



UNIVERSITY OF PRISTINA
SERBIA

THE
UNIVERSITY
THOUGHT

PUBLICATION IN NATURAL SCIENCES

VOL. 5, N° 2, 1998.

PUBLISHED BY UNIVERSITY OF PRISTINA, SERBIA, YUGOSLAVIA

ISSN 0459 - 7226

Vol. V (2), 1998.

Director: Prof. dr Radenko Krulj

Za izdavača: Prof. dr Radenko Krulj

Chief Editor: dr Predrag JAKŠIĆ

Urednik: dr Predrag JAKŠIĆ

Technical Editor: dr Zoran ILIĆ

Sekretar: dr Zoran ILIĆ

Editorial and Advisory Board:

Prof. dr Radivoje PAPOVIĆ, Prof. dr Slobodanka STANKOVIĆ, Prof. dr Dragoslav PEJČINOVIĆ, Prof. dr Slobodan GLIGORIJEVIĆ, Prof. dr Jonče ŠAPKAREV, Prof. dr Jordan N. STAMENOV, Prof. dr Boris KRYŠTUFEK, Prof. dr Ljubiša KOČINAC, Prof. dr Radomir ILIĆ, Prof. dr Radoslav PALIĆ, Prof. dr Čemal DOLIČANIN, dr Mirjana MIRIĆ.

Uređivački i nadzorni odbor:

Editorial Office:

dr Predrag JAKŠIĆ, Prirodno-matematički fakultet, Vidovdanska bb, 38000 Priština, Yugoslavia

The article are translated by authors and by Nikoleta Bašić, Radovan Urošević and Nenad Pejić

SCOPE OF THE JOURNAL

It is the endeavour of the University of Pristina to acquaint the scientific world with its achievements. We would like to affirm the intellectual potential of this region as well as natural resources of the Balkans. We would like to put forward our attitude of principle that science is universal and we invite all scientist to cooperate wherever their scope of research may be. We are convinced that we shall contribute to the victory of science over barriers of all kinds erected throughout the Balkans.

All rights reserved. No part of this journal, excepted abstracts in English, may be reproduced in any form without the permission of the copyright owner.

Ex Libris
Dr Predrag Jakšić

CONTENTS

- [3] IN MEMORIAM
Dr ILIĆ Radomir - Raca
- [5] On the orthogonal Damping Matrices
BAŠIĆ Dragoslav, STOJIĆ Dragoslav & MEŠIĆ Esad
- [9] A Study of the Initial Stages of the Electrochemical Deposition of Thallium on Copper - PART I.
The Linear Sweep Voltammetry Behaviour of polycrystalline and (111) oriented Copper Single Crystal Electrode
JOVIĆEVIC N. Jovan & BEWICK Alan
- [19] A Study of the Initial Stages of the Electrochemical Deposition of Thallium on Copper - PART II.
The Linear Sweep Voltammetry Behaviour of (110) oriented Copper Single Crystal Electrode.
JOVIĆEVIC N. Jovan & BEWICK Alan
- [27] A Study of the Initial Stages of the Electrochemical Deposition of Thallium on Copper - PART III.
The L.S.V. Behaviour of (100) oriented Copper Single Crystal Electrode
JOVIĆEVIC N. Jovan & BEWICK Alan
- [35] Kosovo Lignite as the Raw Material for production of Ammonium-nitro-humate
PETROVIĆ Milena & PETROVIĆ Petar
- [39] Morphographic survey of Relief structure and Internal Regional-geographic Classification of Korita
ALIBAŠIĆ Safeta
- [43] The Yugoslav Part of Sar-planina Mt. Lake Eco-system's Periphyton Alga
UROŠEVIĆ Violeta
- [59] Fritillaria macedonica Bornm. - New Species in Yugoslav flora
AMIDŽIĆ Lidija, KRIVOSEJ Zoran & STEVANOVIĆ Vladimir
- [63] Silene Graefferi Guss. - New Species for Yugoslav flora
KRIVOSEJ Zoran, AMIDŽIĆ Lidija & STEVANOVIĆ Vladimir
- [67] Draba siliquosa Bieb. (D. carinthiaca Hoppe) - a New Species of Flora of Yugoslavia
AMIDŽIĆ Lidija, STEVANOVIĆ Vladimir & KRIVOSEJ Zoran
- [71] Distribution of Butterfly Communities (Lepidoptera: Hesperioidea & Papilioidea) in Plant Communities over the Jazinacko jezero Lake Region on Sar-planina Mt.
JAKŠIĆ Predrag
- [77] Altitudinal Distribution and Biogeographical Division of the Butterflies of Balkan Peninsula (Lepidoptera: Hesperioidea and Papilioidea)
JAKŠIĆ Predrag
- [89] Distribution of some Microelements in muscular Tissue and Organs of the Chubs (Leuciscus cephalus) Caught in the Ibar River.
VUKAŠINOVIC Marija, MIHAJLOVIĆ Randel & PAVLIĆEVIC Nina
- [93] Demographic and Ethnic Problems in Kosovo and Metohija
GOLUBOVIĆ Petar & MARKOVIĆ-KRSTIĆ Suzana
- [101] BOOK REVIEWS - PRIKAZI

IN MEMORIAM

Dr Radomir-Raca Ilić

(1938 - 1998.)



Dana 20.05.1998. godine, ugasio se život istaknutog profesora sa Odseka za geografiju PMF-a u Prištini.

Prof. dr Radomir Ilić je rođen 22.11.1938. godine u selu Rečica, Opština Bojnik. Diplomirao je na Odseku za geografiju PMF-a u Prištini 1974. godine. Magistrirao je 1976. godine na Geografskom fakultetu u Beogradu, i doktorirao na istom fakultetu 1980. godine.

Svoju radnu karijeru profesor Ilić je započeo kao nastavnik u osnovnim školama u Janjevu i Lecu od 1960. godine, a od 1978. godine radio je kao profesor u srednjoj školi u Nišu. Godine 1987., izabran je za docenta, a 1992., za vanrednog profesora PMF-a u Prištini. U toku je bila procedura za njegov izbor u zvanje redovnog profesora, ali to zvanje nije doživeo. Njegovu uzlaznu liniju u naučnoj u pedagoškoj delatnosti prekinula je relativno rana smrt u 60-toj godini života.

Svojim radom na Univerzitetu u Prištini, kako u obrazovnoj, tako i u naučnoj i opšte-društvenoj delatnosti, profesor Radomir Ilić se afirmisao kao veoma istaknut i zaslužan pedagoški i naučni radnik. Njegova predavanja studentima bila su veoma jezgrovita, jasna i sadržajna. Mentorisao je znatan broj diplomskih radova studentima, a "proizveo" je i jednog doktora nauka i pripremao još jednog. Svojom edukacijom, stručnošću i korektnim odnosom, a iznad svega svojom dobrotom, stekao je veliki ugled i bio poštovan među studentima, kao i među svojim kolegama.

Njegov inventivni i kreativni duh je došao do punog izražaja u naučnoj delatnosti. Po oceni eminentnih naučnika, po naučnoj vrednosti spada u sam vrh geografske, posebno hidrološke nauke u nas. Među dvadesetak njegovih radova su i tri vredne knjige. U monografiji Vode- prirodne zakonitosti in-

filtracije padavina, koja je štampana na srpskom i engleskom jeziku i distribuirana u sve velike svetske biblioteke, profesor Ilić prezentira naučnoj javnosti nove, naučne (matematičko-geografske) metode za utvrđivanje prirodnih zakonitosti infiltracije padavina, kojima se rešavaju važna pitanja vodnog bilansa. Za stvaralački opus Radomira Ilića može se reći da ima ne samo teoretsku već i praktičnu odnosno aplikativnu vrednost. Takvu vrednost će imati i njegova najnovija knjiga, koja je u štampi, a u kojoj je takođe došao do novih otkrića u svetskoj hidrologiji. Primenom rezultata istraživanja iz te knjige, doći će do ukidanja skoro svih vodomernih stanica, što bi bila velika ušteda. Kollega Ilić se nije ograničio samo na radove iz Hidrologije. On je jedan od autora Enciklopedije srpskog naroda u kojoj je zastupljen sa 13 odrednicima o Kosovu i Metohiji. Svojim naučnim radom profesor Ilić je dao veliki doprinos razvoju naše i svetske hidrologije. Time, kao i učešćem na brojnim naučnim i stručnim skupovima, u zemlji i inostranstvu, on je dostoјno reprezentovao naš Odsek za geografiju, PMF i Univerzitet u Prištini.

Kao zaslужnom naučnom radniku, Ministarstvo za nauku i tehnologiju Republike Srbije, poverilo mu je dužnost rukovodioca potprojekta "Fizičko-geografski procesi na Kosovu i Metohiji"

Tu dužnost je, na naše zadovoljstvo i zadovoljstvo Ministarstva uspešno izvršavao.

Profesoru Iliću pripadaju velike zasluge za pokretanje i izlaženje našeg Zbornika radova, čiji je bio glavni i odgovorni urednik.

Njegov odlazak na večni počinak predstavlja veliki i nenadoknadiv gubitak za naš Odsek i Univerzitet u Prištini, a posebno za njegove najbliže saradnike. Plemeniti lik našeg dragog Radomira - Race Ilića krasile su najlepše ljudske vrline: poštenje, čestitost, iskrenost, dobromernost i humanost. U naš kolektiv unosio je vedar duh i prijatno raspoloženje. Zaista je bilo veliko zadovoljstvo družiti se s njim. Na žalost, posle potrodične tragedije, koja ga je zadesila smrću njegovih mezmica - kćerki Ljilje i Nele, koje je neizmerno voleo, njegovo emocionalno stanje se znatno promenilo. Bio je često tužan, deprimiran i razočaran. Kao da je želeo da što pre ode u zagrljav svojih kćeri, koje su ga napustile u cvetu svoje mладости. Od tada, smisao svog života nalazi u pisanju naučnih radova, koje posvećuje kćerkama.

No, bez obzira što za sobom nije ostavio biološko potomstvo, profesor Radomir Ilić ipak nije otisao bez traga. Ostavio je vredno naučno delo po kojem će se, njegovo ime večno spominjati i zbog kojeg se, kako je rekao Njegoš, imao rašta i roditi. To delo će inspirisati mlade generacije za nova stvaralaštva.

Naš Odsek za geografiju može biti ponosan što je u svojim redovima imao čoveka takvog kova, kao što je bio prof. dr Radomir Ilić.

Neka mu je večna slava i hvala !

Marko Knežević

Spisak radova

Izvori Gornje Jablanice, Glasnik Srpskog geografskog društva, sv. LVII, br.2, Beograd, 1977., str. 34-39

Water resources of the rivers Veternica, Jablanica and Pusta reka, Collecta simposium, International geographical union, Belgrade, 1978., str. 74-78

Jablanica, Veternica i Pusta reka - hidrološke osobine i vodoprivredni značaj, Posebna izdanja Srpskog geografskog društva, knjiga 46, Beograd, 1978.

Vodni bilans SR Srbije, Doktorska disertacija, Odsek za geografske nauke, PMF, Beograd, 1980.

Hidrološki rejoni Srbije, Glasnik srpskog geografskog društva, sv. LXIII, br.2, Beograd, str. 41-47

Vodni bilans sliva Lepenca, Geografska istraživanja, br.9, Geografsko društvo Kosova, Priština, 1988., str. 115-123

Reka Erenik - veliko vodno bogatstvo, Geografska istraživanja, br. 10, Geografsko društvo Kosova, Priština, 1989., str.37-40

Reka Toplica - hidrološke osobine i zagađivanje, Geografska istraživanja, br. 11, Geografsko društvo Kosova, Priština, 1990., str. 28-32

Zavisnost srednjegodišnjih vrednosti koeficijenta podzemnog oticaja od srednjegodišnje visine padavina u rečnim slivovima SR Srbije, Zbornik radova XIII kongresa geografa SFRJ (1989), Savez geografskih društava Jugoslavije i Geografsko društvo Kosova, Priština, 1991., str. 109-116

Geografski metod proučavanja režima infiltracionih sposobnosti rečnih slivova na primeru Plavске reke i Tise, Glasnik Srpskog geografskog društva, sv. LXXI, br. 2, Beograd, 1991., str. 37-44

Infiltraciona svojstva sliva Sitnice, Geografska istraživanja, br. 12, Geografsko društvo Kosova, Priština, 1991., str. 61-66

Geografski metod proučavanja režima vodopropustljivih sposobnosti rečnih slivova na primeru Belog Drima i Kolubare, Glasnik Srpskog geografskog društva za 1992., str. 9-22.

Vodopropustljiva svojstva sliva Sitnice, Geografska istraživanja, za 1992. Geografsko društvo Ko-sova, u štampi, priložen.

Zavisnost, zasićenost i kapacitet kolektora podzemnih voda (izdani) u rečnim slivovima, priložen. (isto)

Vode I -Prirodne zakonitosti površinskog i podzemnog oticaja. Monografija, NIU Vojska, 1996, Beograd.

Vode II -Monografija, NIP Prosveta, oktobar 1998, Beograd.

Radovi priloženi i prihvaćeni

1. Uticaj antropogenih faktora na promenu elemenata vodnog bilansa, Međunarodni simpozijum o ekologiji gradova, Niš, novembar, 1992. Fakultet zaštite na radu Univerziteta u Nišu.

2. Hidrografske odlike i vodni bilans zapadnih padina Stare Planine, Naučni skup, Geografske promene u pograničnoj zoni Srbije, Geografski fakultet Univerziteta u Beogradu, Zaječar, oktobra 1992.

3. Vode III - Monografija, (u pripremi)

4. Površinsko i podzemno oticanje na zapadnom obodu metohijske kotline- Ilić R., Radovanović D.-Zbornik radova III, Odsek za geografiju, PMF-a, Priština, 1998.

Dragan Radovanović

ON THE ORTHOGONAL DAMPING MATRICES

BASIC Dragoslav, STOJIC Dragoslav, MESIC Esad
University of Pristina

Abstract

The aim of the paper is the derivation of damping matrices for the dynamic systems with the discrete dampers. The experiments indicate that a substantial part of energy absorption takes place in specified points or locations of the system. Testing such systems, one can obtain the modal damping ratios but they can not be used to describe appropriately the damping in a single damper.

The damping of such isolated parts should be described in absolute terms, i.e. viscous damping coefficients. To achieve this objective, the

global damping matrix is formulated in coordinates that represent motion of the system at the ends of a discrete damper. Damping uncoupling is then used to obtain the amount of damping exhibited by each of the dampers. In this paper, the analysis is developed in these terms and general equations are derived. Some standard methods used to construct the orthogonal damping matrices are also presented. This problem is not only significant in physics and engineering, but also in mathematics.

Key words: Damping, orthogonal matrices, dynamic systems, uncoupling.

INTRODUCTION

In the dynamic response analysis of linear elastic systems, it is necessary to define the mass, stiffness and damping properties of the system. It is usually easy to construct the first two matrices but it is extremely difficult to evaluate the damping characteristics. The starting assumption in the dynamic response analysis is the linear viscous character of the damping. This assumption does not affect the form of the damping matrix. For the purpose of the mode superposition approach, the damping is assumed to be uncoupled and is given in each mode as a percentage of the critical damping. The selection of the realistic damping values is usually based on the known physical properties of the system or on experimental evidence for the particular system or from the systems of similar geometry and materials.

The complete damping matrix should be known in the case of direct integration of the equations of motion. If the stiffness properties are non-linear, for example, the direct integration should be performed. Even in that case, it is desirable to retain linear viscous damping. This explains the necessity to develop a complete damping matrix.

The paper is intended to present different methods to develop damping matrices with uncoupling conditions. The first and the simplest damping matrix is the one which represents so called Rayleigh damping. This matrix is directly related to the mass and stiffness matrices through some arbitrary factors. Another widely accepted method is the extension of the Caughey series method. This method develops a damping matrix that is some combination of the mass and stiffness matrices but is not proportional to them. Finally, a method which has the characteristics to be direct evaluation of the damping matrix will be presented.

Beyond these classic methods, the paper is contributing with a method which is appropriate for the

dynamic systems with the discrete dampers. It means the dampers which are located along specific degrees of freedom. The method offers solution for the numerical values of the damping influence coefficients for each of the dampers. The orthogonality condition is used for such a solution. Physically, this could be understood as the distribution of overall energy dissipation among the dampers in the system.

CONDITIONS FOR DAMPING ORTHOGONALITY

In the derivation of the normal-coordinate equations of motion, it has been assumed that the normal-coordinate transformation serves to uncouple the damping forces in the same way that it uncouples the inertia and elastic forces. The vibration mode shapes in the damped system will then be the same as the undamped mode shapes. The mode-shapes have the meaning of eigenvectors.

The equations of motion have the following general matrix form

$$(1) \quad \mathbf{m} + \mathbf{c}\dot{\mathbf{v}} + \mathbf{k}\mathbf{v} = \mathbf{p}(t)$$

where \mathbf{m} , \mathbf{c} , \mathbf{k} , and \mathbf{p} are the mass matrix, the damping matrix, the stiffness matrix, and the force vector, respectively. All degrees of freedom, i.e. coordinates, are included in the vector \mathbf{v} . Two subvectors, group the coordinates with and without damping forces in them.

The uncoupling will occur if the following condition is satisfied

$$(2) \quad \phi_m C \phi_n = 0, \quad m \neq n$$

where ϕ_m and ϕ_n are the mode shapes associated with ω_m and ω_n frequencies, respectively, and c is the damping matrix.

Rayleigh [1] showed that a damping matrix of the form

$$(3) \quad c = a_0 m + a_1 k$$

where a_0 and a_1 are arbitrary proportionality factors, will satisfy the orthogonality condition. It is evident that a damping matrix proportional to the mass and/or stiffness matrices will permit uncoupling the equations of motion.

The general form of a viscous damping matrix with orthogonal properties was originally derived by Caughey [2]. The extension of the Caughey series method [3] produced the damping matrix of the following form

$$(4) \quad c = m \sum_b a_b [m^{-1} k]^b, \\ b = 0, 1, \dots, N-1$$

where a_b is the unknown damping constant and N is the number of dynamic degrees of freedom. Damping constants can be found from the following set of equations

$$(5) \quad \zeta_r = [a_0 / \omega_r + a_1 \omega_r + a_2 \omega_r^3 + \dots + a_{N-1} \omega_r^{2N-3}] / 2, \quad r = 1, 2, \dots, N$$

where ζ_r is the damping ratio and ω_r is the frequency in mode r . For example, to evaluate the coefficients to provide for three specified damping ratios, the equations resulting from eq.(5) would be

$$(6) \quad \begin{bmatrix} \zeta_1 \\ \zeta_2 \\ \zeta_3 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} \omega_1^{-1} & \omega_1 & \omega_1^3 \\ \omega_2^{-1} & \omega_2 & \omega_2^3 \\ \omega_3^{-1} & \omega_3 & \omega_3^3 \end{bmatrix} \begin{bmatrix} a_0 \\ a_1 \\ a_2 \end{bmatrix}$$

While the above procedure for evaluation of damping matrices is sound theoretically, serious numerical difficulties arise that make it impractical when the number of degrees of freedom is large.

Another approach which represents some kind of a direct evaluation of damping matrix leads to the following formula

$$(7) \quad c = m \left[\sum_n (2\zeta_n \omega_n / M_n) \phi_n \phi_n^T \right] m \\ n = 1, 2, \dots, N$$

where M_n is the general mass in mode n . In this equation, the contribution to the damping matrix from each mode is proportional to the mode damping ratio.

It is important to note that the modal damping ratios are the most effective measures of the damping in the system when the analysis is to be carried out by the mode superposition method. Hence the damping matrix will be needed in explicit form primarily when the dynamic response is to be obtained by some other analysis procedure, for example, step-by-step integration.

As it is said in the introductory part of this paper, the aim of the analysis is the derivation of damping matrices for systems with the discrete dampers. Such systems are not imaginary but real and practical systems as those which could be found in structures with flexible

connections [4], [5]. Among them, the timber structures are typical examples. The experiments indicate that substantial part of energy absorption takes place in the flexible connections of these structures, which means that they behave as the systems with the discrete dampers. From the tests on such real systems, one can obtain the modal damping ratios but they can not be used to describe appropriately the damping capacity of a single joint. The damping of such isolated parts should be described in absolute terms, i.e. through the viscose damping coefficients. To achieve this objective, the global damping matrix is formulated in coordinates which represent dynamic degrees of freedom and also the motion of members connected by the discrete dampers. Damping uncoupling is then used to obtain the amount of damping exhibited by each of the discrete dampers.

It should be noted that the modal damping ratios for a system are known either from experiments or from engineering judgement but the damping contribution of each joint which behaves as the discrete damper, is unknown. In the global damping matrix of a system in which the connections are the only dampers, the influence coefficients are actually the coefficients associated with the damping forces in particular connections. If the procedure of deriving uncoupled equations of motion is followed, which also means the satisfaction of orthogonality condition of the damping matrix, a set of equations would be obtained that relate the mode-shapes, the damping coefficients, and the modal damping ratios. From these equations, it is possible to compute either viscous damping coefficient for each of the discrete dampers, or their relative values. It means that the damping uncoupling imposes certain rule on the damping distribution among the discrete dampers. This will be the basis for the approach used further in the analysis.

Under some excitation, the undamped lateral vibrations of a system, for example a frame structure, can be described in a number of displacement components, let say N , which we refer to as the dynamic degrees of freedom. It should be noted that the dynamic degrees of freedom are associated with the displacement coordinates in which significant inertia forces are developed, meaning the lateral displacements in the case of a frame structure.

In general case, the vector of damping forces may be expressed through the damping matrix in the partitioned form

$$(8) \quad f_d = cv = \begin{bmatrix} 0 & 0 & 0 & 0 \dots 0 \dots \\ 0 & c_{r1} & 0 & 0 \dots 0 \dots \\ 0 & 0 & c_{r2} & 0 \dots 0 \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 \dots c_m \dots & v_m \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} \begin{bmatrix} \dot{v}_t \\ \dot{v}_{r1} \\ \dot{v}_{r2} \\ \vdots \\ v_m \end{bmatrix}$$

where the meaning of submatrices is as follows: f_d - the vector of damping forces; c - the system damping matrix; v - the displacement vector; c_r - the damping submatrix for the coordinates in which a discrete damper is located; v_t - the displacement vector for all coordinates without a damper in them; v_r - the

displacement vector with the displacements on both sides of a discrete damper. These displacement vectors and matrices have the following expanded form

$$(9) \quad \begin{aligned} \mathbf{c}_m &= c_n \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \\ \mathbf{v}_t^T &= [v_{11} \ v_{12} \ \dots \ v_{1N}] \\ \mathbf{v}_m &= \begin{bmatrix} v_{m1} \\ v_{m2} \end{bmatrix} \end{aligned}$$

where c_n is the damping coefficient of the dashpot in the joint n .

