ECOLOGICAL RISK ASSESSMENT OF LEAD AND CADMIUM CONTENT IN EGGS FOUND IN ECOTECHNOLOGICAL SYSTEMS

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Abstract: Lead and cadmium studies have been conducted in the egg eco-system trophic chain, which is a continuation study on the chemical heterogeneity of the biosphere, assessed at the ecosystem level. For the realization of the ecologilization, a two-module model of an eco-technical system for production of eggs with models of the two main types of trophic chains is proposed: pasture and detritus type.
The main product of the linearity of the technological processes in livestock breeding is fertilizer. From the point of view of efficient management of eco-technical systems to minimize environmental risk, the ecological assessment of the fertilizer for the purpose of its utilization is appropriate. It belongs to the Odum Classification Conglomerates I (1975), which includes organic substances that are potentials of nutrients and energy, and should be utilized as resources for recipients in agro-ecological or aquatic ecosystems. The fertilizer is materially different from other products under this group due to the large number of pathogenic microorganisms. Organic substances in the fertilizer are a risk factor due to the emission of greenhouse gases and toxic substances to the atmosphere and pathogenic microorganisms are biological pollutants with high risk potential due to the risk of it causing human and animal diseases.
Our research has focused on the quality of products used for human food and the particularities of the movement of matter in eco-technical systems (Baykov, 1994, Baykov & Tyrawska, 1991, Baykov et al., 1996, Baykov et al. 2003). The experiments were carried out in models of eco-technical systems for eggs on the scale of "mesocosmos" via classification of Odum (1986) by analyzing the physicochemical indicators of the two elements of the incoming stream: feedstock and drinking water and an assessment of the chemical heterogeneity at the ecosystem level was performed by analyzing and hygienically assessing the physical characteristics of products used for human food.
Proposed, are criteria for assessing the ecological risk of chemical heterogeneity at ecosystem level: eco-technical Clark (Ec), Clark of safety (Cs), Clark of concentrating (Cc) and Clark of technology (Ct). The results show the possibility of assessing environmental risk through the Cs criterion applied to mass of the egg/ feedstock /and for the processed manure. The ecological risk is managed through the Cs and Ct criteria by regulating the amount of toxic factors in the input stream to guarantee safe for human health secondary biological production.
Keywords: anaerobic fermentation, clark, cadmium, composting, eco-technical system, lead, organic fertilizer

1. INTRODUCTION

The concentration of a large number of farm animals in a restricted area, continuity of production and the lack of the bioreduction unit causes the cyclical movement of biogenic elements, a characteristic of natural ecosystems found in eco-technical systems, to be replaced by linearity in the movement of matter, which is the cause of the production of waste materials.

Purpose of current studies is the modeling of an eco-technical system for eggs in order to manage the technologies in a new doctrine for the functioning of agroecological systems, which is defined as a more environment-friendly technologies. In essence it, it is a combination of economic and environmental priorities in agrocenosis management. The aim is to ensure high economic efficiency of production of town is to minimize environmental risk, which includes safety of food products of animal origin and technological solutions for conversion of the fertilizer to agro-ecological resource, overcoming the linearity of technology.

The aim of this publication is to offer an algorithm for the management of the quality of the secondary organic production based on the information on the movement of the matter in the eco-technical system for eggs and the application of a set of criteria for the chemical heterogeneity in order to limit the ecological risk.

2. MATERIALS AND METHODS

Description of the eco-technical model

The experiment conducted in a dual model of an eco-technical system that reproduces the two main types of trophic chains, functioning in natural ecosystems with related modifications and the intensity and continuous production of secondary organic production and peculiarities of the ecotope: first model of the pasture type and second module of detritus type. The model of movement of matter in a pastoral-type trophic chain is realized in the segment of autotrophic organisms (fodder + water -eggs) in ecotope controlled environment and interrupted circle of matter.

