# LEAD AND CADMIUM CONTENT IN WASHED AND UNWASHED WOOL OF SHEEP REARED IN REGIONS WITH INCREASED TECHNOGENIC CLARC

# СЪДЪРЖАНИЕ НА РВ И CD В ПРАНА И НЕПРАНА ВЪЛНА ОТ ОВЦЕ ОТГЛЕЖДАНИ В РАЙОН С ПОВИШЕН ТЕХНОГЕНЕН КЛАРК

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## **ABSTRACT**

An ICP-ETAAS analyze of unwashed and washed sheep- wool for establishing of Pb and Cd have been conducted. A significant difference in the contents of Pb (15.3- unwashed versus 8.15 mg/kg DM– washed wool) were established. The Cd – content were mean 0.69 (unwashed) versus 0.53 mg/kg DM– washed wool. No statistical differences were established. The authors conclude, that the environment influence significant on the Pb- content of sheep- wool.

Keywords: lead, cadmium, sheep- wool

#### **РЕЗЮМЕ**

Проведен е ICP-ЕТААЅ анализ на прана и непрана овча вълна за установяване на Рb и Сd. Установени са достоверни разлики в съдържанията на Pb (15.3- непрана срещу 8.15 mg/kg ACB- прана вълна). Средното съдържание на Cd е 0.69 (непрана) срещу 0.53 mg/kg ACB (прана вълна). Разликите са статистически достоверни. Авторите заключват, че околното среда влияе достоверно върху съдържанието на Pb в овчата вълна.

Ключови думи: олово, кадмий, овча вълна



#### РАЗШИРЕНО РЕЗЮМЕ

Целта на изследването е да се проучи влиянието на олово и кадмий в почвата, както и ролята на атмосферното и литосферно замърсяване с тези елементи, върху биоакумулацията им във вълната на овце, отглеждани в район с повищен техногенен кларк.

Анализирани бяха 33 броя проби вълна, получени от овце на възраст 1,5-2 години, родени и отгледани в район с повишен техногенен кларк. Храненето на животните бе изцяло с фуражи, произвеждани на място. Пробите вълна бяхаа взети през Април-Май 2004 година. 25 от тях бяха изпрани по стандартна методика, а 8 бяха изследвани непрани.

Анализът извършихме след изсушаване при  $80^{\circ}$ С до постоянно тегло и минерализирахме в киселинна смес от HNO3 и  $H_2O_2$ . Съдържанието на анализираните елементи в пробите-образци определихме по методи на ЛАС след ICP-MS количествен анализ с вътрешни стандарти на подбрани изотопи. Отчитането извършихме на атомно абсорбционен спектрофотометър Perkin Elmer-AAS 5100 Zeeman.

Използвани са критериите: кларк на концентрация (К) по Вернадский (1940)-съдържание на изследвания елемент в почвата към средния кларк на почвата или литосферата; фактор на биоакумулация (ФБ), (Baykov et al., 2003), включващ двата количествени критерия: ФБ1-съдържание на изследвания химичен елемент в проба от 1000 g вторична биологична продукция към съдържание на същия химичен елемент в 1000 g изсушена почва и ФБ2-съдържание на химичния елемент в 1000 g вторична биологична продукция към съдържанието на същия елемент в 1000 g първична биологична продукция от автотрофното равнище на същия екотоп; кларк на разпределение (Кр) -съотношение между количеството токсичен елемент в изследвания орган или тъкан (mg/kg свежа маса) и средното съдържание на химичния елемент в организма (среден кларк). Средният кларк е съотношение между сумарното количество на изследвания химичен елемент във всички изследвани органи и тъкани към сумарното тегло на изследваните органи и тъкани.

Съдържанието на олово и кадмий в непрана вълна е съответно 15.3 и 0.69 mg/kg, а в праната – съответно 8.15 и 0.53 mg/kg. Разликата се дължи на екзогенна литосферна пряка контаминация. Концентрацията на Рb и Сd е многократно по-висока във фината прахова фракция, което създава и реална опасност за аспириране на елементите. Критерият "Кларк на разпределение" в праната вълна показва значително

натрупване на Pb(14.85) и Cd(6.24) спрямо останалите изследвани тъкани.