Performing the undamped free vibration analysis in the extended number of displacement components, the frequencies and the mode-shapes can be obtained. The mode -shape matrix partitioned accordingly would have the following form

$$(10) \quad \Phi = \begin{bmatrix} \phi_l^{(1)} & \phi_l^{(2)} & \dots & \phi_l^{(N)} \\ \phi_{rl}^{(1)} & \phi_{rl}^{(2)} & \dots & \phi_{rl}^{(N)} \\ \phi_{r2}^{(1)} & \phi_{r2}^{(2)} & \dots & \phi_{r2}^{(N)} \\ \vdots & \vdots & \vdots & \vdots \\ \phi_m^{(1)} & \phi_m^{(2)} & \dots & \phi_m^{(N)} \\ \vdots & \vdots & \vdots & \vdots \end{bmatrix}$$

where the superscript means the mode number. The mode-shape subvector, with two components, has the form

$$(11) \quad \phi_m^{(i)} = \begin{bmatrix} \phi_{m1}^{(i)} \\ \phi_{m2}^{(i)} \end{bmatrix}$$

Since the number of displacement coordinates is equal or greater than the number of dynamic degrees of freedom, the mode-shape matrix should not be a square matrix necessarily.

Damping uncoupling is stated with the following relation

$$(12) \quad \Phi^T C \Phi = \begin{bmatrix} 2M_1\xi_1\omega_1 & & & 0 \\ & \ddots & & \\ & & 2M_i\xi_i\omega_i & \\ & & & \ddots \\ 0 & & & 2M_N\xi_N\omega_N \end{bmatrix}$$

Performing detailed matrix multiplication in eq. (12), and also observing the final expression for \mathbf{c}_{rn} in eq.(9), one comes to the following set of equations

$$(13) \quad \left(\sum_n c_n \Delta \phi_m^{(i)} \Delta \phi_m^{(j)} \right)_{i,j=1,2,\dots,N} = \begin{cases} 2M_i\xi_i\omega_i, & i=j \\ 0, & i \neq j \end{cases}$$

in which differences in mode-shape coordinates have the meaning of relative motion on both sides of a discrete damper

(14)

$$\Delta \phi_m = \phi_{m1}^{(i)} - \phi_{m2}^{(i)}$$

In eq.(13), the summation goes over all joints in which there is a discrete damper.

In general case of a dynamic system with N dynamic degrees of freedom, the uncoupling procedure, eq.(13) results in a system of $N(N+1)/2$ equations. It means that we may have just the same number of unknown viscous damping coefficients. In the number of $N(N+1)/2$ unknown parameters some of the modal damping ratios could be included also, but not all of them. At least one of them, preferably the fundamental mode damping ratio, should be known to make the system of equations non-homogenous. The case of a larger number of unknown damping coefficients than the number of available equations will result in relative values between coefficients.

CONCLUSION

In an effort to track the damping sources and their features in some dynamic systems, the present analysis offers a correct analytical procedure for the damping distribution among the discrete dampers.

The experiments demonstrate that substantial part of energy absorption occurs in specified points of some dynamic systems. Examples of such systems are structures, especially the timber structures since they belong to the group of prefabricated systems.

However, the discrete dampers could be found in other fields of engineering and physics also.

Some standard procedures for evaluation of damping matrices are presented in this paper also. The assumption adopted in these procedures is related to unknown sources of damping in a dynamic system. The method developed in the paper offers a correct analytical procedure for evaluation of damping matrices in systems with the discrete dampers. The uncoupling between damping forces is the basis for this approach. The result is not only the damping matrix of the system, but also the amount of energy absorption in each of the discrete dampers.

References

- [1] Clough, R.W., Penzien, J. 1975. Dynamics of Structures, McGraw-Hill.
- [2] Caughey, T.K. 1960. Classical Normal Modes in Damped Linear Systems, Jnl. Appl. Mech. 27.
- [3] Wilson, E.I., Penzien, J. 1972. Evaluation of Orthogonal Damping Matrices, International Journal for Numerical Methods in Eng., Vol 4.
- [4] Basic, D., Mesic,E., Stojic, D. 1995. Flexible Joint Connections in Structure: Methods of Computation and Effects, Facta Universitatis, Series Arch. And Civil. Eng., Vol.1, No1.
- [5] Basic, D. et al. 1996. Flexible Connections as the Dampers in Timber Frame Structures, International Wood Eng. Conference, New Orleans, Louisiana.

Rezime**O ORTOGONALNIM MATRICAMA PRIGUŠENJA**

BAŠIĆ D., STOJIĆ D., MEŠIĆ E.
Univerzitet u Prištini

Cilj ovoga rada je izvodjenje matrice prigušenja za sisteme sa diskretnim prigušivačima. Kod mnogih dinamičkih sistema je testovima utvrđeno da se značajan deo energije apsorbuje u odredjenim tačkama ili lokacijama sistema. Eksperimentima se mogu da dobiju modalni koeficijenti relativnog prigušenja ali oni ne mogu da pokažu koliko se energije apsorbuje u svakom od diskretnih prigušivača. Prigušenje u takvim posebnim delovima sistema treba da bude prikazano

preko apsolutnih pokazatelja, tj. preko koeficijenata viskoznog prigušenja. Da bi se postigao ovaj cilj, globalna matrica prigušenja se formuliše preko koordinata koje predstavljaju pomeranja sistema na krajevima svakog prigušivača. Postupak nevezivanja sila prigušenja se ovde koristi da bi se dobili koeficijenti viskoznog prigušenja u prigušivačima. Ovakvom analizom se došlo do jednačina kojima se proračunavaju ovi koeficijenti. U radu su prikazane i standardne metode za formiranje ortogonalnih matrica prigušenja. Formiranje ortogonalnih matrica prigušenja, sem značaja u fizici i inženjerstvu, značajno je i sa matematičkog aspekta.

Received: November, 1998.

Accepted: December, 1998.

A Study of the Initial Stages of the Electrochemical Deposition of Thallium on Copper - PART I.

The Linear Sweep Voltammetry Behaviour of polycrystalline and (111) oriented Copper Single Crystal Electrode

JOVIĆEVIĆ¹ N. Jovan, BEWICK Alan

Chemistry Department, Southampton University, UK, SO9 5NH

¹Present address: Chemistry Department, Faculty of Natural Sciences & Mathematics, University of Prishtina, 38000 Prishtina, Yugoslavia

ABSTRACT

The underpotential deposition and dissolution of thallium onto carefully chemically polished polycrystalline and single crystal copper (111) electrodes from acetate, sulfate and perchlorate solutions have been investigated using Linear Sweep Voltammetry (L.S.V.).

The voltammetric behaviour of the polycrystalline copper electrodes was shown to be a composite of the various single crystal structures in its surface.

Voltammetry results on Cu(111) single crystal electrode showed thallium forming two underpotential monolayers with close-packed crystalline structure. The assumption that the first closest-packed epitaxial part of the first thallium (more anodic) monolayer was formed by 2D first order phase formation is supported by: ex-

tremely small half height deposition peak widths, ΔE ; deposition peak to dissolution peak potential separation, ΔE_{A-K} ; Frumkin adsorption isotherm factor $g = 3.85$, very close to 4; and the thallium monolayers peak potential dependence on thallium concentration. The full monolayer appears to be completed by higher order phase transformation.

It appears that the deposition of the second thallium monolayer on Cu(111) proceeds similarly to the first layer, but the onset of bulk overpotential deposition does not allow further detailed analysis.

A model of crystalline thallium closest-packed epitaxial monolayer on Cu(111) surface is proposed.

Key words: Underpotential deposition, Linear sweep voltammetry, Cu, Tl, Phase formation, Single crystal

INTRODUCTION

The knowledge gathered about metal deposition so far strongly suggests that the deposition of a metal on a similar substrate and on a dissimilar substrate, although having many features in common, does exhibit important differences.

Phase formation and electocrystallization during deposition processes include incorporation of adatoms (adions) into already existing crystal lattice, or their gathering together to form nuclei of a new crystal lattice¹⁻¹².

In addition, despite extensive studies of metal underpotential deposition there have been some important problems still unresolved. These related principally to the nature of the monolayer (adsorbed or crystalline), the interpretation of the linear sweep voltammogram peaks, phase changes within the monolayer, the kinetics of the crystalline monolayer formation, if any, and the relevance of the UPD monolayer to the overpotential deposition process.

The system selected for the study was thallium on copper polycrystals and single crystals. The underpotential as well as overpotential deposition and their possible mutual interdependence were investigated. The

substrate posses high hydrogen evolution overvoltage and therefore deposition of thallium is not complicated by hydrogen co-adsorption processes.

The techniques employed were linear sweep voltammetry and potential step.

MATERIALS AND METHODS

The experimental work described in this paper was done using linear sweep voltammetry (L.S.V.) technique.

All potential programming of the working electrode was supplied either from a potentiostat ("Hi-Tek Instruments" model DT2101, or two "Chemical Electronics" models V150/1.5A, TR70/2A) in conjunction with a "Chemical Electronics" waveform generator (type R.B.1). The waveform generator provided a ramp type voltage output for L.S.V..

The cell currents were recorded as voltages on an XY recorder (types "Bryans 26000" or "Hewlett Packard 7015A"). To observe and record the current-time transients and other functions too rapid to be followed on an XY or Yt recorder, oscilloscopes ("Tektronix" 547 or 5030) were employed.

The cell used for the L.S.V. experiments is presented in Fig. 1.. The cell was made entirely of glass. The working electrode, C, and Luggin capillary, L, were positioned in syringe barrels to enable adjustment to give the best positions and mutual distances of the two. The counter electrode, A, was either a platinum disc or a platinum mesh disc 1.5 cm² in area, positioned parallel to the working electrode.

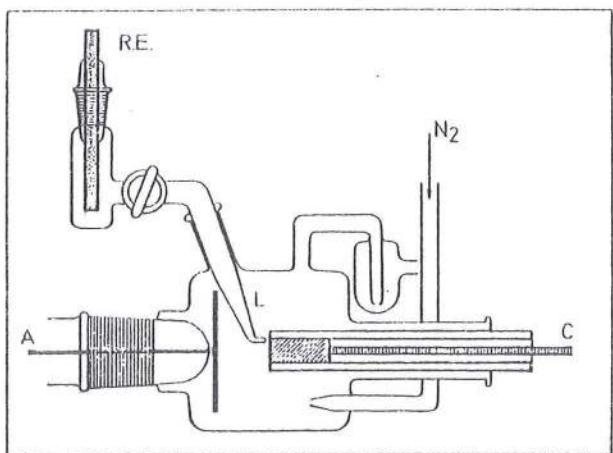


Figure 1. The cell used for most of the L.S.V. and potential step experiments

Working electrodes were small cylinders of polycrystalline ("Koch - Light Laboratories", 99.999%) or single crystal copper ("Metal Research Ltd.", 99.999%) 0.8cm in diameter. These were sealed into Kel-F rod such that only the top surface of the metal cylinder was exposed to the solution. Great care was taken to ensure that no leakage occurred around the side of the metal crystal. This was achieved by cooling the cylinder of copper in liquid nitrogen before mounting in the hollow Kel-F rod (drilled for a tight fit at room temperature), which had been placed in boiling water so that insertion of the metal and contraction of the plastic housing ensured a very tight fit. Electrical contact was made via brass soldered to the copper cylinder. The reference electrodes housed at the end of the Luggin capillary were either a saturated calomel (S.C.E. "Radiometer K401") or lead wire ("Koch - Light Laboratories Ltd.", 99.999%) sealed into the glass holder.

Prior to use all glass-ware was soaked in a mixture containing equal volumes of concentrated nitric and sulfuric acids to remove any possible traces of grease, then it was rinsed thoroughly in tap water, singly distilled and finally triply distilled water. The latter was prepared by slow distillation from a weakly alkaline solution of KMnO₄ and then from solution containing a trace amount of ortho-H₃PO₄.

All solutions were made up from Analar grade chemicals ("B.D.H. Chemicals Ltd." and "Hopkin and Williams Company", without further purification) in triply distilled water. Prior to experiment, solutions were deaerated inside the cell by purging with a stream of purified oxygen-free nitrogen, for about 30-35 minutes. Nitrogen was purified by purging it through a solution of ammonia metavanadate, hydrochloric acid and distilled water lying on top of 25g, of amalgamated zinc¹³.

The importance of electrode surface preparation cannot be overstressed in connection with the metal deposition work. The surface preparation procedures finally adopted for copper single crystal electrodes were result of investigating a number of other methods. Criteria used to judge the success of each method was based on the best reproducibility of experimental data and the clearest delineation of various features on the voltammetric characteristics. The polishing process consisted of two stages, the first mechanical and the second chemical.

Firstly, the electrodes were polished on selvyt cloths ("Buchler Ltd.") impregnated with alumina ("Buchler Ltd." 5.10⁻⁴cm and 3.10⁻⁴cm grade, and "Banner scientific Ltd." 1.10⁻⁵cm and 3.10⁻⁵cm grade). Initially the largest grade was used and then progressively smaller ones down to the smallest, until the electrode had a mirror-like appearance free from scratches or blemishes. These mechanical polishing steps were always performed manually rather than on a polishing machine, which was less convenient to use. Before each experiment copper single crystal electrodes were chemically polished using a modified version of a process described elsewhere m¹⁴.

The three copper single crystals (111), (110) and (100) had to be chemically polished under somewhat different conditions if the result was to be up to the standard. The polishing mixture containing 33vol.% each of concentrated Analar grade HNO₃, glacial acetic acid and orthophosphoric acid, was common to all copper electrodes used. The difference in treatment between polycrystalline and each of the copper single crystals began when the temperature of the polishing agents and the time of immersion was to be decided.

The (111) oriented single crystal was immersed for 3 seconds in the acid mixture heated to over 75°C while stirring, left without stirring for another 3 seconds, then stirred and again left still for 3 seconds, finally the solution was stirred, the electrode removed and washed under a strong stream of tap water and eventually in triply distilled water. The whole procedure was repeated a second time. Then the electrode would be immersed in 30 vol.% solution of orthophosphoric acid and stirred for 10 seconds, washed in tap water and finally with plenty of triply distilled water. If gas evolution occurred on the electrode immersed in the polishing mixture earlier than 3 seconds, then the time which the electrode spent standing still was made shorter.

These polishing processes required a considerable amount of practice before consistent results could be obtained.

Examinations of the polished electrode surfaces under microscope and with X-ray emission spectroscopy revealed no contaminating elements except very minute particles of alumina, but these were very few in number (on the sample investigated one particle of alumina was found in an area of about 0.25cm²).

The amount of the copper dissolved in this chemical polishing process was relatively small. A single crystal polished several hundred times would lose 35% of its volume.

The investigation of a particular electrode solution combination always started with linear sweep voltammetry. In some cases it constituted the whole experiment.

The voltammogram itself was a direct indication of the nature of the electrode surface and consequently could be used to assess the degree to which the chemical polishing had been successful in producing a well defined crystal plane (in the case of the single crystal of course). For any particular system, repeated linear sweep experiments were performed before any additional measurement were made in order to establish an arbiter to which all future voltammetry could be referred. Potential step measurements were made only if the linear sweep voltammetry was identical or very close to the accepted arbitrary standard, which was the clearest delineation of the voltammetric features. The procedure described here for L.S.V. is that which enabled a given solution/electrode combination to be used for a whole day's experiments without any deterioration in the result over this period.

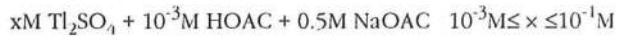
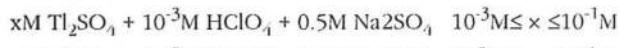
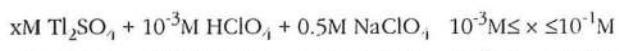
Firstly the cell complete with working electrode (not yet freshly chemically polished) was rinsed thoroughly in tap, and triply distilled water. Then the cell was rinsed with the solution being used and finally filled with it. This was followed by deaeration with a rapid stream of nitrogen (scrubbed by a vanadous ion mixture) for about 35 minutes. During this process the working electrode was polarized at a potential somewhat positive to that where U.P.D. began. After the deaeration period, the working electrode was removed from the cell and chemically (or only mechanically) polished as described earlier and after thorough rinsing was placed back in the cell. Gas purging was continued in the cell sealed with a syringe piston while the chemical polishing was performed. It was resumed for an ad-

ditional 5-10 minutes after the freshly polished working electrode had been put into the cell. The process of polarizing the electrode during the gas purging acted as a mild pre-electrolysis method and impurities were removed from the solution. That this was the case could be seen by carrying out voltammetry with the electrode at the end of the degassing period without chemical polishing, when markedly inferior results were obtained. Before the actual L.S.V. was recorded the cell was sealed off from the air by tight rubber covers being placed on the gas inlet and outlet.

Voltammetric experiments were carried out in the normal way; the potential being cycled continuously and sweeps recorded when necessary at a variety of sweep speeds.

RESULTS

The UPD of thallium was carried out from solutions containing different anions and different thallium concentrations:



For the reasons given earlier^{15,16}, it was not expected that deposition onto polycrystalline surface would be of much interest and this was confirmed by the voltammogram obtained, Fig. 2. Two distinct sets of cathodic and anodic peaks can be easily recognized, but because of their complex shape and because they are spread out over a relatively wide potential range (250mV in the case of K_1), any reliable conclusions about the nature and mechanism of the processes involved, or the character of deposit, were impossible.

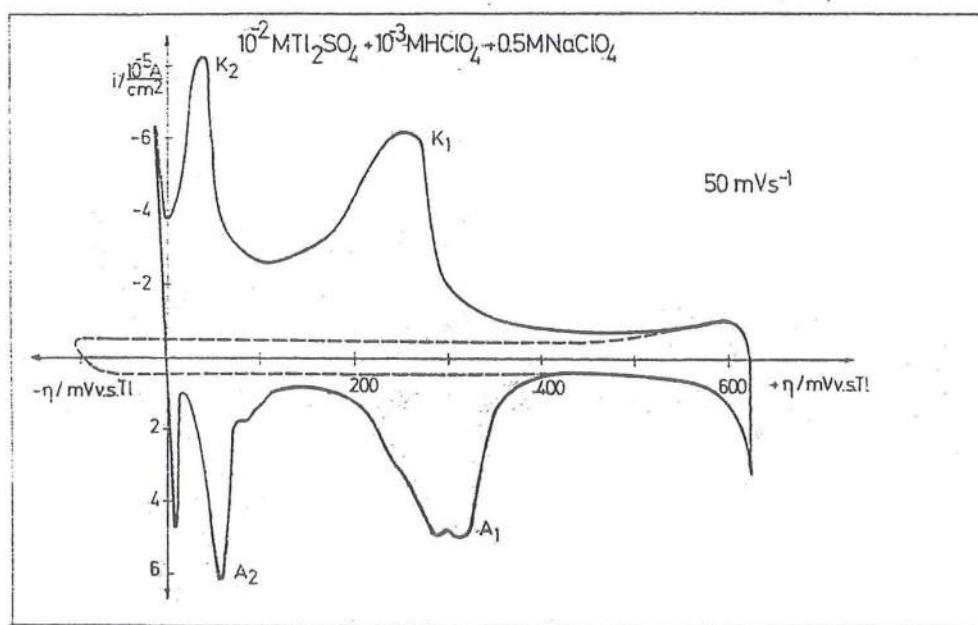


Figure 2. L.S.V. for chemically polished copper electrode in thallium free solution (---); and during thallium underpotential deposition (UPD).

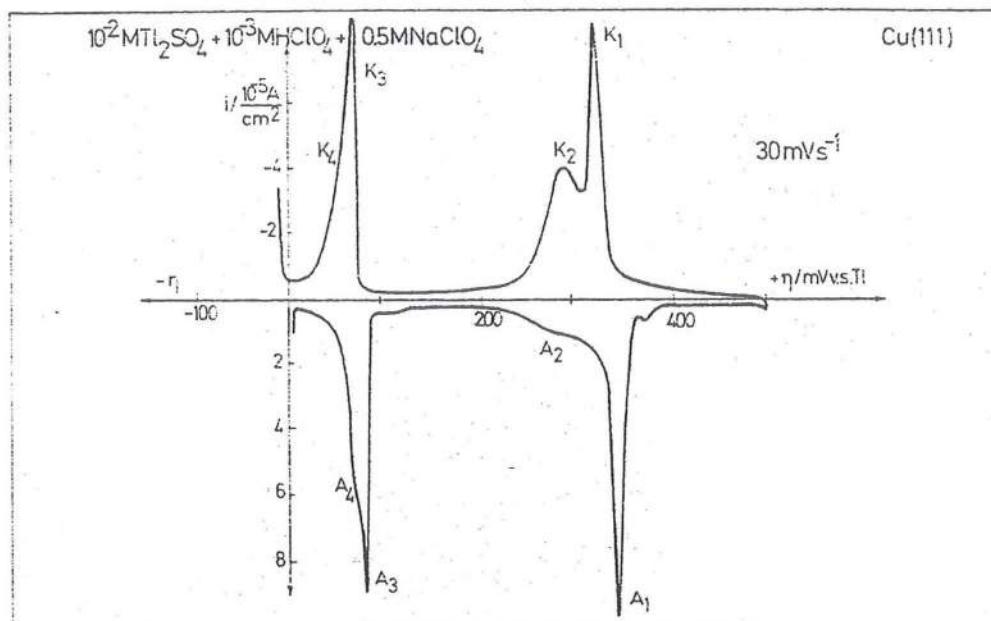


Figure 3.a The L.S.V. behaviour of the Cu (111) oriented electrode surface during thallium UPD.