In the present experiments a scale model "mesocosmos" was used in the Odum classification (1986), which was described in our previous experiments (Baykov, 1987, 1994). The ecotope provides optimal parameters for the living environment and brings in the resources used: air-conditioned industrial building intended for farming of poultry, with size of 20/10 meters when at the same time birds and poultry are farmed and differentiated in treatment groups depending on the purpose of the experiment, under the same parameters of the abiotic factors regulated in Decree 44 of MAF, Ministry of Agriculture and Forestry, for the technological standards of the main abiotic elements as follows: air temperature 16-22^{0}C, relative humidity 50-72%; air speed in the living area -0,2 - 0,5 m/s, intensity of light - 40 lx, content of toxic gases: carbon dioxide - 0,1%, ammonia and hydrogen sulphide - traces. Biological factors are regulated by applying the appropriate prophylactic measures and optimizing the population density of the commercially beneficial species. The birds are hydrated with water from a central water source with physical indices corresponding to Ordinance No. 9, (year 2001) of the Ministry of Health.

The modified trophic chain of the detritus type in the eco-technical system is presented in 3 variants:
1.Trophic chain for aerobic mineralization of organic matter of detritus without a control and management system (such as most of the technologies in the practice of small farms), which correspond to "good agricultural practices".
2.Trophic chain for aerobic mineralization of organic matter under controlled conditions - composting, described by Baykov, 1987;
3.Trophic chain for anaerobic degradation of fertilizer where mineralization is controlled and utilized the obtained energy from gaseous fuel of biogas. The product obtained from the fermentation (biosylate) is used to increase soil fertility or as a solid fuel. For the modeling of this type of trophic chain, it is based on the patent "Fermenter for anaerobic fermentation" - Registry No. 93202/27.11.1992.

In a heat-insulated cabinet is mounted a system comprising 6-12 fermentation vessels. In the tempered fluid (different variants for water and air were developed) 6 to 12 hermetically sealed laboratory bottles with a substrate were placed. A system for removal of the gas obtained and for control of the produced quantity is mounted (this part is visible in the picture). The bottles have a volume of 1.0 - 1.5 liters, which is optimal for a laboratory installation, as the biosylate required for the study is obtained.

Experimental Items: Attempts are carried out with birds of the species *Gallus gallus*, category laying hens breed ISA-Brough (ISA-Brown) at 18 weeks of age for 300 days.

During the experimental period the birds received feed containing: 18% crude/raw protein, 0.44% phosphorus (digestible), 3.83% calcium, 0.91% lysine, 0.76% methionine + cysteine and with a conversion energy of 2750 kcal/kg fodder. The lead content is 1.28 mg and cadmium 1.01 mg per kg of feed with a moisture content of 12%.

A bird receives food and water without any restrictions. The resulting eggs are collected daily and stored after weighing and marking at 4^{0}C.

Biological factors are regulated by applying the established prophylactic programs and by regulating the abiotic factors (the intensity of the air exchange) also by limiting the microbial air pollution. Birds are reared without litter at a density of 6 hens/m^2 of floor area.

Drinking water and fodder were studied at the beginning of experiment, as well as egg mass, shell and fertilizer every 10 days from the beginning of the experiments conducted.

The investigated are pooled fertilizer samples, which are obtained as a 6-point average sample in the room and the manure storage.

The results that are presented represent the average of the 30 samples, including the entire experimental period

Laboratory tests were conducted using the following algorithm: Eggs are collected and tested daily. The egg whites and egg yolks are also mixed as an egg mixture (egg melange) and subjected to lyophilization. The shells are weighed separately. Samples were stored at 0^{0}C until study time (every 10 days). Samples of fertilizer (fresh and mature), biosylate and compost were taken daily, which were tested in 10 days using standardized methods that tested feedstock and drinking water as follows: Determination of the environmental reaction (pH) - BDS EN 12176: 2000; Determination of dry residue and water content - BDS EN 12880: 2003; Determination of total organic carbon ─ BSS EN 13137: 2005; Determination of Cadmium (Cd) and Lead (Pb), - BDS EN-13346: 2000, VM-1: 200. The static processing of the obtained results was done in the statistics program - Origin® 7.0 SR0, V 7.0220 (B220) and using Microsoft ® Excel program. Criterion of statistical reliability was P <0.05.

