weakly fixed compounds of heavy metals (HM) in the anthropogenically transformed soils were studied in the south of Western Siberia. The spatial distribution of HM labile forms was shown to correlate with their quantitative and qualitative composition in the uncontaminated soils of the region. No statistically significant difference between sandy and loamy soils in HM content was found.

1. Introduction

Investigations of soil heavy metal (HM) compound forms and of their transformation mechanisms started more than half a century ago but their urgency has been growing due to necessity to get the adequate assessment of modern soil conditions, to predict HM possible migration processes and accumulation and to find the ways of their improvement [1-3 et al.]. In Siberia region, investigations of fraction-group composition of soil chemical element (CE) compound forms have started recently and become urgent taking into account the necessity of regional peculiarities of CE state in soils to be recorded. The aim of the paper is to investigate group composition of HM compounds in anthropogenically transformed soils of Western Siberia south.

2. Material and methods

Soil samples (0-20 cm) were taken from anthropogenically transformed territories (along large highways P-254, P-255 and P-266 in Novosibirsk, Iskitim Berdsk and others) in the southern part of Western Siberia including Priobskaya high plain, Kolyvan'-Tomsk elevation and the river Ob' valley. Clay content was assessed on GOST 12536-79 and potential acidity (pH_{KCl}) was assessed on GOST 26483-85. Investigated soils were of sandy and loamy granulometric composition and of neutral and close to neutral medium reaction. CE total content was assessed by atomic emission spectrometry method using arc double-jet plasmatron; the amount of weakly fixed forms was assessed by atomic-absorptive method with Quant-2A device. Extraction was carried out by the method of G.A. Solovyova [4], widely and successfully used by T.M. Minkina, G.V. Motuzova and other researchers [2, 5, 6]. As extractants there were used 1 n NH_4Ac (pH 4.8) solutions, EDTA solution of 1% in NH_4Ac and 1 n HCl. They enable to estimate content of the following CE forms in soils: exchangeable ones extracted with 1 n NH_4Ac extract; complex ones calculated on the difference between CE amount extracted with 1 n NH_4Ac and 1% EDTA solution in NH_4Ac ; specifically sorbed ones calculated on the difference between CE amount extracted with 1 n HCl and 1 n NH_4Ac .



3. Results

Since CE content in soils does not follow the law of normal distribution very often [7-9], in the tables there are given average index values and variation limits. In sandy soils, roughly allowable concentrations (RAC) of Ni and Zn total content (on GN 2.1.7.2511-09) are often exceeded. As it has been mentioned before [9], the reason of this fact cannot be attributed to anthropogenic contamination of environment but to the regional geo-chemical specificity of investigated territory that means high natural content of these elements in soils and low RAC values without considering these natural facts.

Total content of CE in the investigated soils does not exceed their uncontaminated data for the soils of Novosibirsk Region [10] though that of some CE can fluctuate within rather wide limits. Weakly fixed compounds have much wider range of CE concentrations. The same wide variation limits of microelement forms content (labile from is ammonium-acetate buffer of pH 4.8 and acid soluble form is of 1 n HCl) in the soils of Western Siberia south have been recorded before [7].