The voltammograms showing thallium UPD on Cu(111) surface from the three solutions used (see above) are shown in Fig. 3.a., b. and c. It appears that the essential characteristics of these remain the same in all solutions, although the exact peak potential values and their shape were to a certain extent dependent on the sweep speed and on whether the anion used in the particular system undergoes significant specific adsorption, Table.1

DISCUSSION

Linear sweep voltammograms obtained for thallium UPD on polycrystalline copper registered only two peak potentials ($E_{K1} = +242 \text{mV}$ and $E_{K2} = +40 \text{mV}$ vs. Ti/Ti^+) and the charges associated with the two broad waves. The charge encompassed by the first "peak" was $260 \cdot 10^{-6} \text{AScm}^{-2}$, which is one and a half times more than that needed for a close-packed thallium

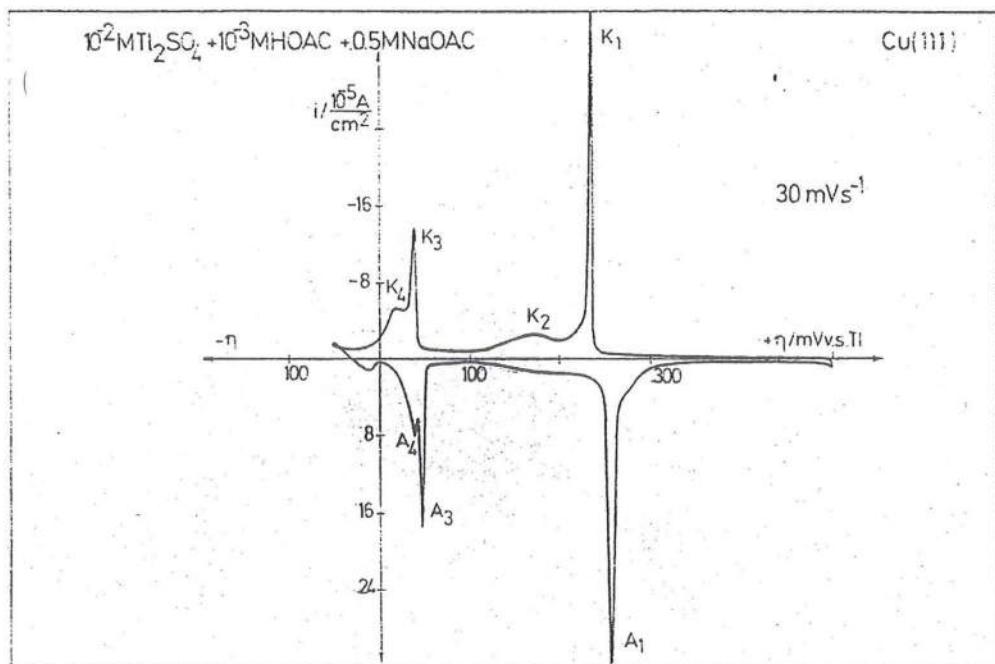


Figure 3.b The L.S.V. behaviour of the Cu (111) oriented electrode surface during thallium UPD.

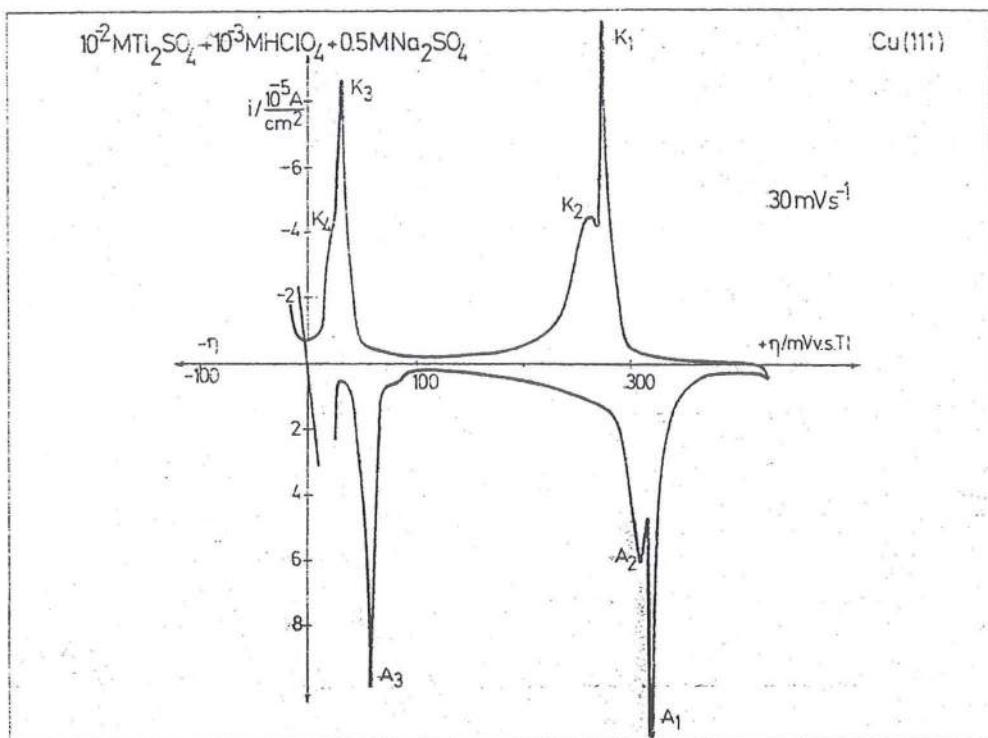


Figure 3.c The L.S.V. behaviour of the Cu (111) oriented electrode surface during thallium UPD.

layer ($160 \cdot 10^{-6}$ As cm $^{-2}$). The total charge under both cathodic peaks anodic to the reversible Tl/Tl $^{+}$ potential is two and a half times greater ($408 \cdot 10^{-6}$ As cm $^{-2}$) than that needed for a close-packed layer.

Since L.S.V. performed in the absence of thallium showed only current flowing due to double layer charging (----- in Fig. 2.), it appears that thallium UPD on copper surface proceeds in two layers.

The complexity of the peaks is most probably due to thallium deposition onto differently oriented copper grains, producing different monolayer structures dependent on the crystallographic orientation of the grains.

In the case of thallium UPD onto Cu(111) surface linear sweep voltammetry reveals two separate sets of peaks, more than 130mV apart.

The first set situated at more anodic potentials, consisted of two peaks, K₁ and K₂. K₁ was generally very sharp (the sharpest recorded having a half peak

width $\Delta E = 3.15$ mV at the sweep speed $v = 10$ mVs $^{-1}$, Fig. 4., and it was markedly sharper than the second peak K₂. The peak width depended on the sweep speed, becoming smaller with decreasing sweep speed, Fig. 5.

The interaction parameter, g, (Frumkin isotherm) calculated^{16,17} from the experimentally obtained half peak width $\Delta E = 3.15$ mV, assuming a fast adsorption process, was $g = 3.85$. On the basis of such a model this would indicate strong lateral interaction among the thallium species deposited at the potentials belonging to the first peak K₁. The charge associated with this peak was approximately $130 \cdot 10^{-6}$ As cm $^{-2}$.

The second peak, K₂, usually started at the potentials more positive than the end potential of the first peak. The charge under this peak was $60 \cdot 10^{-6}$ As cm $^{-2}$.

The second set of peaks presented a problem. The two peaks were merged to such an extent that only their combined characteristics could be obtained. The charge was $120 \cdot 10^{-6}$ As cm $^{-2}$, but even this cannot be

Table 1. Average UPD peak values for 10^{-2} M Tl solutions and $v = 30$ mVs $^{-1}$

Surface orientation	Anion	K ₁ mV vs. Tl	K ₂ mV vs. Tl	K ₃ mV vs. Tl	K ₄ mV vs. Tl	Calc. close-packed layer 10^{-6} As cm $^{-2}$	Calc. epitax layer 10^{-6} As cm $^{-2}$	Measured charge K ₁ 10^{-6} As cm $^{-2}$	Measured charge K ₁ +K ₂ 10^{-6} As cm $^{-2}$	Measured charge K ₃ +K ₄ 10^{-6} As cm $^{-2}$
(111)	ClO ₄ ⁻	+296	+261	+51	+31	160	106	130 ± 5	193 ± 3	110 ± 6
(111)	SO ₄ ²⁻	+277	+262	+55	+31	160	106	128 ± 5	191 ± 5	120 ± 5
(111)	OAc ⁻	+241	+185	+56	+40	160	106	123 ± 3	190 ± 5	122 ± 7

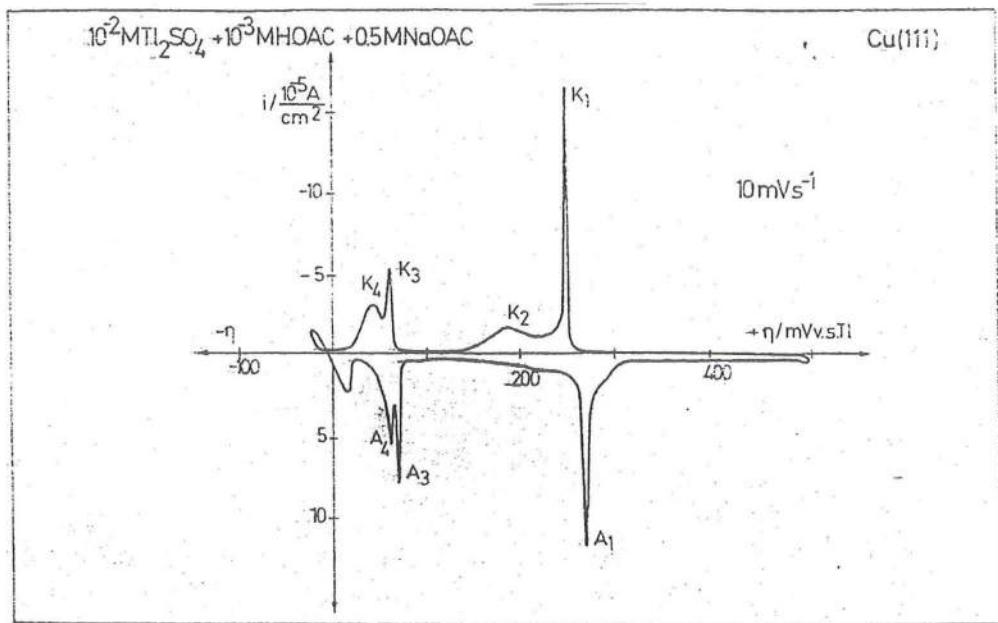


Figure 4. The L.S.V. behaviour of Cu (111) electrode during thallium UPD at lower sweep speeds.

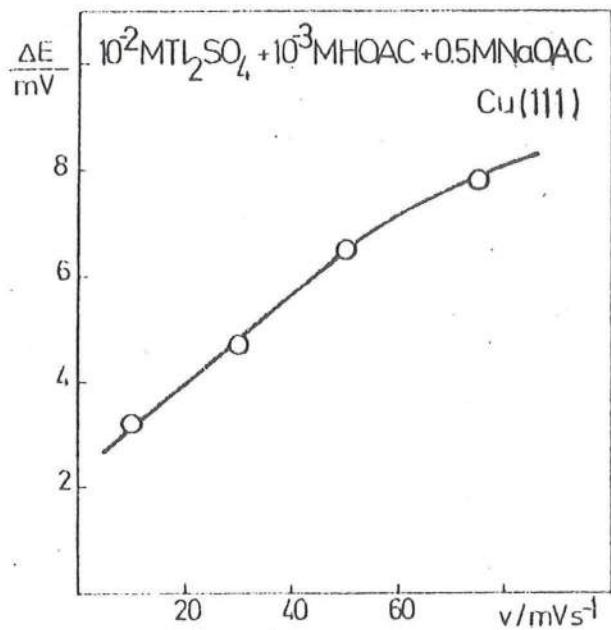


Figure 5. The dependence of the half peak width (ΔE_{K_1}) on the sweep speed.

taken as the total value because the current of the second peak had not fallen to zero before the onset of thallium bulk deposition.

The peak potentials were dependent on the sweep speed, Fig. 6, and the thallium concentration in the solution used, Fig. 7.

The sharpness of the first peak, K_1 , by analogy with the corresponding results for lead^{16,18}, suggests that thallium onto Cu(111) surfaces is also underpotentially deposited in a first order phase formation process.

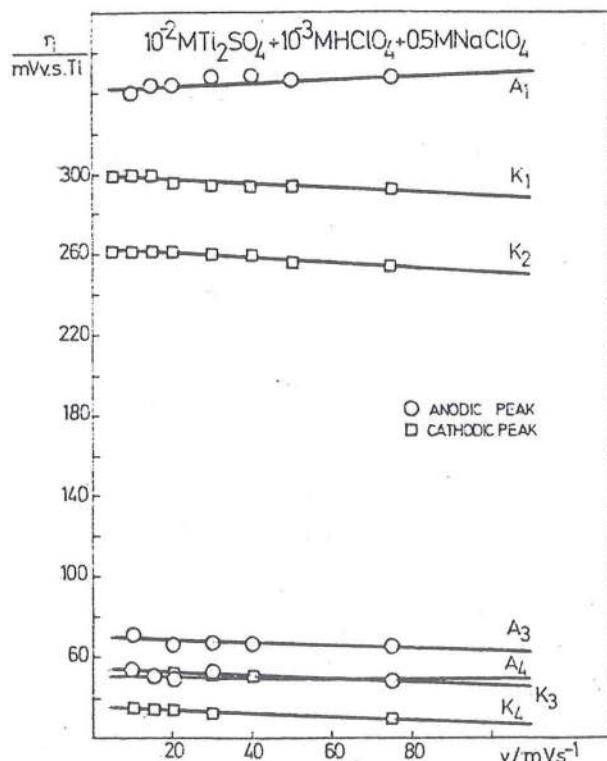


Figure 6. Dependence of the peak potential on the sweep speed.

The charge associated with this peak ($130 \cdot 10^{-6} \text{ Ascm}^{-2}$) is significantly lower than that needed for formation of close-packed thallium layer ($160 \cdot 10^{-6} \text{ Ascm}^{-2}$)¹⁹. It is however in good agreement with that needed for the deposition of the closest-packed epitaxial thallium monolayer ($106 \cdot 10^{-6} \text{ Ascm}^{-2}$), if as before^{16,18} a roughness factor of ≈ 1.1 is taken into account, Fig. 8.

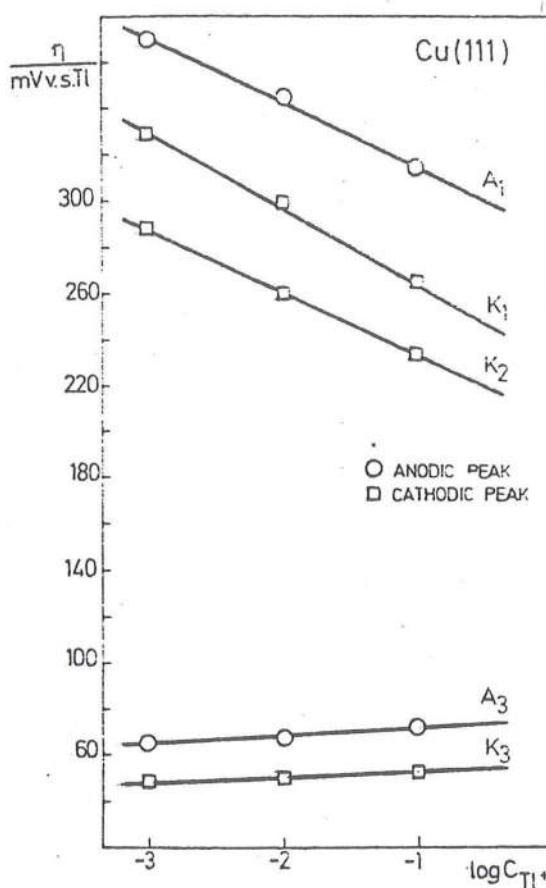


Figure 7. Dependence of the peak potential on thallium concentration.

It is interesting to find, however, that when the charges under the first peak, K₁, and the second peak, K₂, were added together, the sum of 190-6Ascm-2 was very close to the charge needed for a close packed thallium layer (again taking a roughness factor into account). This suggests that the epitaxial layer might be transforming into a close-packed structure at the more negative potentials.

The anodic stripping process, A₁ and A₂, were not symmetrically placed on the potential axis towards K₁ and K₂. The peak potential separation $\Delta E_{A_1-K_1}$ was ≈ 35 mV and $\Delta E_{A_2-K_2}$ was ≈ 40 mV at sweep speed 30mVs^{-1} and both were practically independent of the sweep speed. Anodic peak A₂ contained less charge than K₂, the major part of the stripping process occurring in the large sharp peak A₁.

It appears that unlike the equivalent structure for lead¹⁸ on the same substrate, the thallium closest-packed epitaxial layer, Fig.8., is not the most energetically stable structure at potentials closer to the reversible potential. The difference in the atomic radii of lead and thallium ($r_{Pb} = 1.75 \cdot 10^{-8}\text{cm}$, $r_{Tl} = 1.70 \cdot 10^{-8}\text{cm}$) means that the thallium atoms are less closely packed than the lead atoms in the same epitaxial structure. An additional factor favoring the transition to the close-packed nonepitaxial layer is lower electronegativity of thallium compared to lead²⁰⁻²³. This being the case it is not surprising to find the stripping process for the two structures being reflected in a shoulder (A₂) and a well pronounced peak A₁, where the latter accounts for the dissolution of most of the close-packed layer and carries more than 90% of its total charge.

It should be noted that the apparent interaction parameter, g , obtained from a given half peak width

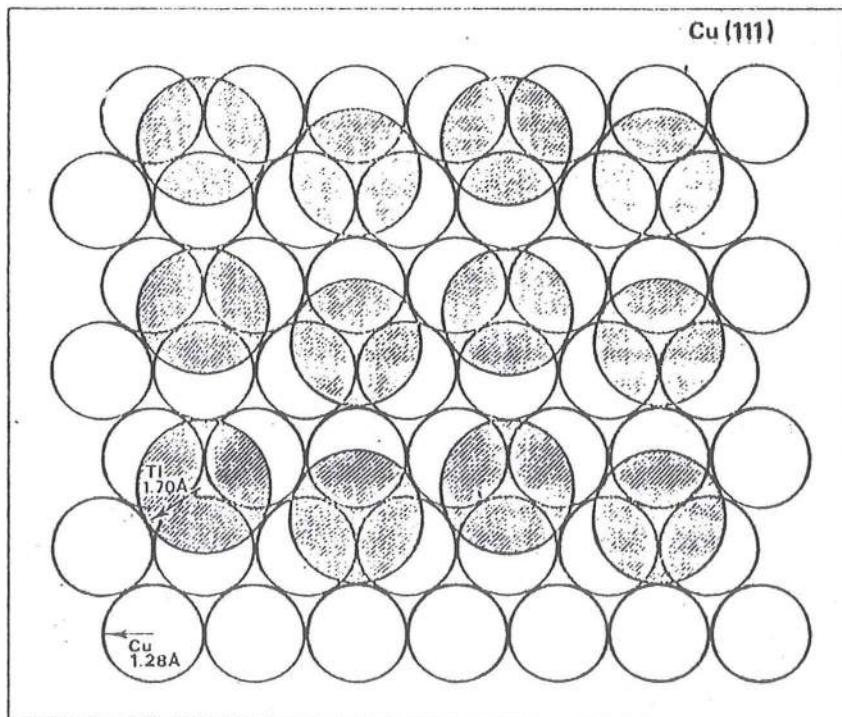


Figure 8. The structure of the epitaxial closest-packed thallium monolayer on Cu (111).

depends upon the valency, z , of the metal ion¹⁷ and the same peak width for lead and thallium corresponds to a large value of g for latter. The apparent value of g for thallium underpotential deposition, 3.85, is very close indeed to the critical value of 4. In such a case it should be remembered that a nucleative phase formation process would be unlikely to give a sufficiently sharp peak to yield an apparent g value of 4¹⁸. This is clear from the analysis of Rangarajan²⁴ which takes account of the slow kinetics of crystal growth. Therefore, whenever a large but apparently sub-critical value for g is found, it is necessary to consider the possibility of a first order phase transition.

It must be concluded, therefore, that K_1 represents the formation of the closest-packed epitaxial layer, Fig. 8., and, by analogy with lead under the same circumstances, it is formed by a 2D nucleative mechanism. The characteristics of the second peak, K_2 , are more in keeping with a higher order phase transformation of this epitaxial structure into the close-packed thallium crystal plane.

The second set of voltammetric peaks is more difficult to characterize. Their charge ($120 \cdot 10^{-6}$ Ascm⁻²), although incomplete because of the onset of bulk deposition indicates that a full close-packed layer is not achieved in the underpotential region. The peak potential separation, EA-K, does not change significantly with sweep speed, Fig. 6., and usually was ≈ 20 mV. The first peak K_3 is very sharp, while the second, K_4 , is less so. It appears that the deposition of the second thallium monolayer on Cu(111) proceeds similarly to the first layer, but the onset of bulk deposition does not allow further detailed analysis.

CONCLUSIONS

Linear sweep voltammograms obtained for thallium UPD on polycrystalline copper registered only two peak potentials ($EK_1 = +242$ mV and $EK_2 = +40$ mV vs. Tl/Tl⁺) and the charges associated with the two broad waves. Since L.S.V. performed in the absence of thallium showed only current flowing due to double layer charging, it appears that thallium UPD on copper surface proceeds in two layers. The complexity of the peaks is most probably due to thallium deposition onto differently oriented copper grains, producing different monolayer structures dependent on the crystallographic orientation of the grains.

In the case of thallium UPD onto Cu(111) surface linear sweep voltammetry reveals two separate sets of peaks, more than 130mV apart. The peak potentials were dependent on the sweep speed, and the thallium concentration in the solution used.

The first set situated at more anodic potentials, consisted of two peaks, K_1 and K_2 . K_1 was generally very sharp and it was markedly sharper than the second peak K_2 . The peak width depended on the sweep speed, becoming smaller with decreasing sweep speed. The interaction parameter, g , (Frumkin isotherm) calculated from the experimentally obtained half peak width $\Delta E = 3.15$ mV, assuming a fast adsorption

process, was $g = 3.85$. The second peak, K_2 , usually started at the potentials more positive than the end potential of the first peak.

The charge associated with the first peak is in good agreement with that needed for the deposition of the closest-packed epitaxial thallium monolayer, $106 \cdot 10^{-6}$ Ascm⁻², if a roughness factor of ≈ 1.1 is taken into account. When the charges under the first peak, K_1 , and the second peak, K_2 , were added together, the sum of $190 \cdot 10^{-6}$ Ascm⁻² was very close to the charge needed for a close packed thallium layer (again taking a roughness factor into account).

The second set of peaks presented a problem. The two peaks were merged to such an extent that only their combined characteristics could be obtained. The charge was measured, but even this cannot be taken as the total value because the current of the second peak had not fallen to zero before the onset of thallium bulk deposition.

It must be concluded, therefore, that K_1 represents the formation of the closest-packed epitaxial layer, and, by analogy with lead under the same circumstances, it is formed by a 2D nucleative mechanism. The characteristics of the second peak, K_2 , are more in keeping with a higher order phase transformation of this epitaxial structure into the close-packed thallium crystal plane.

It appears that the deposition of the second thallium monolayer on Cu(111) proceeds similarly to the first layer, but the onset of bulk deposition does not allow further detailed analysis.