3. RESULTS and DISCUSSION

The results of modeling of the pastoral-type trophic chain are presented in Table 1.

An uneven distribution of the two test elements (lead and cadmium) was detected both at the entrance of the system and in the products forming the two outflows (egg mass + shell) and fertilizer.
Water is the source of 2.58% of lead and 0.20% of cadmium in the two abiotic components of the system: feed, carrier of the characteristic lithospheric area, and drinking water.

Table 1. Dual module model for trophy in ecotehnical system for eggs, modul for trophic chain for pastural type.

№	Indicator	Dimension for chemical elements	Dry mass	Lead in native mass	Lead in dry mass	Cadmium in native mass	Cadmium in dry mass
1.	Output stream	mg/kg	%				
1.1	Forage		88	1.13±0.11	1.28± 0.14	1.01± 0.09	1.14± 0.11
1.2	Water for watering/ submersion		0.2	0.03±0.005	0.03± 0.005	0.02±0.008	0.02± 0.008
2.	Incoming stream	mg/kg	%				
2.1	Egg mass: Egg white+ yolk	mg/kg	90	0.12± 0.05	0.13± 0.04	0.06±0.01	0.07± 0.01
2.2	Egg shell		100	9.62± 0.84	9.62± 0.84	4.04± 0.26	4.04± 0.26
2.3	Fertilizer		22	0.69± 0.07	0.88± 0.08	0.27± 0.01	0.35± 0.02
3.	Clark eco technical (Ce)	Clark					
3.11	Egg mass				0.10±0.02		0.06± 0.01
3.2	Egg shell				7.52±1.06		3.54±0.88
3.3	Fertilizer				0.68±0.12		0.30+0.06
4.	Clark of safety (Cs)	Clark					
4.1	Egg mass			0.04±0.01		0.6±0.08	
4.2.	Egg shell			1.92±0.18		4.04±1.12	
4.3	Fertilizer						
4.3.1	Conventional agriculture				0.007±0.001		0.12±0.05
4.3.2	Biological production				0.02±0.01		0.50±0.002
5.	Clark of concentration (Cc) in egg mass			0.03±0.01		0.02±0.005	
6.	Clark of technology (Ct) in egg mass.			0.46±0.12		0.41±0.22	

The distribution of both elements is also uneven across the output of the system. The lowest is the content of lead in the egg mass (0.12 mg / kg) at humidity of 10%, followed by the fertilizer - 0.88 mg / kg of dry weight. The most intense amount of lead is accumulated in the egg shell - 9.62 mg / kg of dry mass. Similar is the order of cadmium - 0.06 mg / kg in the egg mass, 0.27 - in the fertilizer and 4.04 in the shell.
The results obtained are one-way with the date in Jeng,1997 et al, and Korenekova et al., 2002.The results of the modules of the trophic chain of the detritus type are presented in Table 2.

Table 2. Dual module model of trophy in ecotechnical system for eggs, moduls for trophic chains of the detritus type.

N	Indicator	Dimension	Input: fresh fertilizer	Output: Aged fertilizer	Output: compost	Output: biosylate
1.	**pH**	Units	7.66	7.54	7.84	7.18
2.	**Dry mass**	%	22.0±1.1	36.4±1.2	48.2±1.8	10.8±0.67
3.	**Organic carbon**	% of dry mass/substance	30.72±4.61	20.41±1.96	19.22±1.64	15.12±0.84
4.	**Lead**	Mg/kg dry	0.88±0.12	1.28±0.28	1.44±0.31	1.87±0.36