#### INTRODUCTION

The study on the complex effect of the geochemical factors of the environment on the living matter on the planet (microorganisms, plants, animals, humans) has acquired greater importance when the chemical non-homogeneity of lithosphere as well as of the other component of the biosphere was proved (Vernadskiy, 1940- cited by (2, 6). Investigations on those relationships have been attracting more specialists in different scientific areas: biogeochemists, ecologists, physiologists, biochemists, chemists, veterinary and human doctors, zootechnicians, agriculturists, phytopathologists (7).

The diverse human activity has led to the disturbance of the natural cycles of the chemical elements and to their undesired accumulation or dispersal.

Our studies on the chemical heterogeneity of lead and cadmium at the trophic level of the heterotrophic organisms were an object of previous publications (2, 3, 8, et al.). Our data as well as those in the available literature proved the organotropity typical of each chemical element and its possibility to be used as an indicator for establishing the level of the environmental pollution (9, 12, 13 et al.). For the precise and objective evaluation of the effect of the geochemical environment on animals and for the bioecological monitoring, an accessible and sufficiently objective method is necessary that can also outline the organotropity of a given chemical element. The criteria like coefficient of biological absorption (Cba), Clarc of concentration (Cc), Factor of bioconcentration (FB), proved to be insufficient (2,5). A suitable criterion named Clarc of distribution (Cod) was suggested by (4).

Wool like the other products from the heterotrophic organisms inhabiting a given region could be used as an indicator when evaluating the degree of environmental pollution with toxic chemical elements (7, 13, 10). Collection of samples is easy; it can be carried out at any time without affecting the health status and the normal physiological functions of the animal.

In that relation we set the aim of studying the effect of lead and cadmium in soil and the role of the atmospheric and lithospheric contamination with those elements on their bioaccumulation in the wool of sheep reared in regions with increased technogenic Clarc.

# **MATERIAL AND METHODS**

33 wool samples collected from sheep of 1,5 to 2 years of age, born and reared in a region with increased

Table 1 Content of Pb and Cd in washed and unwashed sheep wool from the contaminated region/ Pb и Cd-съдържания в прана и непрана овча вълна от обременения район:

Wool/Вълна	n	Pb, mg/kg		Cd, mg/kg	
		Mean± Sx	%	Mean± Sx	%
Washed/Прана	25	8.15±1.83*	100	0.53±0.034	100
Unwashed/Непрана	8	15.3±2.43*	188	$0.69\pm0.047$	130
Difference/Разлика		7.15	88%	0.16	30%
Significance/Достове	рност	*-*p<0.01		No stat. sign./He	едостоверно

Table 2 Chemical heterogeneity in antropogenic ecosystem for meat – and wool production (mean values)/

Химична нееднородност на антропогенната екосистема за месо- и вълнопроизводство (осреднени стойности)

месе и вышопроизводетье (осре	диени стоино	C111)
Content/Съдържание, mg/kg	Pb	Cd
Pasture soil/Почва от пасище	118	3.44
Mean for Bulgaria/Средно за България	25	0.07
Coefficient/Коефициент (K)	4.72	49.14
Meadow grass/Пасищна трева	6.63	0.72
FB	0.06	0.21
<u>Cereals/Конц. фуражи</u>	0.68	0.46
FB	0.006	0.13
<u>Air/Въздух</u> (mg/m³)	0.097	0.0027
Wool/Вълна		
Unwashed/Непрана	15.3	0.69
<b>FB</b> 1	0.13	0.20
FB 2	2.31	0.96
Washed/Прана	8.15	0.53
<b>FB</b> 1	0.07	0.15
<b>FB</b> 2	1.23	0.74

technogenic Clarc, were analyzed. The animals were fed only on forages produced on the same location. The samples were collected in April – May 2004. 25 of them were washed following the standard methodology (11) and 8 samples were studied unwashed.

The analyses were carried out after drying at a temperature of 80°C until reaching a constant weight. The samples were mineralized in an acid mixture of HNO3 and H<sub>2</sub>O<sub>2</sub>. The content of the analyzed elements in the samples was determined by the LAS methods after ICP-MS quantitative analysis of selected isotopes with internal standards. The results were reported using atomic absorption spectrophotometer Perkin Elmer-AAS 5100 Zeeman.