Acknowledgment

J.Jovićević wishes to express his gratitude to The Royal Society of London and The University of Southampton for the financial support, which made his work at the University of Southampton possible.

REFERENCES

- 1.- Faraday, M.: Phil. Trans. Roy. Soc. London, 124 (1834) 77.
- 2.- Raub, E., Muller, K.: "Fundamentals of metal deposition", Elsevier Publishing Co., Amsterdam-New York (1967).
- 3.- Bockris, J.O'M., Despic, A.R.: Vol IX-B, Ch.7, p.p.611, "Physical Chemistry", ed. Eyring, Henderson, Jost, Academic Press , London-New York (1970).
- 4.- Conway, B.E., Bockris, J.O'M.: Electrochim. Acta, 3, (1966) 340.
- 5.- Budevski, E.: Electrochimica Metallorum, 2 (1966) 131.
- 6.- Erdey-Gruz, T.: "Kinetics of electrode processes", Adam Higher Ltd., London (1972).
- 7.- Bockris, J.O'M., Reddy, K.N.: Vol.2, "Modern electrochemistry", Plenum Press, Rosetta edition, New York (1970).
- 8.- Markus, R.A.: Electrochim. Acta, 13 (1968) 995.
- 9.- Fleischmann, M., Thirsk, H.R.: Electrochim. Acta, 2 (1960) 22, Electrochim. Acta, 9 (1964) 757.

- 10.- Garner, W.E.: Disc. Faraday Soc., 5 (1949)
- 11.- Burton, W.K., Cabrera, N.: Disc. Faraday Soc., 5 (1949).
- 12.- Bransom, S.H., Dunning, W.J., Millard, B.: Disc. Faraday Soc., 5 (1949)
- 13.- Meites, L.: "Polarographic Techniques", 2nd edition, Interscience, New York (1965).
- 14.- Pinner, R., Electroplating, October and November (1953) 360, 401.
- 15.- Jovićević, J.N., Bewick, A., Univ. Thought, Vol.IV(2) (1997) 29, Pristina
- 16.- Jovićević, J.N., Bewick, A., Univ. Thought, Vol.IV(2) (1997) 39, Pristina
- Thomas, B., Ph.D. Thesis, University of southampton 1976.
- 17.- Thomas, B., Bewick, A., J.Electroanal. Chem., 70 (1976) 239.
- 18.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina
- 19.- Thomas, B., Ph.D. Thesis, University of southampton 1976.
- 20.- Gerischer, H., Kolb, D.M., Przasnyski, M., Surface Science, 43 (1974) 662.
- 21.- Kolb, D.M., Przasnyski, M., Gerischer, H., J. Electroanal. Chem., 44 (1973).
- 22.- Vijh, A.K., Surface Science, 46 (1974) 282.
- 23.- Vijh, A.K., Surface Science, 47 (1975) 713.
- 24.- Rangarajan, S.K., Trans. Faraday Symp. No.12, Southampton, (1977).

REZIME

STUDIJA POČETNOG STADIJUMA ELEKTROTAЛОŽENJA TALIJUMA NA BAKRU - I DIO
PONAŠANJE BAKARNE POLIKRISTALNE ELEKTRODE I ELEKTRODE KRISTALOGRAFSKE ORIJENTACIJE (111) PRI LINEARNOJ CIKLIČKOJ PROMJENI POTENCIJALA

JOVIĆEVIC¹ N. Jovan, BEWICK Alan
 Chemistry Department, Southampton University,
 UK, SO9 5NH

¹Sadašnja adresa: Odsek za hemiju, PMF, Univerzitet u Prištini, 38000 Priština, Jugoslavija.

Ovo je prvi iz serije radova u kojima se iznose rezultati istraživanja početnih stadijuma elektrotaloženja talijuma (iz acetatnih, sulfatnih i perhloratnih rastvora) na polikristalnom i monokristalnom bakru.

Rad predstavlja rezultate dobijene linearnom cikličnom promjenom potencijala (L.S.V.) bakarne polikristalne i monokristalne elektrode površinske orijentacije (111) u području potencijala pozitivnijih od reverzibilnog potencijala talijuma u dатој sredini.

Još jednom se uvjerljivo pokazalo da je pažljivo i uspješno poliranje površine radne elektrode od najvećeg značaja pri ispitivanjima područja potencijala pozitivnijih od reverzibilnog potencijala taloženja/rastvaranja ispitivanog metalu, ukoliko se žele dobiti pouzdani kvantitativni i kvalitativni podaci.

Polikristalna bakarna površina, pri linearnoj cikličnoj promjeni potencijala (L.S.V.) u području poten-

cijala pozitivnijih od reverzibilnog potencijala talijuma (UPD), daje votamogram koji predstavlja zbir karakteristika površina različitih kristalografski orijentisanih zrna, koje su pažljivim hemijskim poliranjem otkrivene i izložene elektrotaloženju olova (ustanovljen faktor rapavosti bararne poršine je bio je 1.3). Dobijeni voltamogrami pokazuju dva široka katodna ($E_{K_1} = +242\text{mV}$ i $E_{K_2} = +40\text{mV}$ vs. Tl/Tl^+) i dva odgovarajuća anodna talasa. Kako ciklička voltametrija u rastvorima bez prisustva talijuma pokazuje samo struje koje su rezultat nabijanja dvojnog sloja, preostaje da se zaključi da se taloženje talijuma na bakru pri potencijalima pozitivnijim od reverzibilnog potencijala odvija depozicijom dva monosloja.

Međutim, elektrotaloženja talijuma na bakarne monokristalne površine kristalografske orijentacije (111) tehnikom cikličke voltametrije otkriva dva odvojena para katodnih strujnih talasa međusobno udaljenih više od 130mV. Potencijali vrhova tih talasa zavisni su od brzine promjene potencijala i od koncentracije talijuma u upotrebljenom elektrolitu.

Prvi par (javlja se pri anodnjem potencijalu) sastoji se od veoma oštrog talasa K_1 i manje oštrog talasa K_2 . Širina poluvrha tih talasa opada sa opadanjem brzine promjene potencijala. Interakcioni parametar, g, Frumkinove izoterme izračunat na osnovu eksperimentalno dobijene širine poluvrise prvog talasa K_1 ($\Delta E = 3.15\text{mV}$) iznosi $g = 3.85$. Drugi talas, K_2 , započinje na potencijalima pozitivnijim od potencijala na kome se završava prvi talas, K_1 .

Količina naelektrisanja ograničena prvim talasom, K_1 , u saglasnosti je sa naelektrisanjem potrebnim da bi se formirao najgušće pakovani epitaksijalni monosloj talijuma na Cu(111) (čiji model je predložen) uvezši faktor rapavosti podloge od 1.1. Kada se naelektrisanje pod K_1 i K_2 talasima sabere, dobija se vrijednost veoma bliska naelektrisanju potrebnom da se formira gusto pakovani sloj talijuma, naravno opet uz faktor rapavosti podloge od 1.1.

Drugi par katodnih talasa je međusobno toliko stopljen da je moguće ozbiljno analizirati samo njihove skupne karakteristike. Čak i mjereno naelektrisanje koje pokrivaju ne može se uzeti kao konačna vrijednost, jer struja drugog talasa K_2 ne pada na nulu pri upotrebljenim brzinama promjene potencijala prije nego što počne elektrotaloženje talijuma uz katodne prenapetosti.

Katodni talas K_1 predstavlja formiranje najgušće pakovanog epitaksijalnog sloja i po analogiji sa olovom na istoj podlozi pod istim uslovima putem dvodimenzionog nukleacionog mehanizma. Karakteristike drugog talasa K_2 su u saglasnosti sa mehanizmima fazne transformacije višeg reda prelaska epitaksijalne strukture monosloja u gustopakovan kristalni monosloj talijuma.

Elektrotaloženje drugog talijumovog monosloja na Cu(111) odigrava se mehanizmom veoma sličnim mehanizmu kojim se odigrava formiranje prvog monosloja, ali započinjanje taloženja pri katodnim prenapetostima onemogućava dalju detaljniju analizu.

Received: March, 1998.

Accepted: April, 1998.



Study of the Initial Stages of the Electrochemical Deposition of Thallium on Copper - PART II. The Linear Sweep Voltammetry Behaviour of (110) oriented Copper Single Crystal Electrode

OVIĆEVIĆ¹ N. Jovan, BEWICK Alan

Chemistry Department, Southampton University, UK, SO9 5NH

Present address: Chemistry Department, Faculty of Natural Sciences & Mathematics, University of Prishtina, 38000 Prishtina, Yugoslavia

ABSTRACT

The underpotential deposition and dissolution of thallium onto carefully chemically polished single crystal copper (110) electrodes from acetate, sulfate and perchlorate solutions have been investigated using Linear Sweep Voltammetry (L.S.V.).

Voltammetry results on Cu(110) single crystal electrode showed thallium forming two underpotential monolayers with close-packed crystalline structure, somewhat distorted by the underlying substrate.

The first closest-packed epitaxial structure of the first thallium (more anodic) monolayer is formed by adsorption. Higher order phase transformation is needed for completion of the first close-packed thallium crystalline monolayer.

It appears that the underpotential deposition of the second thallium monolayer on Cu(110) proceeds similarly to the first layer, but the onset of bulk overpotential deposition does not allow further detailed analysis.

A model of thallium closest-packed epitaxial monolayer on Cu(110) surface is proposed.

Key words: Underpotential deposition, Liner sweep voltammetry, Cu, Tl, Phase formation, Single crystal

INTRODUCTION

Despite extensive studies of metal underpotential deposition¹⁻¹⁴ there have been some important problems still unresolved. These related principally to the nature of the monolayer (adsorbed or crystalline), the interpretation of the linear sweep voltammogram peaks, phase changes within the monolayer, the kinetics of the crystalline monolayer formation, if any, and the relevance of the UPD monolayer to the overpotential deposition process.

The system selected for the study was thallium on copper polycrystals and single crystals. The underpotential as well as overpotential deposition and their possible mutual interdependence were investigated. The substrate posses high hydrogen evolution overvoltage and therefore deposition of thallium is not complicated by hydrogen co-adsorption processes.

The technique employed was linear sweep voltammetry.

MATERIALS AND METHODS

The experimental work described in this paper was done predominantly using linear sweep voltammetry (L.S.V.) technique.

All potential programming of the working electrode was supplied either from a potentiostat ("Hi-Tek Instruments" model DT2101, or two "Chemical Electronics" models V150/1.5A, TR70/2A) in conjunction

with a "Chemical Electronics" waveform generator (type R.B.1), or two "H.Tinsley and Co." potentiometer (type 3387B). The waveform generator provided either a ramp type voltage output for L.S.V.

The cell currents were recorded as voltages on an XY recorder (types "Bryans 26000" or "Hewlett Packard 7015A"). To observe and record the current-time transients and other functions too rapid to be followed on an XY or Yt recorder, oscilloscopes ("Tektronix" 547 or 5030) were employed.

The cell used for the L.S.V. experiments is presented in Fig. 1. The cell was made entirely of glass. The working electrode, C, and Luggin capillary, L, were positioned in syringe barrels to enable adjustment to give the best positions and mutual distances of the two. The counter electrode, A, was either a platinum disc or a platinum mesh disc $\approx 1.5 \text{ cm}^2$ in area, positioned parallel to the working electrode.

Working electrodes were small cylinders of single crystal copper ("Metal Research Ltd.", 99.999%) $\approx 0.8\text{cm}$ in diameter. These were sealed into Kel-F rod such that only the top surface of the metal cylinder was exposed to the solution. Great care was taken to ensure that no leakage occurred around the side of the metal crystal. This was achieved by cooling the cylinder of copper in liquid nitrogen before mounting in the hollow Kel-F rod (drilled for a tight fit at room temperature), which had been placed in boiling water so that insertion of the metal and contraction of the plastic housing ensured a very tight fit. The reference electrodes housed at the end of the Luggin capillary were either a satu-

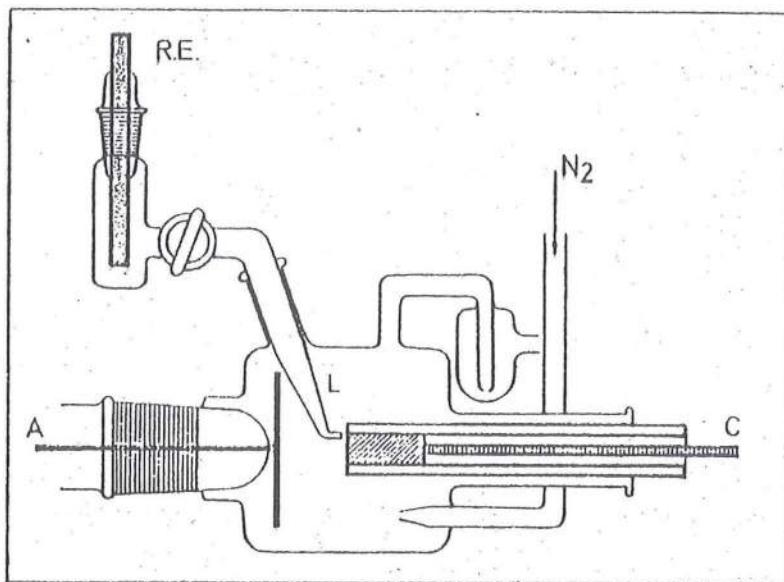


Figure. 1. The cell used for most of the L.S.V. and potential step experiments.

rated calomel (S.C.E. "Radiometer K401") or lead wire ("Koch - Light Laboratories Ltd.", 99.999%) scaled into the glass holder.

Prior to use all glass-ware was soaked in a mixture containing equal volumes of concentrated nitric and sulfuric acids to remove any possible traces of grease, then it was rinsed thoroughly in tap water, singly distilled and finally triply distilled water. The latter was prepared by slow distillation from a weakly alkaline solution of KMnO_4 and then from solution containing a trace amount of ortho- H_3PO_4 .

All solutions were made up from Analar grade chemicals ("B.D.H. Chemicals Ltd." and "Hopkin and Williams Company", without further purification) in triply distilled water. Prior to experiment, solutions were deaerated inside the cell by purging with a stream of purified oxygen-free nitrogen, for about 30-35 minutes. Nitrogen was purified by purging it through a solution of ammonia metavanadate, hydrochloric acid and distilled water lying on top of $\approx 25\text{g}$, of amalgamated zinc¹⁶.

The importance of electrode surface preparation cannot be overstressed in connection with the metal deposition work. The surface preparation procedures finally adopted for copper single crystal electrodes were result of investigating a number of other methods. Criteria used to judge the success of each method was based on the best reproducibility of experimental data and the clearest delineation of various features on the voltammetric characteristics. The polishing process consisted of two stages, the first mechanical and the second chemical.

Firstly, the electrodes were polished on selvyt cloths ("Buchler Ltd.") impregnated with alumina ("Buchler Ltd." $5 \cdot 10^{-4}\text{cm}$ and $3 \cdot 10^{-4}\text{cm}$ grade, and "Banner scientific Ltd." $1 \cdot 10^{-5}\text{cm}$ and $3 \cdot 10^{-5}\text{cm}$ grade). Initially the largest grade was used and then progressively smaller ones down to the smallest, until the electrode had a mirror-like appearance free from scratches or blemishes. These mechanical polishing steps were al-

ways performed manually rather than on a polishing machine, which was less convenient to use. Before each experiment copper single crystal electrodes were chemically polished using a modified version of a process described elsewhere¹⁷.

The three copper single crystals (111), (110) and (100) had to be chemically polished under somewhat different conditions if the result was to be up to the standard. The polishing mixture containing 33vol.% each of concentrated Analar grade HNO_3 , glacial acetic acid and orthophosphoric acid, was common to all copper electrodes used. The difference in treatment between polycrystalline and each of the copper single crystals began when the temperature of the polishing agents and the time of immersion was to be decided.

The (110) oriented single crystal was immersed in the acid mixture heated to 65°C , alternately standing still and stirred every 4 seconds for 4 times. Then it was rinsed with tap water and eventually with triply distilled water. Thereafter the procedure was the same as that previously described for the (111) orientation,^{2,8,11}.

This polishing process required a considerable amount of practice before consistent results could be obtained.

Examinations of the polished electrode surfaces under microscope and with X-ray emission spectroscopy revealed no contaminating elements except very minute particles of alumina, but these were very few in number (on the sample investigated one particle of alumina was found in an area of about 0.25cm^2).

The amount of the copper dissolved in this chemical polishing process was relatively small. A single crystal polished several hundred times would lose 35% of its volume.

The investigation of a particular electrode solution combination always started with linear sweep voltammetry. In this case it constituted the whole experiment.

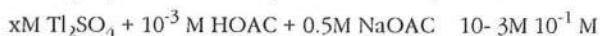
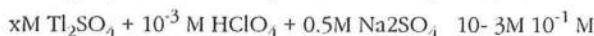
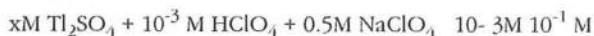
The voltammogram itself was a direct indication of the nature of the electrode surface and consequently could be used to assess the degree to which the chemical polishing had been successful in producing a well defined crystal plane (in the case of the single crystal of course). For any particular system, repeated linear sweep experiments were performed before any additional measurement were made in order to establish an arbiter to which all future voltammetry could be referred. The procedure described here for L.S.V. is that which enabled a given solution/electrode combination to be used for a whole day's experiments without any deterioration in the result over this period.

Firstly the cell complete with working electrode (not yet freshly chemically polished) was rinsed thoroughly in tap, and triply distilled water. Then the cell was rinsed with the solution being used and finally filled with it. This was followed by deaeration with a rapid stream of nitrogen (scrubbed by a vanadous ion mixture) for about 35 minutes. During this process the working electrode was polarized at a potential somewhat positive to that where U.P.D. began. After the deaeration period, the working electrode was removed from the cell and chemically (or only mechanically) polished as described earlier and after thorough rinsing was placed back in the cell. Gas purging was continued in the cell sealed with a syring piston while the chemical polishing was performed. It was resumed for an additional 5-10 minutes after the freshly polished working electrode had been put into the cell. The process of polarizing the electrode during the gas purging acted as a mild pre-electrolysis method and impurities were removed from the solution. That this was the case could be seen by carrying out voltammetry with the electrode at the end of the degassing period without chemical polishing, when markedly inferior results were obtained. Before the actual L.S.V. was recorded the cell was sealed off from the air by tight rubber covers being placed on the gas inlet and outlet.

Voltammetric experiments were carried out in the normal way; the potential being cycled continuously and sweeps recorded when necessary at a variety of sweep speeds.

RESULTS

Copper single crystal with (110) oriented surface, was examined in solutions containing three different anions:



This relatively wide variation in solution composition and concentration was necessary to understand all the variables affecting the UPD.

Typical voltammograms recorded during thallium UPD on Cu(110) substrate from the three solutions used, are presented in Fig. 2. a, b and c.

The essential features of all voltammograms were the same, Table.1., except for peak potential variations due to specific adsorption of the acetate anion in solution of higher concentration.

Two sets, of two peaks each, were observed. The resolution between the two peaks in the first set situated at more anodic potentials could be improved by decreasing the sweep speed, but not to the point of separating them. The second peak, K₂, which obviously starts at potentials still within the first peak, seems to be very sharp. The first peak K₁ is well defined but not nearly as sharp as K₂.

The charge associated with K₁ was approximately $120 \cdot 10^{-6} \text{ Ascm}^{-2}$, and that due to the second peak, K₂, was $70 \cdot 10^{-6} \text{ Ascm}^{-2}$.

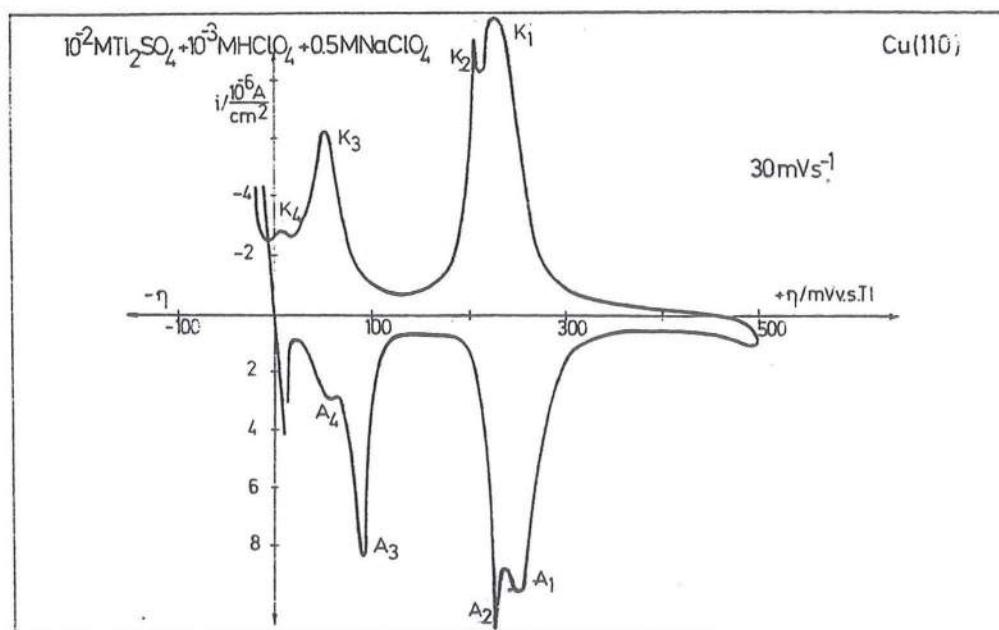


Figure. 2.a. Linear sweep voltammogram for thallium underpotential deposition on Cu(110).