		mass/substance				
5.	**Cadmium**	„	0.35±0.08	0.53±0.11	0.68±0.23	0.84±0.34
6.	**Clark of Safety**					
6.1	In the fertilizers of conventional agriculture	Units				
6.1.1	Lead		0.007±0.001	0.01±0.005	0.01±0.005	0.02±0.008
6.1.2	Cadmium		0.12±0.08	0.18±0.09	0.23±0.08	0.33±0.09
6.2	In the fertilizers of biological production					
6.2.1	Lead		0.02±0.008	0.03±0.009	0.03±0.08	0.04±0.10
6.2.2	Cadmium		0.50±0.11	0.76±0.24	0.97±0.36	1.20±0.14

Minor changes in fresh fertilizer pH were observed compared to those stored in accordance with "Good Agricultural Practice" recommendations -180 days with conditions for isolation from external influences. In both models of aerobic treatment of the fertilizer, dry matter is increased - up to 36.4% for DSP and 48.2% for composting. The anaerobic digestion was found to be significantly of about 10.8% (with 51%) reduction in dry matter. Organic carbon losses in three patterns of the detritus type trophic chain are significant. The largest carbon losses in anaerobic digestion are 50.8% of the baseline, and this is understandable because the main purpose of this technology is the production of biogas, a mixture of two carbon-containing compounds: methane and carbon dioxide. There is also a significant reduction in the amount of carbon in the aerobic control (composting) by 37.5%. The lowest is the reduction in anaerobic treatment type DSP - 33.6%. The indicator organic carbon, is important to make an agrotechnical assessment, as an indicator of the degree of decomposition of the organic substances, which determines the possibilities for utilization of nutrients (the biogenic elements) by plants - autotrophic organisms utilize biogenic elements only mineralized forms.

Table 2 show that in all three patterns of detrimental trophic chains, the content of lead and cadmium in the products is increased, which is produced to increase fertility of the soil. The highest amount of lead in the biosylate (by 140% relative to the fresh substance), followed by compost (64%) and the aged fertilizer - 45%. One-way results are also for cadmium: 140%; 94% and 50%.

This increase in both toxic elements is due to the redistribution of chemical elements in the substrate due to the modeling of two main types of the biodegradation process of organic substances found in natural ecosystems. In aerobic digestion /storage under DPS and composting/, which is widespread in natural trophic chains of detritus type, under the influence of oxygen substantial amounts of organic substances are oxidized to generate carbon dioxide and water, significant part of which is evaporated and. In anaerobic digestion, and as widespread in natural ecosystems, a significant portion of biogenic element components leave the system as they form a biogas (mainly made of methane and carbon dioxide).

In the present paper on solving tasks in two main directions: food safety and fertilizer processing for use as a resource and criteria for chemical heterogeneity are applied in the eco-technical system:

Clark ecotechnical (Ce) - the ratio of the studied chemical element in dried egg mass, shell and fertilizer to their feed quantity. It is defined in units, such as more than 1, is when there is a concentration, and less than 1, means there is dilution of the respective chemical element. With this criterion, we replace the "Bioconcentration Factor" proposed by Dobrovolsky (1988) and used in our other publications because of the uniformity of dimensions defining chemical heterogeneity in the biosphere. It is important to note, that it is only in one of the heterogeneity characteristics (aggregate, energy, spatial), that we accept the name of the criterion "Clark" for all aspects of chemical heterogeneity.

Clark of concentration (Cc), (Baykov, 1987), which is the ratio of studied chemical element in 1 kg native egg mass to the amount of the same element throughout the whole quantity of fodder and water, which is also required for production of 1 kg egg mass presented as the dimension is mg/kg of native mass.

Clark of safety (Cs), (Kirov et al., 2018) is the criterion for assessing the ecological risk due to bioaccumulation of toxic elements in secondary biological production. The criterion is the ratio of the content of toxic factor in mg/1 kg of fresh secondary organic production to the regulated and admissible content in the same quantity according to the current legislation and documents (MRLs). It is proposed to be a user-friendly expert assessment of the environmental risk of increased content of toxic elements in secondary biological production and human health hazards. Interpretation of the Cs is elementary: at values above 1, the product is dangerous to human health and at values below 1, it is safe.