Table 1. Total content and weakly fixed compounds of TM, mg/kg

CE	Sandy soils (n = 30)				Loamy soils (n = 30)			
	total content	weakly fixed compounds			total content	weakly fixed compounds		
		exchan geable	complex	specifically sorbed		exchang eable	complex	specifically sorbed
Cd	<u>0,40</u> 0,31-0,46	<u>0,04</u> 0,02-0,07	<u>0,01</u> 0,01-0,03	<u>0,02</u> 0,01-0,05	<u>0,40</u> 0,30-0,43	<u>0,06</u> 0,03-0,08	<u>0,02</u> 0,02-0,03	<u>0,03</u> 0,01-0,05
Co	<u>10,8</u> 6,3-16,3	<u>0,8</u> 0,4-1,5	<u>0,8</u> 0,4-1,7	<u>0,5</u> 0,1-1,0	<u>12,2</u> 6,7-14,3	<u>0,9</u> 0,5-1,5	<u>1,2</u> 0,6-1,8	<u>1,3</u> 0,4-2,4
Cu	<u>13,5</u> 8,5-31,8	<u>0,38</u> 0,22-0,64	<u>4,2</u> 2,5-6,2	<u>4,5</u> 3,0-9,0	<u>23,8</u> 16,5-42,3	<u>0,44</u> 0,20-0,73	<u>4,7</u> 3,5-7,4	<u>7,4</u> 4,4-11,4
Ni	<u>40,8</u> 29,0-45,3	<u>1,3</u> 0,6-1,9	<u>0,8</u> 0,3-1,7	<u>1,1</u> 0,6-3,0	<u>41,2</u> 31,4-44,4	<u>1,3</u> 1,0-2,0	<u>1,4</u> 0,3-1,9	<u>2,3</u> 0,5-3,8
Pb	<u>16,5</u> 12,8-27,6	<u>1,9</u> 0,9-3,0	<u>3,7</u> 0,9-5,4	<u>5,6</u> 3,1-6,8	<u>17,4</u> 10,9-22,6	<u>2,3</u> 1,6-4,1	<u>3,8</u> 1,1-6,1	<u>6,0</u> 3,6-10,6
Zn	<u>62,2</u> 47,2-95,9	<u>6,0</u> 1,6-10,5	<u>1,3</u> 0,9-6,8	<u>4,8</u> 3,0-13,2	<u>75,0</u> 53,1-107,0	<u>6,6</u> 2,2-11,0	<u>4,9</u> 0,9-7,8	<u>11,0</u> 3,3-14,8
Fe	<u>24850</u> 15600- 35800	<u>29</u> 15-61	<u>475</u> 315-835	<u>977</u> 824-1716	<u>29400</u> 14800- 32900	<u>32</u> 14-58	<u>386</u> 246-809	<u>1022</u> 728-1578
Mn	<u>537</u> 357-683	<u>108</u> 58-157	<u>10</u> 3-21	<u>84</u> 54-130	<u>577</u> 387-809	<u>112</u> 83-169	<u>11</u> 3-16	<u>117</u> 60-200

Note: numerator – average values, denominator – variation limits.

In sandy soils, HM total content and amount of HM weakly fixed compounds forms are a bit higher than those of loamy soils, though statistically significant difference has not been found. We have recorded this before in the case of HM total content [9]. Chemical elements average contents were summarized for sandy and loamy soils by V.B. Ilyin and A.I. Syso [11].

The percentage of Cd and Mn exchangeable forms is about half of all forms of weakly fixed compounds while Cu and Fe hardly ever form exchangeable compounds (Table 2). Complex forming of Mn and Zn is least revealed. Specifically sorbed compounds fractions are dominant in case of Fe, Cu, Ni and Pb.

Almost the same pattern of HM weakly fixed compounds distribution in the regional uncontaminated soils was recorded. It enables to assume that investigated anthropogenically transformed soils were not contaminated ones. This assumption is confirmed with the fact that maximum allowable concentrations (MAC) of CE labile forms on GN 2.1.7.2041-06 were not exceeded. Contaminated soils with MAC exceeding of Pb and Zn labile forms taken for comparison

(with occasional RAC exceeding on GN 2.1.7.2511-09) had the percentage of Pb weakly fixed compounds of 92-94% total content, that of Zn 61-69% and of Cd 44-63 % total content.