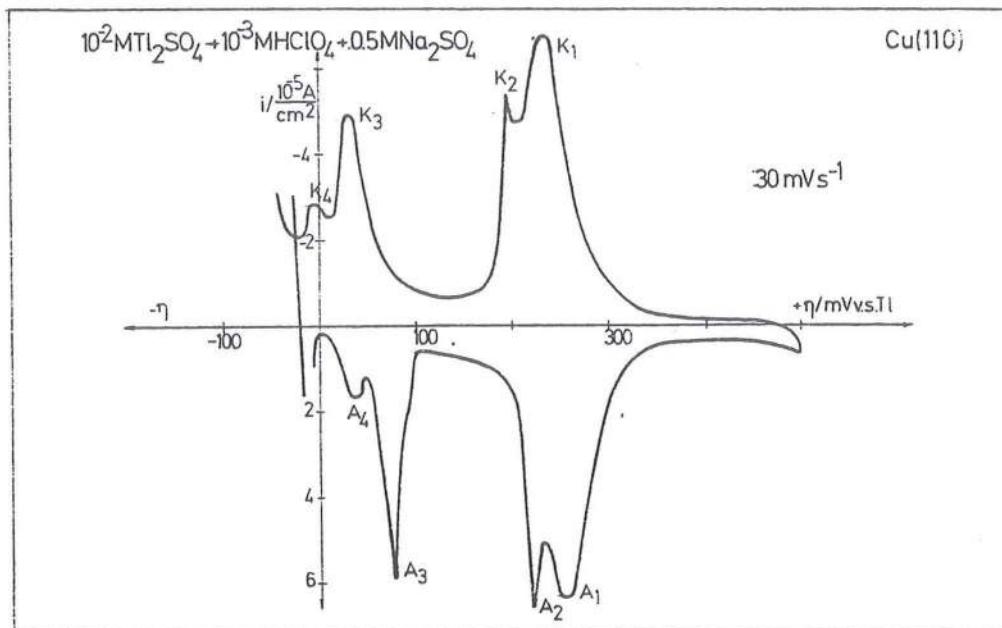


Figure. 2.b. Linear sweep voltammogram for thallium underpotential deposition on Cu(110).

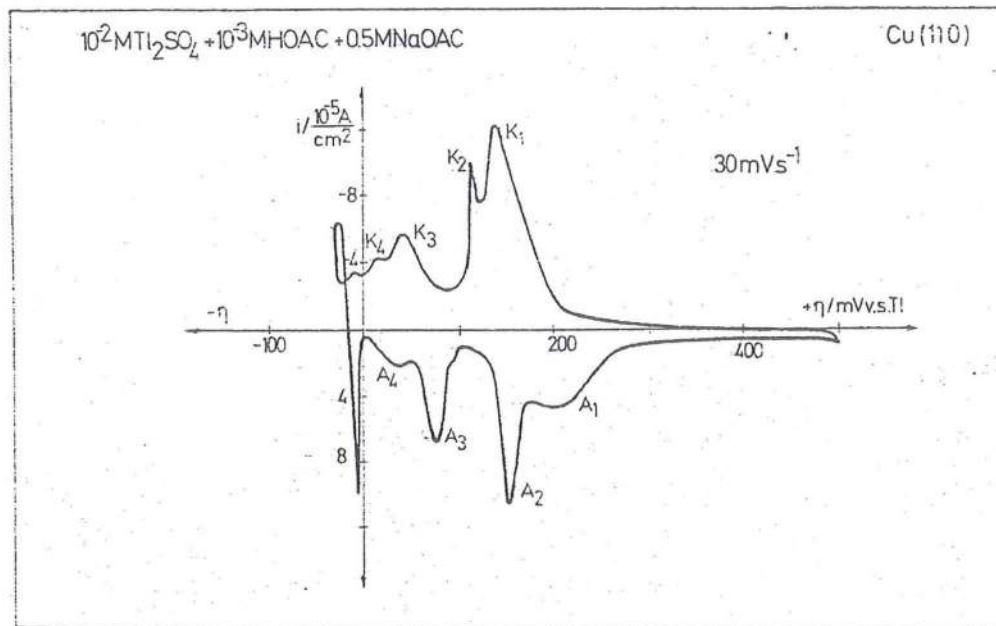


Figure. 2.c. Linear sweep voltammogram for thallium underpotential deposition on Cu(110).

Table. 1. Average UPD values measured for 10^{-2}M Tl solutions and $v=30\text{mVs}^{-1}$.

Surface orientation	Anion	K ₁ mV vs. Tl	K ₂ mV vs. Tl	K ₃ mV vs. Tl	K ₄ mV vs. Tl	Calc. close-packed layer $10^{-6} \text{ As cm}^{-2}$	Calc. epitax layer $10^{-6} \text{ As cm}^{-2}$	Measured charge $K_1 + K_2 10^{-6} \text{ As cm}^{-2}$	Measured charge $K_3 + K_4 10^{-6} \text{ As cm}^{-2}$
(110)	ClO_4^-	+245	+218	+73	+39	160	90	122 ± 5	195 ± 4
(110)	SO_4^{2-}	+240	+204	+43	+17	160	90	120 ± 3	193 ± 5
(110)	OAc^-	+143	+114	+52	+22	160	90	120 ± 3	193 ± 7

The stripping peaks, A_1 and A_2 , are more or less good inverted replicas of their deposition counterparts, except for a shift along the potential axis. The peak potential separations were $\Delta E_{A_1-K_1} \approx 12\text{mV}$ and $\Delta E_{A_2-K_2} \approx 14\text{mV}$ at $v = 10\text{mVs}^{-1}$.

The peak potentials were dependent on sweep speed, Fig. 3., and the thallium concentration, Fig. 4.

The second set of peaks situated at potentials very close to the reversible Tl/Tl^+ potential, consisted basically of two peaks, K_3 and K_4 . The first one, K_3 , was more pronounced, while the second, K_4 , was incomplete in the UPD region in all cases. The current due to K_4 did not fall to zero value before the onset of bulk deposition. Therefore, the measured charge for these two peaks ($115 \cdot 10^{-6} \text{ Ascm}^{-2}$) is not the full value. The peak separations were $\Delta E_{A_3-K_3} \approx 32\text{mV}$ and $\Delta E_{A_4-K_4} \approx 32\text{mV}$ and these did not change significantly with changing sweep speed.

DISCUSSION

Comparison with the L.S.V. results obtained for thallium UPD on $\text{Ag}(110)_1$ shows significant similarities, but an even better resemblance to the voltammogram for lead UPD on the same substrate⁹ was observed.

On account of its less sharp features and its charge values ($120 \cdot 10^{-6} \text{ Ascm}^{-2}$), K_1 could be attributed to the adsorption of thallium. When a roughness factor (≈ 1.1) is taken into account the charge recorded is still somewhat higher than the charge needed for the epitaxial closest-packed thallium layer on the $\text{Cu}(110)$ surface ($\approx 90 \cdot 10^{-6} \text{ Ascm}^{-2}$) in Fig. 5. But when the charge of the overlapping K_2 ($\approx 70 \cdot 10^{-6} \text{ Ascm}^{-2}$) is added to it, the sum ($\approx 190 \cdot 10^{-6} \text{ Ascm}^{-2}$) is quite close to the value of $160 \cdot 10^{-6} \text{ Ascm}^{-2}$ needed for the close-packed thallium layer.

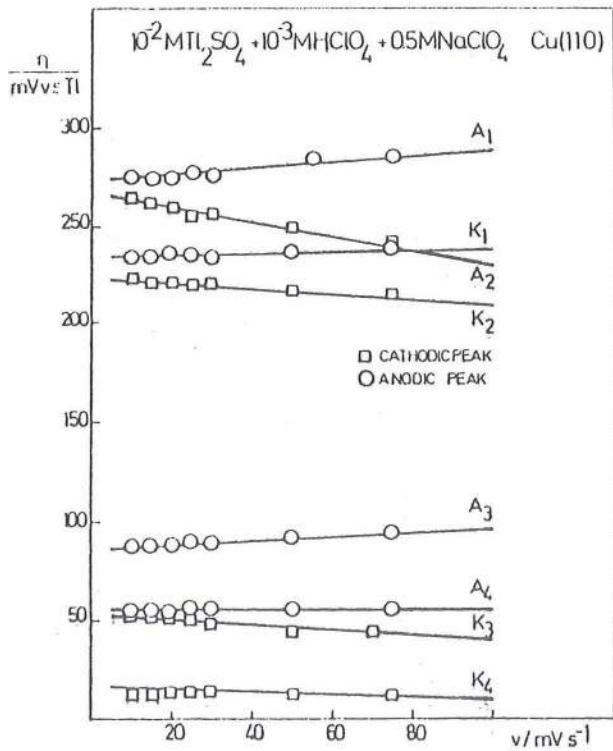


Figure 3. The dependence of peak potentials on the sweep speed.

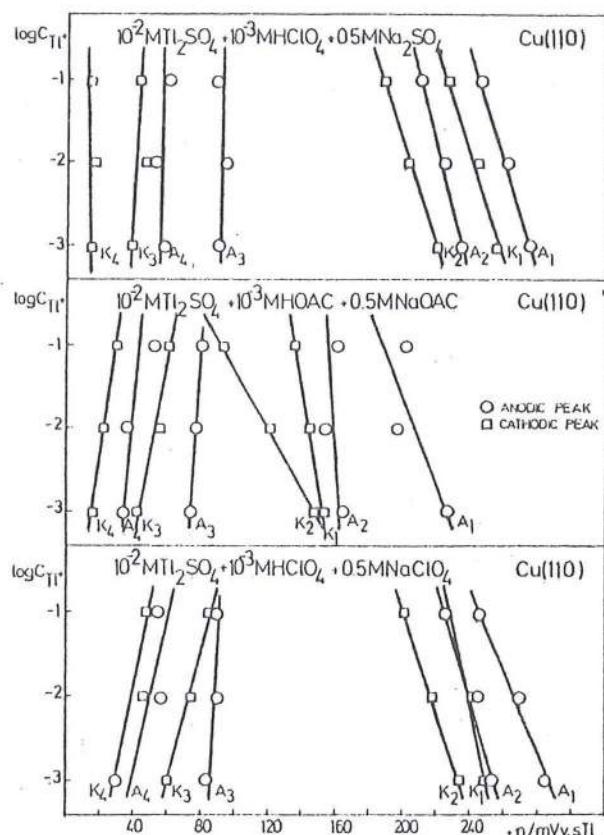


Figure 4. The dependence of peak potential on the thallium concentration.

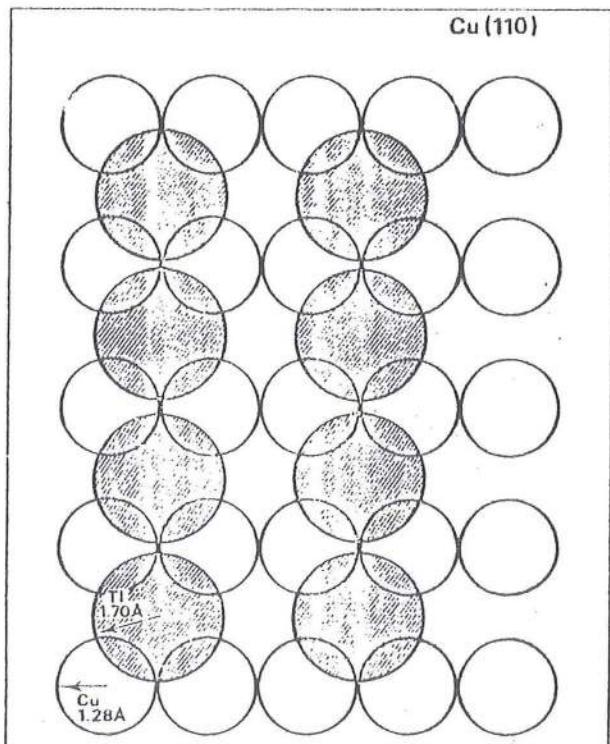


Figure 5. The structure of the epitaxial closest-packed thallium monolayer on the $\text{Cu}(110)$ surface.

Therefore, it seems realistic to attribute K_1 to an adsorption process leading to the closest-packed epitaxial thallium layer, and K_2 is probably due to a higher order phase transformation of such a structure into a crystalline close-packed thallium plane. The final monolayer will most probably be distorted to a certain extent by structure of the underlying substrate. The parallelism and the conclusions reached for the UPD of lead on Cu(110)⁹ and of thallium on Ag(110)¹ is clear.

The second thallium monolayer, formed in K_3 and K_4 seems to produce the same deposition characteristics irrespective of the substrate. The peak potentials K_3 and K_4 are very similar on all three copper single crystal orientations^{8,10}, as are charges ($\approx 100 \cdot 10^{-6} \text{ Asec}^{-2}$) and in each case bulk deposition commences before K_4 is completed.

Nevertheless, the data available do not allow further conclusions other than the simple acknowledgement of its presence as a second thallium monolayer put down before bulk deposition starts in a way probably similar to the first UPD monolayer.

CONCLUSIONS

The essential features of all voltammograms were the same, except for peak potential variations due to specific adsorption of the acetate anion in solution of higher concentration.

Two sets, of two peaks each, were observed. On account of its less sharp features and its charge values, K_1 could be attributed to the adsorption of thallium, and it seems realistic to attribute K_1 to an adsorption process leading to the closest-packed epitaxial thallium layer. The second peak, K_2 , is probably due to a higher order phase transformation of such a structure into a crystalline close-packed thallium plane. The final monolayer will most probably be distorted to a certain extent by structure of the underlying substrate. The parallelism and the conclusions reached for the UPD of lead on Cu(110)⁸ and of thallium on Ag(110)¹ is clear.

The second thallium monolayer, formed in K_3 and K_4 seems to produce the same deposition characteristics irrespective of the copper single crystal substrate used in this series of experiments. Nevertheless, the data available do not allow further conclusions other than the simple acknowledgement of its presence as a second thallium monolayer put down before bulk deposition starts in a way probably similar to the first UPD monolayer.

Acknowledgment

J.Jovićević wishes to express his gratitude to The Royal Society of London and The University of Southampton for the financial support, which made his work at the University of Southampton possible.

REFERENCES

- 1.- Thomas, B., Ph.D. Thesis, University of Southampton 1976.
- 2.- Jovićević, J.N., Ph.D. Thesis, University of Southampton 1978.
- 3.- Bewick, A., Jovićević, J.N., Thomas, B., Trans. Faraday Disc., 12 (1977) 24
- 4.- Thomas, B., Bewick, A., J.Electroanal. Chem., 65 (1975) 911.
- 5.- Thomas, B., Bewick, A., J.Electroanal. Chem., 70 (1976) 239.
- 6.- Thomas, B., Bewick, A., J.Electroanal. Chem., 84 (1977) 127.
- 7.- Jovićević, J.N., Bewick, A., Univ. Thought, Vol.IV(2) (1997) 29,Pristina.
- 8.- Jovićević, J.N., Bewick, A., Univ. Thought, Vol.IV(2) (1997) 39,Pristina.
- 9.- Jovićević, J.N., Bewick, A., Univ. Thought, Vol.IV(2) (1997) 51,Pristina.
- 10.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 11.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 12.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 13.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 14.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 15.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 16.- Meites, L.: "Polarographic Techniques", 2nd edition, Interscience, New York (1965).
- 17.- Pinner, R., Electroplating, October and November (1953) 360, 401.

REZIME

STUDIJA POČETNOG STADIJUMA ELEKTRO-TALOŽENJA TALIJUMA NA BAKRU - II DIO
PONAŠANJE BAKARNE POLIKRISTALNE ELEK-TRODE I ELEKTRODE KRISTALOGRAFSKE ORIJEN-TACIJE (110) PRI LINEARNOJ CIKLIČKOJ PROMJENI POTENCIJALA

JOVIĆEVIĆ¹ N. Jovan, BEWICK Alan
Chemistry Department, Southampton University,
UK, SO9 5NH
¹Sadašnja adresa: Odsek za hemiju, PMF, Univerzitet
u Prištini, 38000 Priština, Jugoslavija.

Ovo je drugi iz serije radova u kojima se iznose rezultati istraživanja početnih stadijuma elektrotaloženja talijuma (iz acetatnih, sulfatnih i perhloratnih rastvora) na polikristalnom i monokristalnom bakru.

Rad predstavlja rezultate dobijene linearnom cikličnom promjenom potencijala (L.S.V.) bakarne monokristalne elektrode površinske orientacije (110) u području potencijala pozitivnijih od reverzibilnog potencijala talijuma u datoj sredini.

Još jednom se uvjerljivo pokazalo da je pažljivo i uspješno poliranje površine radne elektrode od najvećeg značaja pri ispitivanjima područja potencijala pozitivnijih od reverzibilnog potencijala taloženja/rastvaranja ispitivanog metala, ukoliko se žele dobiti pouzdani kvantitativni i kvalitativni podaci.

Elektrotaloženja talijuma na bakarne monokristalne površine kristalografske orientacije (110) tehnikom

cikličke voltametrije otkrivaju po dva odvojena para katodnih strujnih talasa međusobno udaljenih više od 100mV. Potencijali vrhova tih talasa zavisni su od brzine promjene potencijala i od koncentracije talijuma u upotrebljenom elektrolitu.

Prvi par katodnih strujnih talasa (javlja se pri anodnijim potencijalima) sastoji se od manje oštrog (anodnijeg) talasa, K₁, i vrlo oštrog (katodnijeg) talasa, K₂. Na osnovu oblika promjene gustine struje sa potencijalom i na osnovu količine razmjenjenog naelektrisanja koje predstavlja, prvi talas (K₁) vjerovatno odražava proces adsorpcije talijuma koji vodi formiranju najgušće pakovanog epitaksijalnog monosloja talijuma na Cu(110) podlozi. Drugi katodni talas, K₂, koji je mnogo oštiji, vjerovatno predstavlja faznu transformaciju tog epitaksijalnog monosloja u kristalnu gustopakovanu dvodimenzionu strukturu talijuma koja je donekle poremećena pod uticajem oblika bakarme monokristalne podloge. Oblik i položaj komplementarnog anodnog para A₁ i A₂ (koji predstavljaju procese rastvaranja struktura predstavljenih sa K₁ i K₂) na skali potencijala, potvrđuju ovakve pretpostavke, pogotovo kada se uzmu u obzir zavisnost potencijala vrhova talasa od koncentracije talijuma u upotreblje-nim rastvorima i njihovi međusobni odnosi.

Drugi par katodnih strujnih talasa, K₃ i K₄, (i njima komplementarnih anodnih talasa A₃ i A₄) po obliku i karakteristikama, veoma su slični prвome paru (K₁, K₂, odnosno A₁, A₂), te se formiranje drugog monosloja talijuma pri potencijalima pozitivnijim od reverzibilnog potencijala talijuma u dатoj sredini najvjerovaljnije odigrava na isti način kao i prvi monosloj. Međutim, detaljna analiza mehanizma formiranja ovoga drugoga monosloja onemogućena je činjenicom da se primjenjenom tehnikom ne može napraviti razlika između trenutka kada nastupa kraj formiranja monosloja od trenutka kada započinje elektrotaloženje talijuma uz katodne prenapetosti.

Oblici strujnih talasa (katodnih-taloženje, K₁, K₂, K₃ i K₄, odnosno komplementarnih anodnih-rastvaranje, A₁, A₂, A₃ i A₄), količina naelektrisanja koju ograđuju, razlika u potencijalima vrhova komplementarnih katodnih i anodnih parova talasa, zavisnost potencijala vrhova talasa od koncentracije talijuma i brzine promjene potencijala, snažno podržavaju iznijete pretpostavke o mehanizmu formiranja talijumovih mono-slojnih kristalnih faza na Cu(110) pri potencijalima pozitivnijim od reverzibilnog potencijala talijuma u ispitivanim sredinama.

Received: March, 1998.

Accepted: April, 1998.

A Study of the Initial Stages of the Electrochemical Deposition of Thallium on Copper - PART III. The L.S.V. Behaviour of (100) oriented Copper Single Crystal Electrode

JOVIĆEVIĆ¹ N. Jovan, BEWICK Alan

Chemistry Department, Southampton University, UK, SO9 5NH

¹Present address: Chemistry Department, Faculty of Natural Sciences & Mathematics, University of Prishtina, 38000 Prishtina, Yugoslavia

ABSTRACT

The underpotential deposition and dissolution of lead onto carefully chemically polished single crystal copper (100) electrodes from acetate, sulphate and perchlorate solutions have been investigated using Linear Sweep Voltammetry (L.S.V.).

Voltammetry results on Cu(100) single crystal electrode showed thallium forming two underpotential monolayers with close-packed crystalline structure, somewhat distorted by the underlying substrate.

The crystalline closest-packed epitaxial structure of the first thallium (more anodic peak K1 of the set) monolayer is formed by higher order phase formation. At more negative potentials (characteristic to less anodic peak K2 of the set)

the free energy change favours the deposition of additional thallium which provokes a higher order phase transformation of this epitaxial crystalline structure into energetically more stable close-packed thallium crystalline plane, most probably somewhat distorted by the underlying substrate.

It appears that the underpotential deposition of the second thallium monolayer on Cu(100) proceeds similarly to the first layer, but the onset of bulk overpotential deposition does not allow further detailed analysis.

A model of crystalline thallium closest-packed epitaxial monolayer on Cu(100) surface is proposed.

Key words: Underpotential deposition, Liner sweep voltammetry, Cu, Tl, Phase formation, Single crystal

INTRODUCTION

Despite extensive studies of metal underpotential deposition¹⁻¹⁸ there have been some important problems still unresolved. These related principally to the nature of the monolayer (adsorbed or crystalline), the interpretation of the linear sweep voltammogram peaks, phase changes within the monolayer, the kinetics of the crystalline monolayer formation, if any, and the relevance of the UPD monolayer to the overpotential deposition process.

The system selected for the study was thallium on copper polycrystals and single crystals. The underpotential as well as overpotential deposition and their possible mutual interdependence were investigated. The substrate posses high hydrogen evolution overvoltage and therefore deposition of thallium is not complicated by hydrogen co-adsorption processes.

The technique employed was linear sweep voltammetry.

MATERIALS AND METHODS

The experimental work described in this paper was done predominantly using linear sweep voltammetry (L.S.V.) technique.

All potential programming of the working electrode was supplied either from a potentiostat ("Hi-Tek Instruments" model DT2101, or two "Chemical Electronics" models V150/1.5A, TR70/2A) in conjunction with a "Chemical Electronics" waveform generator (type R.B.1), or two "H.Tinsley and Co." potentiometer (type 3387B). The waveform generator provided either a ramp type voltage output for L.S.V.

The cell currents were recorded as voltages on an XY recorder (types "Bryans 26000" or "Hewlett Packard 7015A"). To observe and record the current-time transients and other functions too rapid to be followed on an XY or Yt recorder, oscilloscopes ("Tektronix" 547 or 5030) were employed.

The cell used for the L.S.V. experiments is presented in Fig. 1. The cell was made entirely of glass. The working electrode, C, and Luggin capillary, L, were positioned in syringe barrels to enable adjustment to give the best positions and mutual distances of the two. The counter electrode, A, was either a platinum disc or a platinum mesh disc $\approx 1.5 \text{ cm}^2$ in area, positioned parallel to the working electrode.