Clark of technology (Ct) – is a new criterion related to risk management by controlling and regulating the content of toxic factors at the input part of the system. The aim is to exclude the environmental health risk of the toxic concentrations from studied food factors, which are possible due to the specificity of bioaccumulation along the trophic chain. It is determined that the amount of toxic factor in food (lead and cadmium) in 1000 g of native egg is divided by the quantity of the same elements contained in 1000 g of native mass (feed and water) by the incoming stream. In contrast to Cc, which is indicative of the dynamics of movement of matter, Ct is a derivative thereof which allows to regulate Cs values in foods by varying the amounts of toxic elements at the input of the system, based on the conditions established for the particular conditional values of Ct, with the fodder-water ratio established in the model. Our studies show that the content of cadmium and lead in drinking water is relatively constant in the central water supply and that it is actually impossible to adjust the set values, thus, the only feasible option is to manage the environmental risks by changing the quantities of lead and cadmium in the feed to values that guarantee that Cs in eggs is under 1, i.e., they are safe for humans, and they can be determined using the criterion Ct.

The proposed criteria allow interpretation of results and the possibilities of ecologicalization of the egg production technology in two main directions:

Optimizing the amount of the two toxic elements at the input of the system by regulating their amount in the feed (constant values in water are assumed within the experiment and should be controlled without any possible changes to them in order to produce safe foods that are defined with a Cb value below 1).

2.Control and certification of the other products in the secondary organic production: egg shell - used as feed additive and fertilizer - intended to increase the fertility of the crops after appropriate processing also by using the criterion Cs as defined by specific national and international regulations.

The incoming stream contains 1.13 mg of lead and 1.01 kg of cadmium in 1 kg of feed with 12% water content. The corresponding elements in drinking water are 0.03 mg/l and 0.002 mg/l. In graphs 6 and 8 the data for dry matter are given. Water is the source of 2.3% of lead and 1.7% of cadmium in the substrate of the incoming stream. In our previous experiments, the amount of the two toxic elements in the ration was measured in accordance with the Maximum Residues Limit (MRL) in Ordinance No. 5 of the Ministry of Public Health (SG 39/44) - lead up to 0.5 and cadmium up to 0.10 mg per kg of feed. In the current trials, the quantities of the two toxic elements were modeled on the basis of the data from 140 samples tested and on the the availability of updated limit values and/limit values of Annex 1 to Directive 2002/32 / EC of the European Parliament / 7 May 2002 /: whereby MRL of lead is 5 mg and for cadmium, it is 1 mg to 1 kg feed with a 12% moisture content. In said model parameters of the input / w 1.1 and 1.2 in column 6 /Clark ecotechnological /(Ce) for lead is 0.10 in egg mass, 7.72 for egg shells and 0.68 for the fertilizer. For cadmium, the corresponding values are 0.06; 3.54 and 0.30.

The presented results show that in the modeling of parameters for lead and cadmium content at the entrance of the eco-technical system, that the secondary production used for human food / egg mass / and the fertilizer meet the food safety norms, respectively, of resources for increasing fertility of the soil.