Table 2. Group composition of HM compounds forms

CE	WF/TF*	Sandy soils (n = 30)			Loamy soils (n = 30)			
		weakly fixed compounds **			weakly fixed compounds **			
		exchange-able	complex	specifically sorbed	WF/TF*	exchange-able	complex	specifically sorbed
Cd	18 (14-34)/82	<u>58</u> 43-65	<u>22</u> 13-32	<u>24</u> 12-35	20 (18-36)/80	<u>50</u> 45-74	<u>21</u> 12-27	<u>28</u> 14-40
Co	22 (13-33)/78	<u>35</u> 27-53	<u>31</u> 18-46	<u>26</u> 16-38	32 (19-39)/68	<u>22</u> 16-43	<u>36</u> 22-43	<u>44</u> 29-49
Cu	68 (46-77)/32	<u>4</u> 3-6	<u>46</u> 39-47	<u>50</u> 48-58	55 (44-71)/45	<u>3</u> 2-5	<u>44</u> 36-49	<u>52</u> 49-62
Ni	9 (6-16)/91	<u>30</u> 21-43	<u>26</u> 14-35	<u>38</u> 22-49	12 (6-20)/88	<u>24</u> 18-27	<u>26</u> 12-32	<u>48</u> 31-55
Pb	76 (41-82)/24	<u>18</u> 16-27	<u>30</u> 16-37	<u>51</u> 47-58	70 (51-84)/80	<u>22</u> 15-30	<u>27</u> 17-36	<u>57</u> 47-58
Zn	23 (12-38)/77	<u>40</u> 29-50	<u>15</u> 10-22	<u>43</u> 34-57	29 (13-36)/71	<u>31</u> 22-40	<u>20</u> 13-24	<u>48</u> 42-57
Fe	7 (4-14)/93	<u>2</u> 1-3	<u>33</u> 24-45	<u>65</u> 54-75	5 (3-15)/95	<u>2</u> 1-3	<u>25</u> 20-36	<u>73</u> 61-80
Mn	36 (33-46)/64	<u>53</u> 41-65	<u>6</u> 1-10	<u>42</u> 34-50	40 (33-47)/60	<u>50</u> 39-59	<u>3</u> 1-7	<u>48</u> 34-56

Note. There are given average values, variation limits are in brackets and denominators. *- weakly/strongly fixed compounds, % of total content, ** - % of weakly fixed compounds content.

Received data comparison with the characteristics of group composition and HM compounds lability of the Lower Don soils shows a lot of significant differences. For example, Cd total content in Siberian soils corresponds to the least values given by T.M. Minkina et al. [6]. There is noted that sharp increasing of Cd exchangeable forms occurs in contaminated soils. The percentage of weakly fixed compounds is slightly higher than that of the Don uncontaminated soils but the percentage of exchangeable forms takes more than a half (not only in anthropogenically transformed soils but in uncontaminated and contaminated ones). Specifically sorbed compounds dominate in Mn of HM weakly fixed compounds of the Don uncontaminated soils while their percentage approximately coincides with that of exchangeable forms in Siberian region. Lability of Cu and Pb differs sharply; their weakly fixed compounds percentage is more than 40% of total content and about 70 % on average. It can be caused by the influence of granulometric and mineralogical soil composition and soil-forming rocks that is by little amount of original soils stable minerals enriched with given CE and low content of clay minerals capable of strong metal fixing and carbonates absence. All the above confirms once more that while estimating ecological soil condition regional peculiarities and character of investigated territory should be taken into account.

4. Conclusion

Thus, HM total content and weakly fixed compounds forms in the soils of Western Siberia south vary within a wide range. In anthropogenically transformed soils there has not revealed any uncontaminated contents exceeding, though Ni and Zn RAC exceeding on GN 2.1.7.2511-09 are often recorded for loamy soils that can be explained with regional geochemical specificity of the territory and also with insufficient actual standards. In loamy soils, HM total content and the amount of their weakly fixed compounds are generally a little bit higher than those of sandy soils though statistically significant

difference has not been revealed. Distribution of HM weakly fixed compounds in anthropogenically transformed soils generally coincides with that of regional uncontaminated soils. The percentage of Cd and Mn exchangeable forms is about a half of all weakly fixed compounds amount and Cu and Fe hardly ever form exchangeable compounds. Manganese and zinc have shown weak complex forming. Specifically sorbed compounds fraction dominates in Fe, Cu, Ni and Pb.

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