Working electrodes were small cylinders of single crystal copper ("Metal Research Ltd.", 99.999%) $\approx 0.8\text{cm}$ in diameter. These were sealed into Kel-F rod such that only the top surface of the metal cylinder was exposed to the solution. Great care was taken to ensure that no

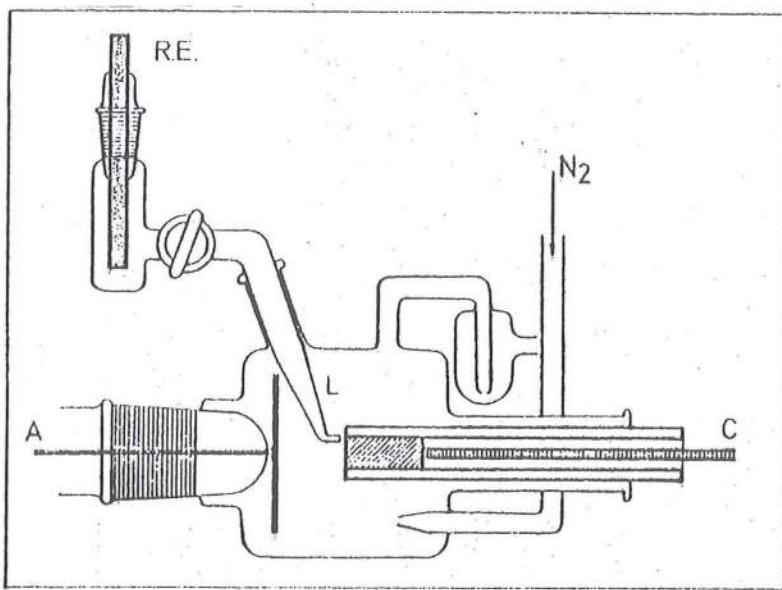


Figure. 1. The cell used for most of the L.S.V. and potential step experiments.

leakage occurred around the side of the metal crystal. This was achieved by cooling the cylinder of copper in liquid nitrogen before mounting in the hollow Kel-F rod (drilled for a tight fit at room temperature), which had been placed in boiling water so that insertion of the metal and contraction of the plastic housing ensured a very tight fit. The reference electrodes housed at the end of the Luggin capillary were either a saturated calomel (S.C.E. "Radiometer K401") or lead wire ("Koch - Light Laboratories Ltd.", 99.999%) sealed into the glass holder.

Prior to use all glass-ware was soaked in a mixture containing equal volumes of concentrated nitric and sulphuric acids to remove any possible traces of grease, then it was rinsed thoroughly in tap water, singly distilled and finally triply distilled water. The latter was prepared by slow distillation from a weakly alkaline solution of KMnO_4 and then from solution containing a trace amount of ortho- H_3PO_4 .

All solutions were made up from Analar grade chemicals ("B.D.H. Chemicals Ltd." and "Hopkin and Williams Company", without further purification) in triply distilled water. Prior to experiment, solutions were deaerated inside the cell by purging with a stream of purified oxygen-free nitrogen, for about 30-35 minutes. Nitrogen was purified by purging it through a solution of ammonia metavanadate, hydrochloric acid and distilled water lying on top of 25g, of amalgamated zinc19.

The importance of electrode surface preparation cannot be overstressed in connection with the metal deposition work. The surface preparation procedures finally adopted for copper single crystal electrodes were result of investigating a number of other methods. Criteria used to judge the success of each method was based on the best reproducibility of experimental data and the clearest delineation of various features on the voltammetric characteristics. The polishing process consisted of two stages, the first mechanical and the second chemical.

Firstly, the electrodes were polished on selvyt cloths ("Buchler Ltd.") impregnated with alumina ("Buchler Ltd." $5 \cdot 10^{-4}$ cm and $3 \cdot 10^{-4}$ cm grade, and "Banner scientific Ltd." $1 \cdot 10^{-5}$ cm and $3 \cdot 10^{-5}$ cm grade). Initially the largest grade was used and then progressively smaller ones down to the smallest, until the electrode had a mirror-like appearance free from scratches or blemishes. These mechanical polishing steps were always performed manually rather than on a polishing machine, which was less convenient to use. Before each experiment copper single crystal electrodes were chemically polished using a modified version of a process described elsewhere²⁰.

The three copper single crystals (111), (110) and (100) had to be chemically polished under somewhat different conditions if the result was to be up to the standard. The polishing mixture containing 33vol.% each of concentrated Analar grade HNO_3 , glacial acetic acid and orthophosphoric acid, was common to all copper electrodes used. The difference in treatment between polycrystalline and each of the copper single crystals began when the temperature of the polishing agents and the time of immersion was to be decided.

The (100) oriented single crystal was immersed in the acid mixture heated to 70°C, and alternately kept still and stirred every 3 seconds four times. Then it was rinsed with tap water and eventually with triply distilled water. Thereafter the procedure was the same as that previously described for the (111) and (110) copper surface orientation^{2,8,11}.

This polishing process required a considerable amount of practice before consistent results could be obtained.

Examinations of the polished electrode surfaces under microscope and with X-ray emission spectroscopy revealed no contaminating elements except very minute particles of alumina, but these were very few in number (on the sample investigated one particle of alumina was found in an area of about 0.25cm^2).

The amount of the copper dissolved in this chemical polishing process was relatively small. A single crystal polished several hundred times would lose 35% of its volume.

The investigation of a particular electrode solution combination always started with linear sweep voltammetry. In this case it constituted the whole experiment.

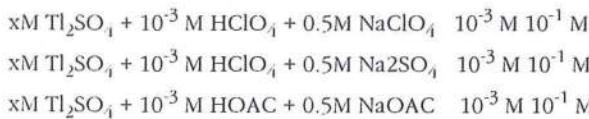
The voltammogram itself was a direct indication of the nature of the electrode surface and consequently could be used to assess the degree to which the chemical polishing had been successful in producing a well defined crystal plane (in the case of the single crystal of course). For any particular system, repeated linear sweep experiments were performed before any additional measurement were made in order to establish an arbiter to which all future voltammetry could be referred. The procedure described here for L.S.V. is that which enabled a given solution/electrode combination to be used for a whole day's experiments without any deterioration in the result over this period.

Firstly the cell complete with working electrode (not yet freshly chemically polished) was rinsed thoroughly in tap, and triply distilled water. Then the cell was rinsed with the solution being used and finally filled with it. This was followed by deaeration with a rapid stream of nitrogen (scrubbed by a vanadous ion mixture) for about 35 minutes. During this process the working electrode was polarised at a potential somewhat positive to that where U.P.D. began. After the deaeration period, the working electrode was removed from the cell and chemically (or only mechanically) polished as described earlier and after thorough rinsing was placed back in the cell. Gas purging was continued in the cell sealed with a syringe piston while the chemical polishing was performed. It was resumed for an additional 5-10 minutes after the freshly polished working electrode had been put into the cell. The process of polarising the electrode during the gas purging acted as a mild pre-electrolysis method and impurities were removed from the solution. That this was the case could be seen by carrying out voltammetry with the electrode at the end of the degassing period without chemical polishing, when markedly inferior results were obtained. Before the actual L.S.V. was recorded the cell was sealed off from the air by tight rubber covers being placed on the gas inlet and outlet.

Voltammetric experiments were carried out in the normal way; the potential being cycled continuously and sweeps recorded when necessary at a variety of sweep speeds.

RESULTS

Copper single crystal with (100) oriented surface, was examined in solutions containing three different anions:



This relatively wide variation in solution composition and concentration was necessary to understand all the variables affecting the UPD.

Typical linear sweep voltammetry results obtained for thallium underpotential deposition on Cu(100) are presented in Fig. 2.a., b. and c., and Table 1.

It is clear that the character of the processes involved is not changing when the anion is changed, although the peak potentials for the acetate solutions were shifted to somewhat more negative potentials.^{17,18}

Once again^{15,16}, two sets of cathodic peaks (and anodic counterparts) were present.

In the first (more anodic) set, K₁ and K₂ were merged together, and although at slower sweep speeds a tendency towards separation was observed it was not fully accomplished. Their anodic counterparts, A₁ and A₂, showed an "overpotential" shift along the potential axis, producing peak potential separation of $\Delta E_{A_1-K_1} \approx 50 \text{ mV}$ and $\Delta E_{A_2-K_2} \approx 34 \text{ mV}$ at $v=10 \text{ mVs}^{-1}$, which increased with increasing sweep speed. This, of course, was yet another example of the familiar tendency^{8-10,15,16} of the voltammogram peak potentials to change with changing sweep speeds, Fig. 3. Yet another feature already established as regular^{8-10,15,16} was observed, namely the change of peak potential with changing thallium concentration, Fig. 4. The charge associated with K₁ (the charge measured to the point X in Fig. 2.a., b. and c.) was $\approx 147 \cdot 10^{-6} \text{ Ascm}^{-2}$ and the charge under K₂ $\approx 18 \cdot 10^{-6} \text{ Ascm}^{-2}$.

The second set of peaks, K₃, closer to the thallium reversible potential, also could not be separated. Peak potential dependence on the sweep speed applied and thallium concentration used, was recorded again. However, this process was not completed before the start of bulk deposition. The total charge associated with this voltammetric feature was $\approx 80 \cdot 10^{-6} \text{ Ascm}^{-2}$.

DISCUSSION

The peak separation of about 50mV observed for K₁ and A₁ at slow sweep speeds strongly suggests that the process connected with these peaks may be a phase formation. Adsorption processes are not normally associated with such large "overpotentials".

The charge measured under K₁ ($147 \cdot 10^{-6} \text{ Ascm}^{-2}$) does not differ much from the value needed ($147 \cdot 10^{-6} \text{ Ascm}^{-2}$) for deposition of the closest-packed epitaxial crystalline structure on Cu(100), Fig. 5., when a roughness factor (≈ 1.1) is taken into account.

This part of the voltammogram closely resembles the deposition and stripping of the first thallium monolayer on Ag(100)¹. At the same time, there appears to be striking similarities with the results obtained for lead on the same surface orientation of copper¹⁰.

Therefore, it must be concluded that thallium underpotential deposition on Cu(100) starts with a phase formation process producing the thallium crystalline lattice (this time closest-packed epitaxial monolayer) shown in Fig. 5. This 2D phase formation is most probably of a higher order.

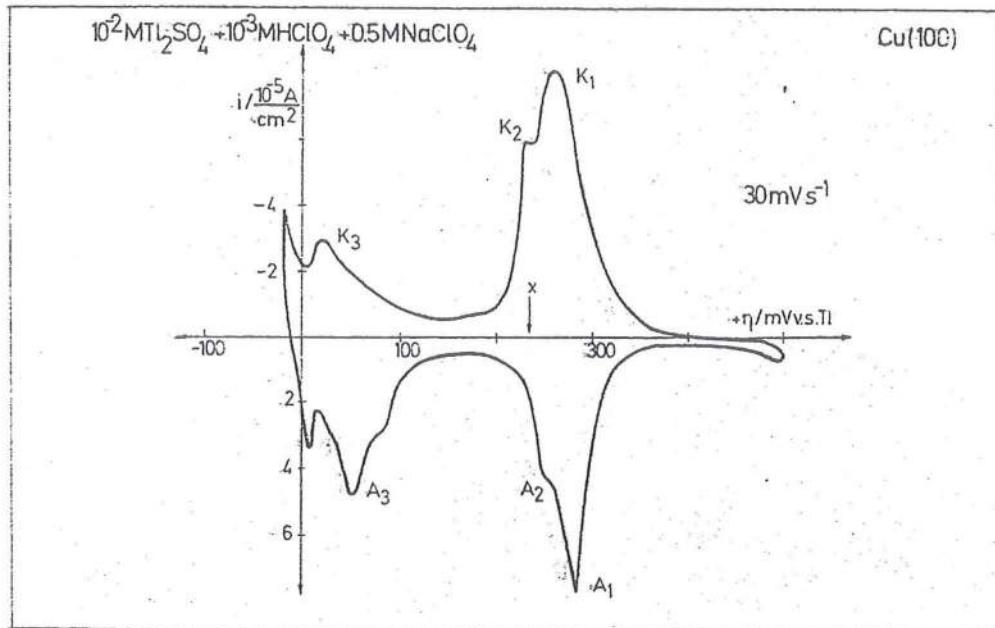


Figure. 2.a. Linear sweep voltammogram for thallium underpotential deposition on Cu(100).

At more negative potentials, characteristic to K₂, the free energy change favours the deposition of additional thallium ($\approx 48 \cdot 10^{-6} \text{ As cm}^{-2}$) which produces a higher order phase transformation into energetically more stable close-packed thallium crystalline plane ($197 \cdot 10^{-6} \text{ As cm}^{-2}$ charge measured).

The data for the second UPD monolayer is once again difficult to interpret. However, it has features very similar to those of the second UPD thallium monolayer formed on the Cu(111) and the Cu(110) oriented electrodes.

CONCLUSIONS

In the case of thallium underpotential deposition onto carefully chemically polished Cu(100) surface, linear sweep voltammetry reveals two separate sets of cathodic (and anodic) peaks, more than 150 mV apart. The peak potentials were dependent on the sweep speed, and the thallium concentration in the solution used. Voltammetric features, however did not depend on the anion used, except in the case of acetate when peak potential shift to more cathodic potentials was observed^{17,18}.

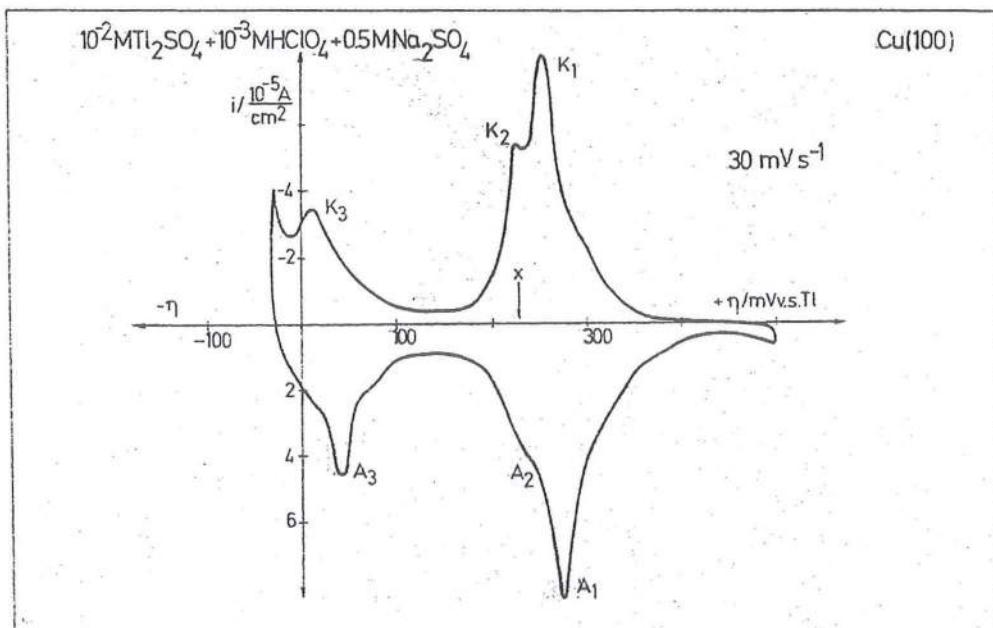


Figure. 2.b. Linear sweep voltammogram for thallium underpotential deposition on Cu(100).

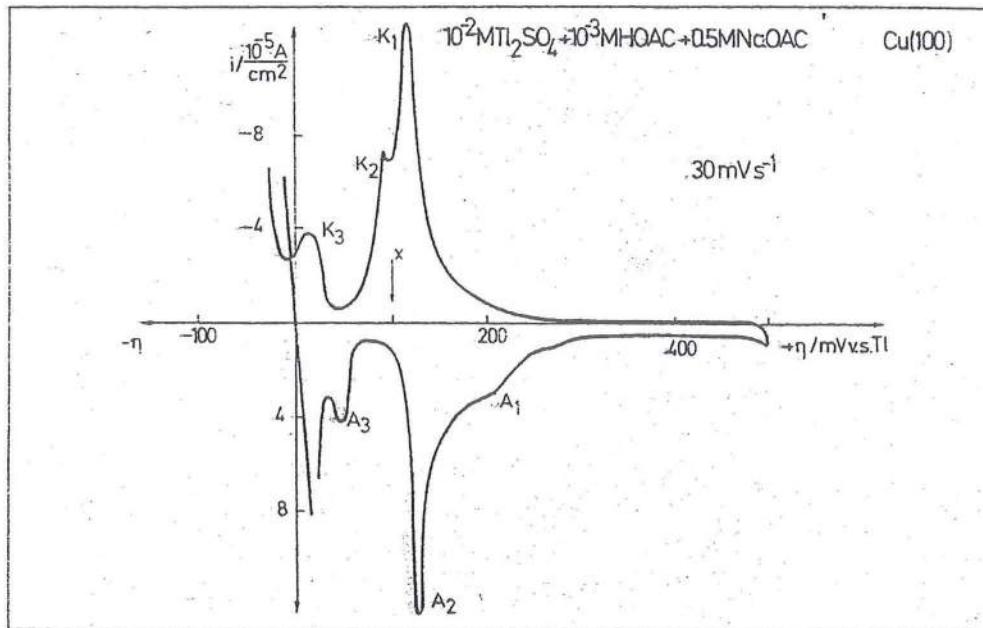


Figure. 2.c. Linear sweep voltammogram for thallium underpotential deposition on Cu(100).

The first set situated at more anodic potentials, consisted of two peaks, K₁ and K₂, merged together, and although at slower sweep speeds a tendency towards separation was observed it was not fully accomplished. The second peak, K₂, usually started at the potentials more positive than the end potential of the first peak. Their anodic counterparts, A₁ and A₂, showed an "overpotential" shift of $\approx 50 \text{ mV}$.

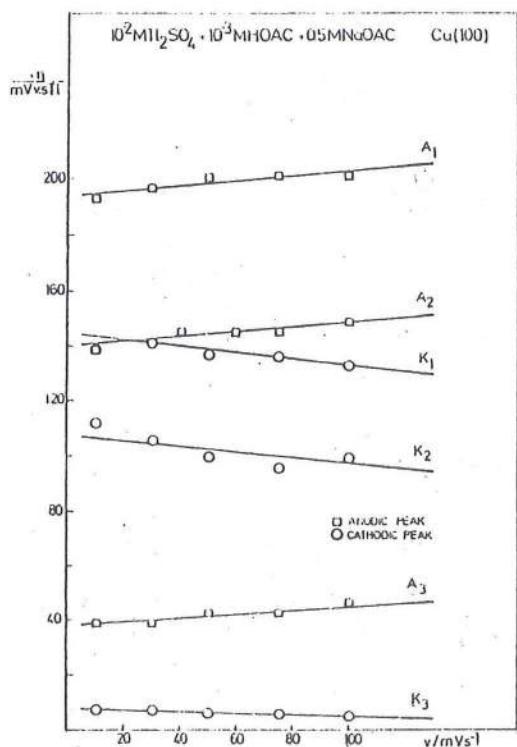


Figure. 3. The dependence of peak potentials on the sweep speeds applied.

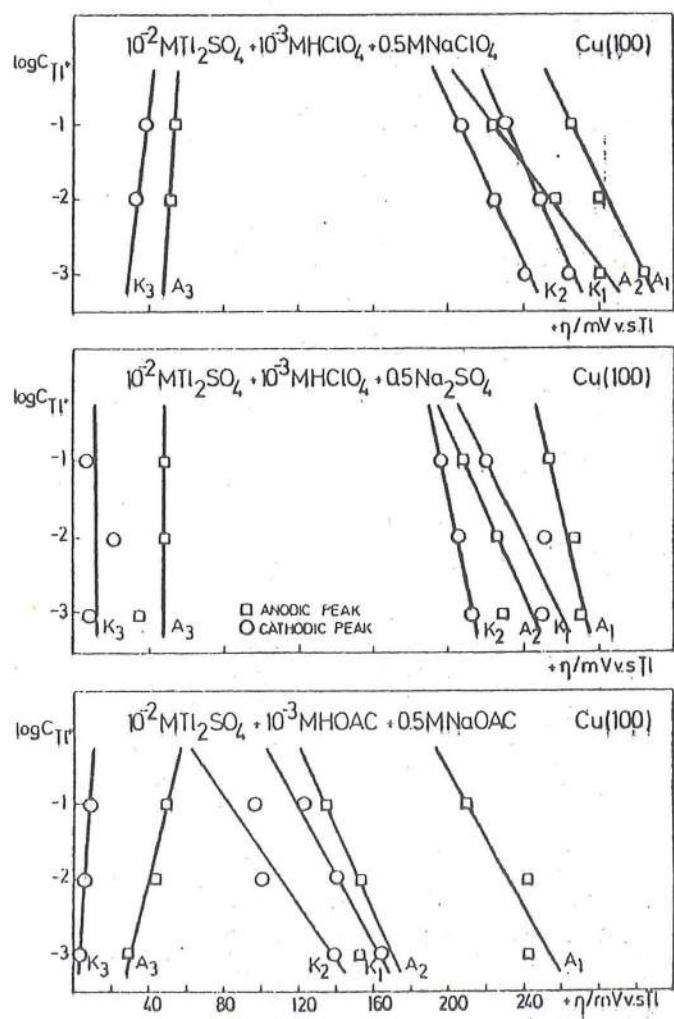


Figure. 4. The dependence of peak potentials on thallium concentration.

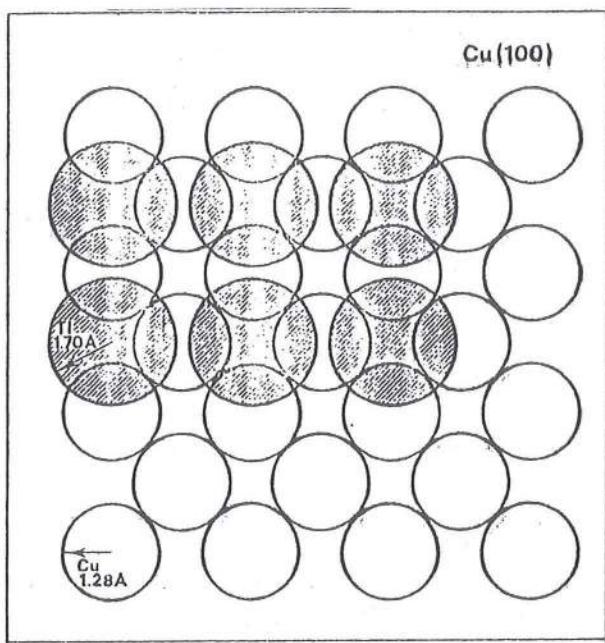


Figure 5. The structure of the epitaxial closest-packed thallium monolayer on the Cu(100) surface.