The developed model allows control of chemical heterogeneity, allowing those criteria to apply for managing the system to limit the environmental risk of increased content of toxins in food / egg mass / by controlling the amount of two elements on the system / primary in feed as it is assumed that the quantities in water are constant. To make management possible, we offer a new criterion, Clark of technology (Ct). The model shows that for the production of 1 kg of egg mass, 2.721 kg of feed containing 3.07 mg of lead and 4.126 L of water containing 0.12 mg of lead is needed. The production of 1 kg of egg mass requires 6.857 kg of resources (in which the feed / water ratio is 40:60) containing 3.19 mg of lead. The Clark of concentration is 0.03 /0.12:3.19/. Using an analogous algorithm, we determine Cc of cadmium to be 0.02. This information indicates the intensity of moving the materials and allows management decisions to be made related to limiting the environmental risk as a result of chemical heterogeneity and the movement of lead and cadmium in the segment: autotrophic organisms + water - egg mass. For movement management, we offer a new indicator of chemical heterogeneity – Clark of technology (Ct). Determined on the basis of the results obtained in the model but recalculated for 1000 g of system input /feed + water/: consumed were 6.857 kg of resource containing 3.19 mg of lead, which means that 1 kg of resource at the entrance contains 0.46 mg of lead. The Ct value for lead is 0.26. Ct value for cadmium determined by the same algorithm is 0.41. These data values make it possible to recalculate the values of the toxic elements in the input (feed + water) under specified requirements (MRL) for food /(egg mass).

The developed dual module system for the trophic chain integrates a second module: a detritus food chain. The objective is to assess the movement of the two toxic elements in a biotechnological chain in three described processing technologies that limit the environmental risk of pathogenic microorganisms and partially mineralize the organic substances of the substrate. The most widely used aerobic extensive fertilizer storage technology according to IMP requirements /180 days in space isolation/ 1 group /due to redistribution of the chemical elements/ emission of greenhouse gases/is responsible for increasing the amount of lead by 45% and of the cadmium by 51%. Cs is as follows: for conventional agricultural production 0.007, and for organic production, it is 0.02. When composting in a laboratory installation with a dosed oxygen supply (2nd group) the amount of lead increased by 54% and the values of Cs were 0.01 and 0.03. The most important are differences in anaerobic digestion in biogas plants (3rd group) - increased content by 112% and Cs values of 0.02 and 0.04.

Similar is the dynamics of cadmium in the three technologies. In group 1, the amount of cadmium is increased by 51% and Cs is 0.12 and 0.50, respectively. In group 2 the indicators are: 94% and 0.23 and 0.97. The most important to change into 3 groups are the following: an increase of cadmium by 140% and a Cs of 0.33 for conventional production and of 1.20 for organic, which means that the product is unfit for organic food production in agriculture.

The experiments in the two-module model for ecotechnical system for eggs allows control of the movement of toxic elements throughout the entire tropical food chain, combining the two main types of food chains: the pasture type and detritus type. The control restricts the environmental risk due to bioaccumulation of toxic factors in secondary production, ensuring food safety. The model allows the control and evaluation of lead and cadmium in processed manure, standardized for fertilization or fuel, which is an alternative to the linearity of technologies.

In this publication we analyze the possibilities for limiting environmental risk through a system for controlling and managing the movement of toxic elements, i.e., we focus on the chemical heterogeneity of the living substance at the population level.

CONCLUSIONS

The current management stage of ecotechnical systems combines business with environmental priorities and is defined as the greening or ecologization of technology. The lead and cadmium studies conducted in the trophic chain of the eco-technical system for eggs are a continuation and a more in depth look at the investigation from the 1994 research study on the chemical heterogeneity of the biosphere evaluated at ecosystem level, with experiments with two significant for Bulgaria toxic elements of lithospheric origin: lead and cadmium. For An integrated two-module model of an ecotechnical system for the production of eggs is proposed for realizing ecologicalization in animal breeding, which includes models of two main types of trophic chains: of the pastural type and the detritus type. This integrated model is a basis for greening or ecologicalization technology as it combines two essential requisites for providing safe food and allowing for the overcoming of the linearity of technology. Criteria for environmental risk assessment are proposed: Clark ecotechnical, Clark of safety, Clark of concentration, and Clark of technology. The results presented show the possibility of assessing the environmental risk through Cs which is applied both for the egg (food resource) and for the processed fertilizer. Through using Cc and Ct, it is possible to manage the system by regulating the amount of toxic factors in the input stream to ensure a safe for human health - secondary organic production.

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