The chemical heterogeneity of soil and the level of lead and cadmium bioaccumulation in different organs and tissues of the animals were determined by means and methods described in our previous announcements (3, 4, 8 et al. The following criteria were used: Clarc

of concentration (Cc) by Vernadskiy- the content of the studied element in soil to the mean Clarc of soil or lithosphere; Factor of bioaccumulation (FB), (3,4) including the two quantitative criteria: FB1 – the content of the studied chemical element in a sample of 1000 g of secondary biological produce to the content of the same element in 1000 g of dried soil and FB2 - the content of the chemical element in 1000 g of secondary biological produce to the content of the same element in 1000 g of primary biological produce at the autotrophic level of the same ecotope; Clarc of distribution (Cod), (4) - the ratio between the amount of the toxic element in the studied organ or tissue (mg/kg fresh weight) and the mean content of the chemical element in the organism (mean Clarc). The mean Clarc is the ratio between the total amount of the studied chemical element in all the investigated organs and tissues to the total weight of the investigated organs and tissues.

The results obtained were submitted to statistical variation processing, using the program BIOSTAT-2.

Table 3 Clarc of distribution (**Kod**) of Pb and Cd in lamb's tissues and organs from the contaminated region (mean values)/ Кларк на дистрибуция в агнешки тъкани и органи от обременения район (средни стойности)

Organs and tissues/Органи и тъкани	Pb	Cd
Liver/Челен дроб	2.91	10.47
Kidney/Бъбреци	2.0	13.3
Abdominal muscle/Абдом. мускулатура	1.51	2.71
Unwashed wool/Непрана вълна	27.87	8.12
Washed wool/Прана вълна	14.85	6.24

Table 4. Pb and Cd contents in litospheric dust depended of size of fragments/Съдържание на Pb and Cd в литосферен прах в зависимост от размера на частиците:

Place of sample collections/ Място на пробовзимане	n	Pb – mg/kg mean±SD	Cd– mg/kg mean±SD
School yard/Училищен двор		mean=5D	meun±5D
< 1 mm	3	108.2±30.5	2.7±1.5
< 5 μm	3	$162.0\pm34.5$	$5.7 \pm 1.0$
Private yard/Частен двор			
< 1 mm	5	$160.6\pm90.6$	$4.4 \pm 3.0$
< 5 μm	5	421.6±64.4	$3.2 \pm 1.8$

# **RESULTS AND DISCUSSION**

Wool is a product used by man as a raw material in light industry. The toxic elements contained in it do not affect human health directly. However as a technological raw material, and, above all, as an element of the trophic level of the heterotrophic organisms, it carries information about the distribution and accumulation of the toxic chemical elements in their organism.

Data in Table 1 show the relatively high lead level in wool – 8.15 mg/kg. In unwashed wool the lead content was almost twice higher – 15.3 mg/kg and the difference was statistically significant (p<0.01). The cadmium content was also quite high (0.53 mg/kg) but the difference between its content in washed and unwashed wool was about 30 %.

When following out the data in Table 2, characterizing the chemical heterogeneity of the anthropogenically formed trophic chain of a pasture type, Pb and Cd dispersal in the meadow grasses was observed, which was about 0.01 n and 0.1 n, respectively. In cereals the dispersal level of lead was higher (about 0.001 n), while for cadmium the same tendency was preserved. The increased Clarc of concentration of lead (4.72) and cadmium (49.14) in soil did not cause their concentration at the level of the autotrophic organisms. Evaluated by FB1 criterion at the level of phytophages, wool also did not show concentrating, while evaluated by FB2

criterion wool showed concentration of lead (2.31) and less concentration of cadmium (0.96).

Information about the real dynamics and distribution of the toxic elements, which entered the animal organism with the forage, water and air, was obtained by the criterion Clarc of distribution (Cod) – Table 3.

Data contained in the table showed differences in lead and cadmium distribution in the studied tissues and organs of the animals, meanwhile giving new information about bioaccumulation of those elements.

The content of toxic chemical elements in air was extremely low –  $0.097~\text{mg/m}^3$  for lead and  $0.0027~\text{mg/m}^3$  for cadmium, respectively. The aerosol way of dispersal of those elements was insignificant (only 0.001~%), which was also proven in our other previous studies (8). Similar data (for the Pb and Cd – contents in the atmospheric air were also reported for the same region by [1].

It is well known that sheep spend the bigger part of the day and night on the pasture. Moving in big herds, they create 'whirls of air' sweeping along fine soil particles. They proved to be rich in Pb and Cd – Table 4. The finer the dust aerosol, the higher the content of the elements in a unit of volume was. A part of that aerosol was breathed by the sheep, but the bigger part was deposited over their fleece while the animals were moving or lying. The secret of the sebaceus and sudoriferous glands also contributed for that.