Peak potentials and cathodic to anodic peak potential separation values, were dependent on thallium concentration and sweep speeds applied.

It must be concluded, therefore, that K_1 represents the formation of the closest-packed epitaxial crystalline monolayer, and, by analogy with lead under the same circumstances, it is formed by higher order phase formation. At more negative potentials, characteristic to K_2 , the free energy change favours the deposition of additional thallium which produces a higher order phase transformation into energetically more stable close-packed thallium crystalline plane, most probably somewhat distorted by the underlying substrate.

It appears that the deposition of the second thallium monolayer on Cu(100) proceeds similarly to the first layer, but the onset of bulk deposition does not allow further detailed analysis.

Acknowledgement

J.Jovićević wishes to express his gratitude to The Royal Society of London and The University of Southampton for the financial support, which made his work at the University of Southampton possible.

Table. 1. Average UPD values measured for $10^{-2}M$ Tl solutions and $v=30mVs^{-1}$.

Surface Orientation	Anion	K_1 mV vs. Tl	K_2 mV vs. Tl	K_3 mV vs. Tl	K_4 mV vs. Tl	Calc. close- packed layer $10^{-6} As$ cm^{-2}	Calc. epitax layer $10^{-6} As$ cm^{-2}	Meas- ured charge K_1 $10^{-6} As$ cm^{-2}	Meas- ured charge K_1+K_2 $10^{-6} As$ cm^{-2}	Meas- ured charge K_3 $10^{-6} As$ cm^{-2}
(100)	ClO_4^-	+240	+214	+36	+39	160	118	149±5	198±5	80±5
(100)	SO_4^{2-}	+240	+194	+12	+17	160	118	147±5	197±5	82±5
(100)	OAC^-	+142	+102	+6	+22	160	118	145±5	195±5	50±5

The charge associated with the first peak is in good agreement with that needed for the deposition of the closest-packed epitaxial thallium monolayer, if a roughness factor of ≈ 1.1 is taken into account. When the charges under the first peak, K_1 , and the second peak, K_2 , were added together, the sum of $\approx 197 \cdot 10^{-6} As cm^{-2}$ was very close to the charge needed for a close packed thallium layer (again taking a roughness factor into account).

In the case of the second set, the two peaks (both cathodic and anodic) were merged to such an extent that only their combined characteristics could be obtained. The charge was measured, but even this cannot be taken as the total value because the current of the second peak had not fallen to zero before the onset of thallium bulk deposition.

REFERENCES

- 1.- Thomas, B., Ph.D. Thesis, University of Southampton 1976.
- 2.- Jovićević, J.N., Ph.D. Thesis, University of Southampton 1978.
- 3.- Bewick, A., Jovićević, J.N., Thomas, B., Trans. Faraday Disc., 12 (1977) 24
- 4.- Thomas, B., Bewick, A., J.Electroanal. Chem., 65 (1975) 911.
- 5.- Thomas, B., Bewick, A., J.Electroanal. Chem., 70 (1976) 239.
- 6.- Thomas, B., Bewick, A., J.Electroanal. Chem., 84 (1977) 127.
- 7.- Jovićević, J.N., Bewick, A., Univ. Thought, Vol.IV(2) (1997) 29, Pristina.

- 8.- Jovićević, J.N., Bewick, A., Univ. Thought, Vol.IV(2) (1997) 39, Pristina.
- 9.- Jovićević, J.N., Bewick, A., Univ. Thought, Vol.IV(2) (1997) 51, Pristina.
- 10.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 11.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 12.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 13.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 14.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 15.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 16.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 17.- J. N. Jovićević, V. D. Jović, A. R. Despić: "The influence of adsorbing substances on the lead UPD onto (111) oriented silver single crystal surface - Part I", *Electrochim. Acta*, 29, 1625 (1984).
- 18.- V. D. Jović, J. N. Jovićević: "The influence of adsorbing substances on the UPD of lead onto the (111) oriented silver single crystal surface - Part II", *Electrochim. Acta*, 30, 1455 (1985).
- 19.- Meites, L.: "Polarographic Techniques", 2nd edition, Interscience, New York (1965).110tl
- 20.- Pinner, R., *Electroplating*, October and November (1953) 360, 401.

REZIME

STUDIJA POČETNOG STADIJUMA ELEKTRO-TALOŽENJA TALIJUMA NA BAKRU - III DIO
PONAŠANJE BAKARNE ELEKTRODE KRISTALOGRAFSKE ORIJENTACIJE (100) PRI LINEARNOJ CIKLIČKOJ PROMJENI POTENCIJALA

JOVIĆEVIC¹ N. Jovan, BEWICK Alan
Chemistry Department, Southampton University,
UK, SO9 5NH
¹Sadašnja adresa: Odsek za hemiju, PMF, Univerzitet
u Prištini, 38000 Priština, Jugoslavija.

Ovo je treći iz serije radova u kojima se iznose rezultati istraživanja početnih stadijuma elektrotaloženja talijuma (iz acetatnih, sulfatnih i perhloratnih rastvora) na polikristalnom i monokristalnom bakru.

Rad predstavlja rezultate dobijene linearnom cikličnom promjenom potencijala (L.S.V.) bakarne monokristalne elektrode površinske orientacije (100) u području potencijala pozitivnijih od reverzibilnog potencijala talijuma u datoj sredini.

Još jednom se uvjerljivo pokazalo da je pažljivo i uspješno poliranje površine radne elektrode od najvećeg značaja pri ispitivanjima područja potencijala

pozitivnijih od reverzibilnog potencijala taloženja/rastvaranja ispitivanog metala, ukoliko se žele dobiti pouzdani kvantitativni i kvalitativni podaci.

Elektrotaloženja talijuma na bakarne monokristalne površine kristalografske orientacije (100) tehnikom cikličke voltametrije otkrivaju po dva odvojena para katodnih (i komplementarnih anodnih) strujnih talasa međusobno udaljenih više od 150mV. Potencijali vrhova tih talasa zavisni su od brzine promjene potencijala i od koncentracije talijuma u upotrebljenom elektrolitu.

Prvi par katodnih strujnih talasa K₁ i K₂ (i komplementarnih anodnih strujnih talasa A₁ i A₂) javlja se pri anodnijim potencijalima u odnosu na reverzibilni potencijal talijuma u posmatranoj sredini. Na osnovu oblika promjene gustine struje sa potencijalom, na osnovu razlike od preko 50mV u potencijalima vrhova komplementarnih katodnih i anodnih talasa i na osnovu količine razmijenjenog naielektirisanja koje predstavljaju, prvi talas (K₁) najvjerovatnije odražava proces formiranje kristalne najgušće pakovane epitaksijalne talijumove 2D strukture na Cu(100) podlozi mehanizmom višeg reda fazne transformacije. Drugi katodni talas, K₂, najvjerovatnije predstavlja faznu transformaciju višeg reda tog epitaksijalnog monosloja u kristalnu gusto-pakovanu dvodimenzionu strukturu talijuma koja je donekle poremećena pod uticajem oblika bakarne monokristalne podloge. Do ovoga dolazi zbog promjene slobodne energije predhodnog epitaksijalnog monosloja na potencijalima talasa K₂, koja izaziva dodatno taloženje talijuma radi kompletiranja za te uslove stabilnije dvodimenzionalne konfiguracije talijumovog kristalnog gusto-pakovanog monosloja. Oblik i položaj komplementarnog anodnog para A₁ i A₂ (koji predstavljaju procese rastvaranja struktura predstavljenih sa K₁ i K₂), potvrđuju ovakve pretpostavke, pogotovo kada se uzmu u obzir zavisnost potencijala vrhova talasa od koncentracije talijuma u upotrebljenim rastvorima i njihovi međusobni odnosi.

Drugi par katodnih strujnih talasa, K₃ i K₄ (i njima komplementarnih anodnih talasa A₃ i A₄), po obliku i karakteristikama, veoma su slični prvome paru (K₁, K₂, odnosno A₁, A₂), te se formiranje drugog monosloja talijuma pri potencijalima pozitivnijim od reverzibilnog potencijala talijuma u datoj sredini najvjerovatnije odigrava na isti način kao i prvi monosloj. Međutim, detaljna analiza mehanizma formiranja ovo-ga drugoga monosloja onemogućena je činjenicom da se primjenjenom tehnikom ne može napraviti razlika između dva strujna talasa koji čine ovaj par, niti se može napraviti razlika između trenutka kada nastupa kraj formiranja monosloja i trenutka kada započinje elektrotaloženje talijuma uz katodne prenapetosti.

Received: March, 1998.

Accepted: April, 1998.

KOSOVO LIGNITE AS THE RAW MATERIAL FOR PRODUCTION OF AMMONIUM-NITRO-HUMATE

Milena Petrović¹ and Petar Petrović² 1 The faculty of science and Mathematics, Priština 2 The Faculty of science of Economics, Priština

ABSTRACT

Four samples of Kosovo lignite from different localities were examined for the purpose of pointing out possibilities of its application in production of ammonium-nitro-humate. On the basis of the results of technical analysis, determini-

nation of humic acids content and elementary analysis we have concluded that the lignite from the surface excavation site „Dobro Selo“ is the most suitable raw material for production of ammonium-nitro-humate.

Key words: ammonium-nitro-humate, humic acids, extraction.

INTRODUCTION

Kosovo coal basin is an enormous raw material base in our country, with favourable mining-geological conditions. They enable usage of contemporary mechanization for surface digging up of coal. Thus the basin is of a great importance, firstlz for production of capacities of electrical energy and also for development of some chemical industry branches.

The lack of organic fertilizers in our country imposes a question of production of humus-mineral fertilizer based on the coal, having in mind the fact that for a long time positive effect of coal scraps to fertility of the soil i. e. their stimulative effect to growth and development of plants has been noticed.

Former examination of possibilites in applying Kosovo lignite in agriculture (Djokić and Mitrović, 1968, Petrović, 1978, Petković, 1983, Petrović et al., 1997) has shown that Kosovo lignite as well as the products obtained by its processing can be used as raw material base for production of organic-mineral fertilizer.

So the purpose of our work was to examine the samples of Kosovo lignite from different localities. And on the basis of the results of technical analysis, determination of humic acids content and elementary analysis to estimate what lignite sample is the most suitable raw material for production of ammonium-nitro-humat.

MATERIAL AND METHODS

We have selected to examine four samples of Kosovo lignite from different localities as follows:

1. the lignite from the surface excavation site "Dobro Selo", position 401, eastern shaft, elevation 407, floor II.
2. the lignite from the surface excavation site "Belačevac", position 103, elevation 489, floor II.
3. the lignite from the hole in the middle part of Kosovo basin elevation 161-166, and
4. the lignite from the hole in the middle part of Kosovo basin elevation 268,0-272,0.

The lignite was firstly ground then sifted so that granulation was max. 0,1, afterwards. Such prepared lignite was used in all of our research examination.

Technical analysis of raw lignite: determination of humidity ash, sulphur, volatile substances, combustion substances, coke, C-fix and thermal values. Classic laboratory analisys used. Results are given in table 1.

Chemical analysis: ash content for quality and quantity was determined. Results are given in table 2.

Humic acids content in the examined lignite samples was determined by extraction of humic acids in 1 M sodium-hydroxide solution then extraction was repeated with more diluted solution of sodium-hydroxide (0,5 and 0,1 M) with water rinsing until the extract became light brown and clear. When the unsoluble part of lignite was separated, humic acids from extracts were settled by making then sour to pH 2 with hydro-chloric acid. Filtrat was separated from humic acids by centrifugation. Humic acids were dried at 105OC. Results are given in table 3.

Elementary content was determined in all the four samples. Carbon and hydrogen content was determined by dry combustion method as per Pregl, nitrogen -per Dumas and sulphur -per Schoninger, while oxygen was determined by calculation. Results are given in table 4.

GRATITUDE: We thank Ministry of Science and Technology of Republic of Serbia for material help to make this work.

RESULTS AND DISCUSSION

Results of technical analysis of lignite samples as given in table 1 show all samples of lignite having high content of humidity. A bit greater humidity content was found in the lignite of "Belačevac" site although it ranges in the limits of the average for Kosovo basin. The samples of lignite from the holes are of considerably less content of humidity than those from surface excavation sites.

Tab. 1 - Technical analysis of raw lignite

	"Dobro Selo"	"Belaćevac"	The hole 3	The hole 4
Humidity, %	43,87	45,70	24,52	31,70
Ash, %	19,59	11,48	27,35	22,51
Coke, %	33,03	19,56	45,27	39,15
C-fix, %	13,44	19,56	17,92	16,64
Volatile matters, %	23,10	23,36	30,21	29,15
Combustion matters %	36,54	42,82	48,13	45,79
LTP, KJ/kg	7079	9051	10720	9980
S (total), %	0,90	0,73	1,22	1,37
S (in ash), %	0,74	0,60	1,01	1,02
S (combustible), %	0,16	0,13	0,21	0,35

Regarding ash content the lignite from "Dobro Selo" site is classified into the third class, the lignite from "Belaćevac" site into the first class and the lignite from the holes in the fourth class of Kosovo basin. The ash of samples is of light red colour showing presence of ferric oxides. Differences in ash content are probably in connection with genesis of the coal itself i.e. with conditions under which accumulation of original material happened.

The samples of lignite contain relatively small amount of volatile substances, which is on the contrary to the rule that younger kinds of coal contain greater amount of volatile substances, while the coals of higher carbonification level contain less amount of volatile matters. Both lignite samples from the holes had greater content of volatile components than those samples from surface excavation sites.

Higher percentage of combustion substances shows the better quality of the lignite from "Belaćevac" and from the holes in comparison with those from "Dobro Selo".

Coke or coke remiat is the hard remiat which is obtained after separation of volatile matters. It includes organic matter, ash and a part of the remaining volatile substances. The sample from "Belaćevac" has the least content of coke.

On the basis of results for coke and ash content the content of linked carbon, C-fix was calculated i.e. coke without ash having the highest content in the samples of lignite from "Belaćevac".

Lower thermal power in the lignite sample from "Dobro Selo" is considerably less than the one from "Belaćevac" and especially than those from the holes. When content of combustion substance is compared with values of the lower thermal power direct proportionality can be seen. The same depandance is obtained when content of C-fix values is comared with lower thermal power.

Regarding the total sulphur content the sample from "Belaćevac" belongs to more qualitative coal in comparison with the other examined samples of lignite.

Relatively low values for combustible sulphur show that the greatest quantites of sulphur are found in the ash i.e. in the mineral components.

Results of technical analysis show that the examined samples of lignite are found at the low carbonification level belonging to the kind which is at the transition between soft brown and brown lignite bearing coals. The samples of lignite from "Belaćevac" and from the both holes are richer in content of combustion substances and thermal values than those from "Dobro Selo" thus having certain advantages as energetic material. On the other side the sample of lignite from "Dobro Selo" belongs to the coals of less maturity level thus having certain advantage as potential raw material for production of organic-mineral fertilizers.

Results of chemical analysis of ash in the examined samples of lignite given in table 2 show that CaO and SiO₂ prevail in all the examined samples: Al₂O₃, Fe₂O₃ and MgO are present in less extent while presence of other oxides is much less.

Tab. 2 -Chemical analysis of ash

Components, %	"Dobro selo"	"Belaćevac"	the hole 3	The hole 4
Si O ₂	32,95	30,16	33,81	31,49
CaO	38,76	35,81	32,87	32,94
F ₂ O ₃	6,02	8,28	9,11	9,45
Al ₂ O ₃	7,86	7,04	9,80	8,92
MgO	2,57	4,31	3,08	3,68
SO ₃	8,90	10,61	9,23	11,32
MnO	0,22	0,18	0,19	0,21
Na ₂ O	0,44	1,94	0,66	0,76
K ₂ O	0,53	0,57	0,49	0,61

Results of determination of humic acids content were calculated for lignite with total humidity and ash (t.h.a.), for lignite without humidity (w.h.) and for lignite without humidity and ash (w.h.a) are given in table 3.

Table 3 -Results of determination of humic acids content

Lignite	t.h.a., %	w.h., %	w.h.a., %
"Dobro selo"	17,09	30,46	46,79
"Belaćevac"	8,44	13,12	19,71
The hole 3	13,06	17,19	27,12
The hole 4	12,69	19,15	28,57

Table 3 shows that humic acids content in the sample of lignite "Dobro Selo" is as follows: calculated for the lignite with total humidity and ash -17,09%, calculated for the lignite without humidity and ash - 46,79%. Considerably less amount of humic acids was extracted from the lignite samples of the holes 3 and 4 and especially from the lignite of "Belaćevac". On the basis of results for determination of humic acids content it can be concluded that the lignite from "Dobro Selo" has advantage for production of organic-mineral fertilizers in comparison with the other examined samples.

Results of elementary analysis of lignite given in table 4 show that elementary composition in all the four samples of lignite ranges within the limits usual for younger kinds of coals. The lignite from "Dobro Selo" contains the least amount of carbon and is therefore the poorest energetic material of all the examined samples.

Table 4 -Elementary components of lignite, in mass %

Lignite	C	H	N	S	O	Ash
"Dobro selo"	59,35	6,22	0,93	0,41	33,09	19,59
"Belaćevac"	61,02	5,35	0,87	0,31	32,45	11,48
The hole 3	61,98	6,03	0,98	0,47	30,54	27,35
The hole 4	59,85	5,70	1,06	0,53	32,86	22,51

CONCLUSION

While examining the four samples of lignite from different localities with the purpose of showing possibility of their application in producing ammonium-nitro-humate we have concluded the following:

1. The examined samples of lignite belong to the coals of low carbonification level and at the transition between soft brown and brown lignite bearing coals.

2. The samples of lignite from the surface excavation site "Belaćevac" and from the holes of the middle part of coal layer of Kosovo basin are richer in carbon and thus they are more qualitative as energetic material than the samples of lignite from the surface excavation site "Dobro Selo".

3. During extraction of humic acids from the samples of lignite "Dobro Selo" 46,79% of humic acids were extracted calculated for lignite without humidity and ash and considerably less amount of humic acids was extracted from other examined samples.

4. Compared with other examined samples of lignite, the lignite from the surface excavation site "Dobro Selo" is the most suitable raw material for production of ammonium-nitro-humate.

REFERENCES

Djokić, M., Mitrović, M (1968): Amonizacija lignita iz basena Kosovo, Rudarski institut, Beograd.

Petrović, P. (1978): Prilog proizvodnji huminskih djubriva na bazi kosovskog lignita, Doktorska disertacija, Univerzitet u Beogradu, Beograd.

Petković, D. (1983): Razvoj tehnološkog postupka dobijanja stimulatora rasta biljaka na bazi ekstrakcije lignita, Doktorska disertacija, Univerzitet u Beogradu, Beograd.

Petrović, M., Jablanović, M., Petrović, P. and Milićević, Z. (1997): The University Thought, 4, 1, (61-64).

REZIME

KOSOVSKI LIGNIT KAO SIROVINA ZA PROIZVODNJU AMONIJUM-NITRO-HUMATA

Milena Petrović¹ i Petar Petrović² 1 Prirodno-matematički fakultet, Priština 2 Ekonomski fakultet, Priština

Četiri uzorka kosovskog lignita, sa različitim lokalitetima, ispitivani su s ciljem da se ukaže na mogućnost njegove primene za proizvodnju amonijum-nitrohumata. Na osnovu rezultata tehničke analize, određivanja sadržaja huminskih kiselina i elementarne analize došli smo do sledećih konstatacija: 1. Ispitivani uzorci lignita pripadaju vrsti ugljeva niskog stepena karbonifikacije i na prelazu su između mekih mrkih i mrkolignitskih ugljeva. 2. Pri ekstrakciji huminskih kiselina sa površinskog kopa "Dobro Selo" ekstrahovano je 46,79% huminskih kiselina, obračunato na lignit bez vlage i pepela a iz ostalih ispitivanih uzoraka znatno manja količina huminskih kiselina. 3. Lignit sa površinskog kopa "Dobro Selo" je, od svih ispitivanih uzoraka lignita, najpogodnija sirovina za proizvodnju amonijum-nitro-humata.

Received: May, 1998.

Accepted: June, 1998.

MORPHOGRAPHIC SURVEY OF RELIEF STRUCTURE AND INTERNAL REGIONAL-GEOGRAPHIC CLASSIFICATION OF KORITA

ALIBAŠIĆ Safeta, assistant at the Department for geography,
Faculty of Sciences and Mathematics in Pristina

Abstract:

This survey focuses on the regional-geographic classification of Korita on the basis of the relief structure. Applying the principle of a

unique relief structure type a few entities included on relief of this high plateau are singled out.

Key words: Regional classification.

Introduction

Korita is situated on the north- east part of the community Bijelo Polje, and it got its name because of trough shape of the relief of the whole area.

This rather specious, clearly individual limestone plateau, is morphologically differentiated from the neighboring areas / Pester Plateau to the north- east, Gornji Bihor to the south- east and Donji Bihor to the west/ 1,130/. The area of Korita is, as we already stated in the previous study grooved by dry valleys and hollows in the direction of SE-NW, which is also the direction of is sloping/ towards Bistricka i.e. Djalovska gorge/. Regarding the internal relief structure, Korita plateau is characterised by the three dry trough-shaped valleys in SE-NW direction. They occupy southeast and southwest part of Korita, and in the middle/ between them/ is a so-called central plateau of Korita.

Methods

For a treatment regionally- geographical differentiation of Korita, the methods of unique type of the relief structure are applied, which are conditionally homogeneous.

Results and discussion

Regional-Geographic Classification of Korita

Applying the principle of a unique relief structure type with aim of evaluating conditionally homogeneous regional-geographic differentiation/ 2,409-416 and 13-28/ of Korita, it is possible to single out several entities that are encompassed into relief of this high plateau area, and which are of the crucial importance in shaping global appearance of the natural landscape. Applying this principle, the following entities of the internal regional-geographic structure of Korita have been singled out:

- 1.Licinska valley
- 2.Lazovska-Dupljacka-Djalovska valley

3.Central Koritas plateau

4.West Koritas area

5.Mountain frame

This survey (3,26) presents for the first time in our regional geography literature a concept of internal regionalisation of Korita. According to this concept relief structure is of a primary importance (Fig. 1).

These entities have micro-relief and microclimatic-ecological characteristics, which is obviously shown through the main types of pedologic and micro- vegetation blanket.

The main characteristics of each regional geographic entities of Korita will be presented in the following text.