The high content of lead and cadmium both in unwashed

and even in washed wool confirmed once again the doctrine that the major source of toxic chemical elements is the lithosphere and the ways of absorption are exo- as well as endogenic (through the organism).

#### **CONCLUSIONS**

Lead and cadmium contents in unwashed wool was 15.3 and 0.69 mg/kg, respectively, and, in washed one -8.15 and 0.53 mg/kg, respectively. The difference was due to the exogenic lithospheric direct contamination.

Pb and Cd concentrations are many times higher in the fine dust fraction, which provides a real threat for breathing in the elements.

Clarc of distribution criterion in washed wool showed significant accumulation of Pb (14.85) and Cd (6.24) in comparison with the other studied tissues.

## **REFERENCES**

- 1. Alandjiysky, D., S. Ishpekov, D. Penkov, 2001, Imissions of Pb and Cd in atmosphere air over populated place with increased health risk-content and tendences, Res. Works Agric. Univ.- Plovdiv, vol. 46 (3), 353-356
- 2. Baykov B., 1994, An objective method for assessment of the movement of chemical elements in anthropogenic ecosystem (domestic animal farms). Toxicol. Environ. Chem., 42, 227-233.
- 3. Baykov B., Hr. Hristev, D. Penkov, B. Zaharinov, Yu. Georgieva, Ch. Willeke-Wetstein, J. Stenbach, 2003, Movement of cadmium and lead in anthropogenically formed trophic chains of a pasture type. J. Central European Agriculture, vol.4, 389-398.
- 4. Baykov, B., A. Hallak, K. Kirov, G, Georgiev, 2006, Assessment of safety and distribution of Pb and Cd in the organism of rabbits through criteria Clarc of distribution, J. of Anim. Sci., 43 (1), 65-69 (BG)
- 5. Baykov, B., Hr. Hristev, D. Penkov, Ch. Willeke-Wetstein, J. Steinbach, M. Kitanova, B. Saharinov, 2003, Investigation on the chemical heterogeneity of Pb and Cd in trophic chain: autotrophic organisms small ruminants in antropogenic cosystems with increased

- technogenic clarc. Proceedings of conference "50 years University of forests- Sofia", 55-57
- 6. Baykov, B., R. Gjurov, 2004, Biogeochemistry, New Bulg. Univ., p. 154
- 7. Gabrashansky, P., V. Kovalskiy, M. Rish, L. Nedkova, A. Daskalova, Y. Raezkaya, D. Abdulaev, 1979, Microelments and microelemetosis in the intensive animal husbandry, Zemizdat+Kolos (BG+RU)
- 8. Hristev H., B. Baykov, D. Penkov, C. Willeke-Wetstein, J. Steinbach, 2003, Study on the chemical heterogeneity of cadmium and lead in the biosphere bioaccumulation of cadmium and lead in the organism of young ruminants from anthropogenic ecosysteme with an increased technogenic clarc. J. Central European Agriculture, vol.4, 23-30.
- 9. Mochizuki M., R. Hondo, K. Kumon, R. Sasaki, H. Matsuba, F. Ueda, 2002, Cadmium contamination in wild birds as an indicator of environmental pollution. Environmental Monitoring and Assessment, vol. 73, 229-235.
- 10. Nedkova, L., 1976, On the relations between some microelements by domestic an wild animals, regarding clearing up of the microelmetosis patogenesis, PhD Thesis, Sofia (BG)
- 11. Tyankov, S., V. Lazarov, I. Stankov, 1993, Handbook of sheep breeding, p. 74
- 12. Wayland M., A. Fernandez, E. Neugebauer, H. Gilchrist, 2001, Contaminations of cadmium, mercury and selenium in blood, liver and kidney of common eider ducks from the Canada Arctic. Environmental Monitoring and Assessment, vol. 71, 255-267.
- 13. Yanchev, I., 2001, Influence of geochemical ecological factors on some hematological and biochemical indexes in sheep blood in Chiprovtsi region, J. of Anim. Sci., 6, 41-43 (BG)
- 14. Yanchev, I., L. Dicheva, K. Krastev, 1997, Influence of different As- loading through contaminated fodder, on it's accumulation in sheep' wool, J. of Vetrinary Sci., 1-2, 588-592 (BG)