1.Licinska valley is named after the village of Licina, the notion of valley covering wider area. We can study it in the narrower or wider sense. According to our opinion, the valley in the narrower sense deserves more attention due to several reasons. Under this notion, Licinska valley is an area starting south D east of the village Licina and ending to the northwest, with the widening of Milovo Polje ,edging with area of Kosmatica. Spreading direction of this valley is SE-NW. Licinska valley is framed by areas of Homar, Ostra Glava, Kosa, Vrance, Ostronosa, Kosmatica i Crni Vrh. The valley has a wide flattened bottom (cc. 100-150 m) with the gently sloping concave sides. The valley drop is low as a result of its well advanced morphologic evolution.

Water is present only in the southeast part, where the river Licinska springs at the foot of the Begluk mountain and periodically runs (depending on meteorological conditions) all the way to the abyss Jama to the north edge of Milovo Polje were it sinks and reappeared in Bistricka gorge. Consisting amount of water the Licinska river gets from the spring of Licina situated close to the river Licinska in the village of Licine.In this valley there is only one settlement under the name of Licine.

2.Lazovska-Dupljacka-Djalovska valley in the regional-geographical sense represents

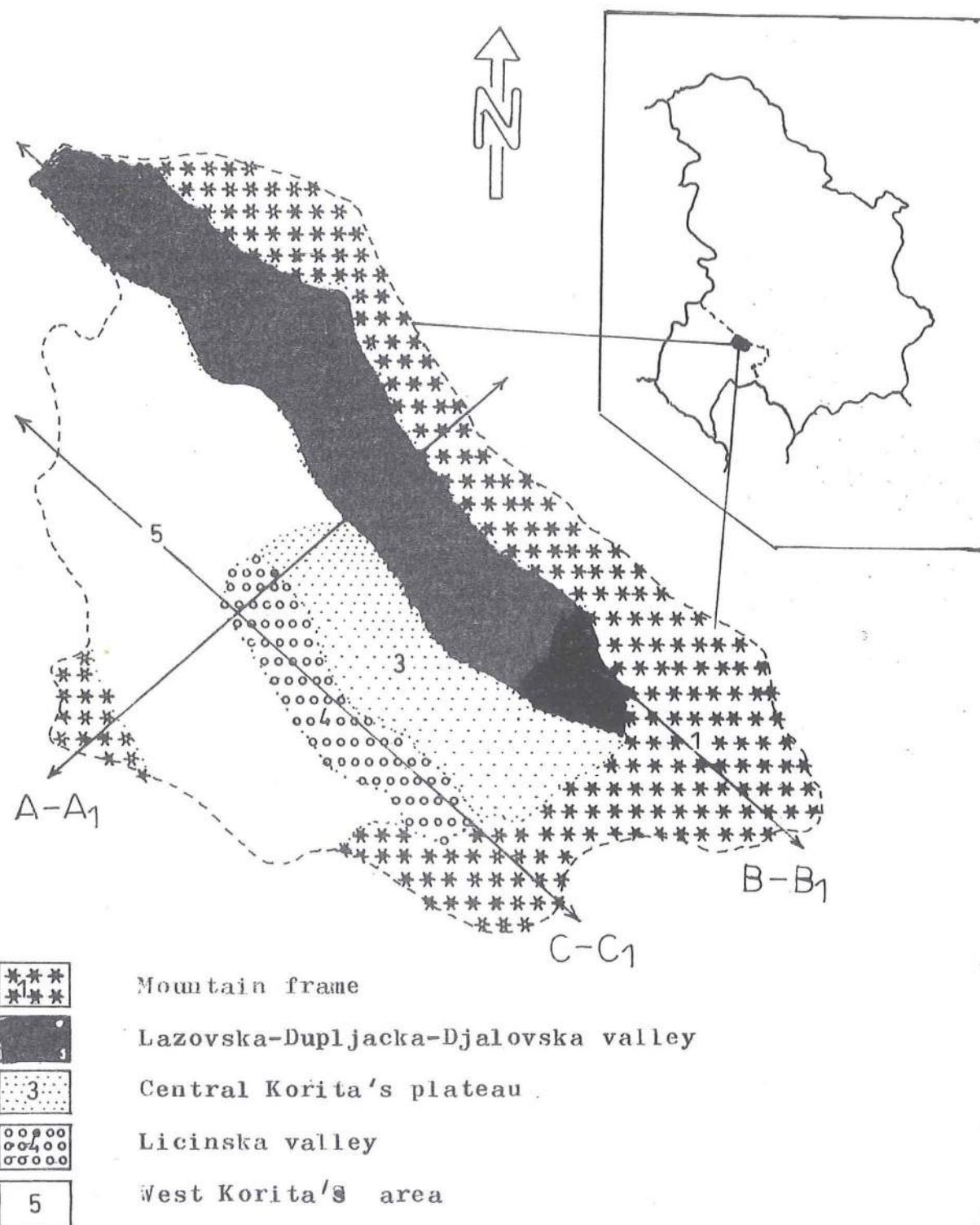


Fig. 1. INTERNAL REGIONAL STRUCTURE OF KORITA

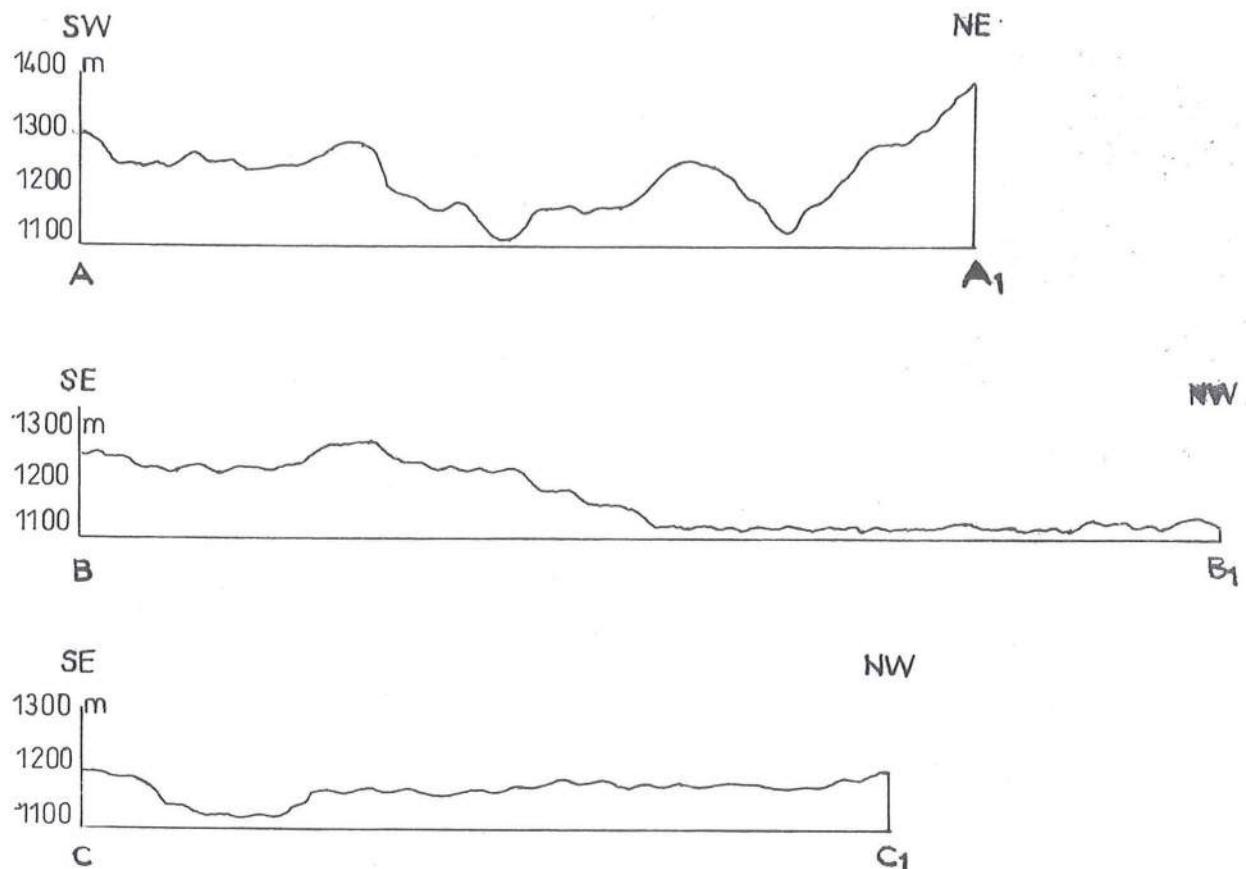


Fig. 2. MORPHOLOGICAL PROFILE OF THE KORITAS PLATEAU

A-A₁ – morphological profile of Korita SW-NE

B-B₁ – morphological profile of Lazovska-Dupljačka-Djelovska Valley SE-NW

C-C₁ – morphological profile of Licinska valley and Central plateau

a uniform valley area, as it is treated in this survey. However, our viewpoint is that these are two interconnected karst valleys (Lazovka to the south-east and Djelovska-Dupljacka to the north-west), separated by a low limestone threshold to the south of village Dupljaci.

(a) **Lazovska valley** is located to the south-east of Lazovic village in the southeast – southwest direction. At Milovo Polje this valley merges with Licinska valley. In this valley there is the Susica brook that springs at the foot of Tutnji hill, close to Lazovici village. For 3 km from its source it runs over the surface and then sinks and most probably merges with the Licinska river in the abyss of Jama close to Milovo Polje. In this valley Lazovici village and the hamlet Susuca are located.

(b) **Dupljako-Djelovska valley** spreads south-east from Dupljaci village to Bistricka (Djelovska) gorge in the southeast-northwest direction. It occupies the north part of Korita to the west of Vrhovi and to the south of Sneznica and east of Maljevsko Polje high plateau. Its flattened bottom is 60-

130m wide with a gently sloping concave sides. There are two settlements in this valley (Lazovci and Djelovici) and one hamlet (Campari).

All the three valleys (Licinska, Lazovska and Dupljacka-Djelovska) have got the same spreading direction, the same geological structure, similar physiognomy and morphology.

3. Central Korita's plateau is a uniform area spreading between Lazovska-Dupljacka-Djelovska and Licinska valley. It has characteristics of the limestone plateau of more than 1.200 m in high, and is represented with a typical karst surface like Vrcane (south-west of Lazovici, north-east of Licina). Both Central Korita's plateau area and Licinska valley are considered in narrower sense, although in the wider sense Petrovo Brdo and Maljevac can be included in this area. However we decided to include highly karsted Maljevicko Polje together with highly karsted areas to the west, into a uniform area entitled West Korita's area. Southeast parts of the Central Korita's plateau (Vrcane area) have characteristics of a typical rocky ground with a number of depressions with a sporadic appearances of hard karst. It is worth

noting that majority of Central Korita's area is deforested, with the exception of Crni Vrh, with a mixed coniferous and deciduous vegetation.

4. West Korita's area covers west part of Korita, characteristic uniform karst area of 1.200m in high. West Korita's area is a uniform high plateau composed of several area: Koprivna, Kosi, Mladenovci, Ostrotrone, Kosmatica, Gradac, etc. In the west of Korita area are a few spacious hollows where the following settlements are located: Sipanje, Negobratina and Sipovica. With a view at the economy, this area is better valorized because the large part of it is covered with meadows and pastures, but it lacks water significantly.

5. Mountain frame to the west, east and south, morphologically individualizes the plateau of Korita. It is separated from Pester by: Katuniste, Sneznica, Vrhovi, Zilindar, Ugljanski Krs and Moravacki Krs. These are mountains with relative high from 1.300 to 1.600m, with highly developed karst relief and in most parts deforested. The mountain frame towards Gornji Bihor / the Lesnica river basin / is composed by: Moravacki Krs, Ostra Glava, Begluk and Nikin Krs, and in the direction of Gornji Bihor: Paljevine, Venac, Gvozd and Dijelovi. In the natural valorization, the best utilized mountains Kruscica and Moravac, with the forms of traditional cattle breeding economy, are used not only by cattle breeders from Korita, but also from Pester and Gornji and Donji Bihor and even from Metohija (Fig. 2).

Conclusion

According to this, it can be said that Korita is a part of a unique complex of Dinaric-Karst area, without constant river courses, cruel climate and strong wind during the whole year.

REFERENCES

1. Lutovac V.M. Bihor and Korita, Serbian Ethnographic Proceedings, LXXXI Book, Serbian Academy of Science and Arts, Beograd, 1967.

2. Rogic V. Regionalisation of Central Mountains Area of Yugoslavia, Proceedings from IX Congress of Yugoslav Geographers, Sarajevo, 1974.

3. Rogic V. Regionalisation of Yugoslavia. Geografski glasnik, No. 35. Zagreb, 1973.

4. Alibahic S. Regional-Geographic Studies of Korita /master work/, Postdiplomski Studij Prirodnih Znanosti, područje Geografija, Zagreb, 1991.

REZIME

MORFOGRAFSKI PRIKAZ RELJEFNE STRUKTURE I INTERNA REGIONALNO-GEOGRAFSKA PODELA KORITA

ALIBAŠIĆ Safeta Asistent, PMF, Odsek za geografiju, Vidovdanska bb, 38000 Priština, Jugoslavia

Uzimajući u obzir internu reljefnu strukturu, Koritu karakterišu tri suve koritske doline smera JI - SZ.

One zauzimaju severoistočni i jugozapadni deo Korita, a u sredistu / izmedju njih / pruža se central-nokoritski plato.

Primenom metode jedinstvenog tipa reljefne strukture, izdvojeno je nekoliko celina ovog visokopovrskog prostora.

To su:

1. Ličinska dolina
2. Lazovsko-Dupljacko-Djalovska dolina
3. Centralnokoritski plato
4. Zapadnokoritska površ
5. Planinski okvir (Fig. 1, Fig. 2).

Received: November, 1998.

Accepted: December, 1998.

THE YUGOSLAV PART OF SAR-PLANINA MT. LAKE ECO-SYSTEM'S PERIPHERYON ALGAE

UROSEVIC Violeta Faculty of Sciences and Mathematics, University of Pristina, Vidovdanska bb,
38000 Pristina, Yugoslavia

ABSTRACT

The paper presents the results of the periphyton algae research in 19 lakes of the Yugoslav part of Sar-planina Mt. The research was made within the period of 1984 to 1998, in the lakes, as follows: glacial - 13, nivational - 4, and solifluctual - 2. Some 541 taxa were determined in these lakes, as follows: Cyanophyta - 54, Pyrro-

phyta - 4, Chrysophyta - 2, Bacillariophyta - 273, Xanthophyta - 4, Euglenophyta - 11, and Chlorophyta - 196.

The differences existing in the vegetation and flora between the glacial and nival lakes were determined. Bacillariophyta representatives dominated in glacial lakes, while Chlorophyta in the nival ones, respectively.

INTRODUCTION

Republic of Serbia represents a real natural resource regarding the waters. The respective, first of all, refers to non-polluted, potable and healthy waters, not often present in many other countries, long time ago already. Diverse healing waters of many spas, hot and cold, mineral were already used by Romans. Even nowadays, Serbia abounds in rivers rich in waters, in clear mountain creeks, in springs, in geysers and waterfalls. The lakes occupy a special position, as these are significant water resources. Vlasinsko Lake has been, at present, the most research one, and was described by the group of authors (Blazencic ed., 1987).

A special group of 19 lakes, located on the Serbian part of Sar-planina Mt. has been researched, since 1984 up to present time (Urosevic, 1994, 1994 a, 1997 a, 1997 b, 1997 c, 1998).

THE SAR-PLANINA Mt. GENERAL CHARACTERISTICS

Sar-planina Mt. is located at the border between Macedonia, Albania and Serbia. Its bordering zone is the Lepenac River and Ljuboten mountain peak at east, while, Mavrovo Lake at southeast. It spreads along the mountain crest in a length of 83-km (Figure 1). Sar-planina Mt. is classified within young mountains (Tertiary), formed during Alpine Oro-genesis, and is still under the process of corrugation.

From the geologic aspect, Sar-planina Mt. is made of crystal schist and marble, including its famous Ljuboten marble board. Its pedological composition: 20 soil types.

A special significance is given to its abundant flora and fauna. Its 140 lakes (Cukic, manuscript), of which, 19 were researched by the team, could be divided in three groups:

I - Glacial (glacier erosion): 1. Veliko Jazinacko Lake (2,128 m/as/l), 2. Mali Vir Lake 1 (2,160 m/a/s/l), 3. Mali Vir Lake 2 (2,159 m/a/s/l), 4. Malo Jazinacko

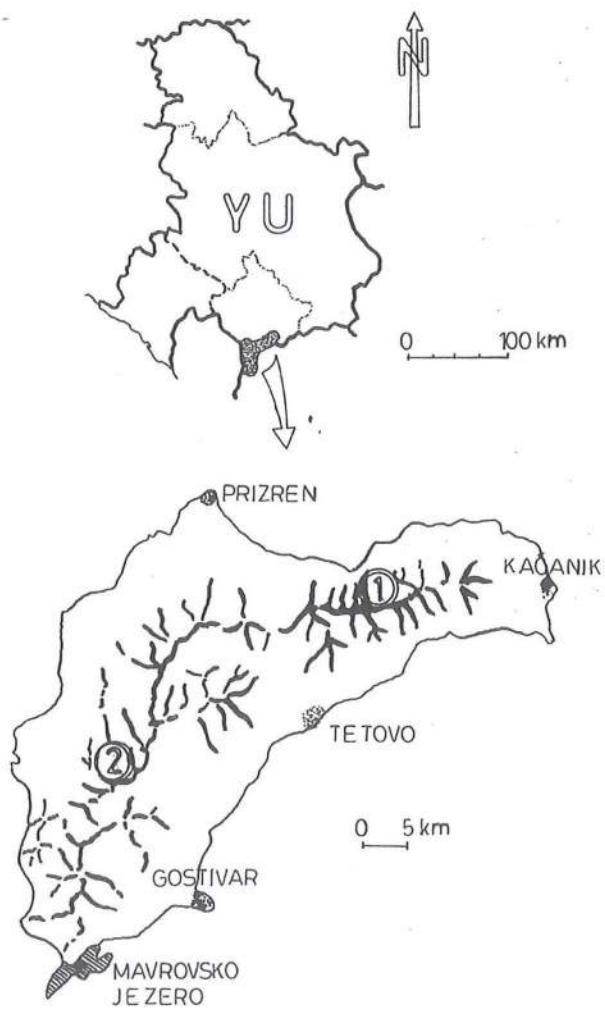


Fig. 1

Lake (2,220 m/a/s/l), 5. Veliki Vir Lake (2,345 m/a/s/l), 6. Gornje Blatesticko Lake (2,215 m/a/s/l), 7. Srednje Blatesticko Lake (2,210 m/a/s/l), 8. Donje Blatesticko Lake (1,950 m/a/s/l), 12. Livadicko Lake (2,173 m/a/s/l), 15. Donje Veljinbesko Lake (2,085 m/a/s/l), 16. Srednje Defsko Lake (2,080 m/a/s/l), 17. Gornje Ginevodno Lake (2,250 m/a/s/l), and 18. Srednje Ginevodno Lake (2,250 m/a/s/l).

II - Nival (nev  erosion): 9. Gornja Sija Lake 1 (1,860 m/a/s/l), 10. Gornja Sija Lake 2 (1,860 m/a/s/l), 11. Mekus Bor Lake (1,840 m/a/s/l), 19. Gornje Veljinbesko Lake (2,110 m/a/s/l).

III - Solifluctional lakes (between glacial and nival): 13. Gornje Tupankamensko Lake (1,950 m/a/s/l), and 14. Donje Tupankamensko Lake (1,560 m/a/s/l).

THE PAPER RESULTS AND DISCUSSION

The periphyton alga research was made within the period of 1984 to 1998 at 19 lakes of Sar-planina Mt. Some 541 taxa were determined in these lakes, as follows: Cyanophyta - 54, Pyrrophyta - 4, Chrysophyta - 2, Bacillariophyta - 273, Xanthophyta - 4, Euglenophyta - 11, and Chlorophyta - 196 (table 1).

Table 1.

Species	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
C Y A N O P H Y T A																			
Anabaena affinis LEMM.															+				
Anabaena flos-aquae BRÉB.															+			+	
Anabaena sp.														+					
Aphanothecæ globosa ELENK.							+												
Aphanothecæ stagnina (SPRENG.)																			
B. PETERS. et GEITL.						+									+				
Calothrix parietina THURET.					+	+	+	+						+					
Calothrix sp.																+			
Chamaesiphon incrassans GRUN.								+											
Chamaesiphon polymorphus BR. et GR.							+												
Chroococcus helveticus NAG.													+	+					
Chroococcus minor (KTZ.) HOLERB.																			
Chroococcus limneticus (KTZ.) HOL.						+									+				
Chroococcus sp.								+											
Coelosphaerium kützingianum NÄG.														+					
Coelosphaerium proboscideum BOHL.														+					
Dactylococcopsis raphidoides HANS.																			
Dichothrix gypsophylla KTZ.								+											
Gloeocapsa gigantea (W. WE.) HOLL.							+												
Gloeocapsa rupestris KTZ.							+												
Gloeocapsa turgida (KTZ.) HOLL.							+							+					
Gloeocapsa sp.							+												
Haplosiphon sp.																			
Hydrocoleus brebissonii KTZ.								+											
Microcystis aeruginosa KTZ.															+				
Microcystis aeruginosa f. marginata (MENECH.) ELENK.														+					
Microcystis elabens MENECH.																			
Microcystis marginata (MENECH.) KTZ.								+	+										
Microcystis sp.								+											
Microcystis sp.																+			
Merismopedia elegans A. BR.									+	+									
Merismopedia punctata MEYEN.					+	+													
Merismopedia tenuissima LEMM.																			
Nostoc disiforme FRITSCH.																			
Nostoc linckia FREMY																+			
Nostoc kihlmannii LEMM.														+	+	+			
Nostoc palidosum KTZ.														+	+	+			
Oscillatoria geminata (MENECH.) GOM														+	+				
Oscillatoria princeps VAUCH.																			
Oscillatoria splendida GREV.																			
Oscillatoria terbriformis (AG.) ELENK.																			
Phormidium ambiguum GOM							+												
Phormidium autumnale (AG.) GOM.									+	+	+	+	+						
Phormidium favosum GOM.									+	+									
Phormidium papuraceum GOM.									+										
Phormidium uncinatum																			
Phormidium sp.									+										
Phormidium sp.														+					

Species	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
<i>Scytonema mirabile</i> AG.	+													+					
<i>Symploca mucorum</i> (AG.) GOM..	+													++					
<i>Synechococcus aeruginosa</i> NAG.																+			
<i>Spirulina</i> sp.					+													+	
<i>Stigonema ocellatum</i> (DILLV.) THUR.	+				+														
<i>Stratonostoc linckia</i> (ROTH.) BORN.					+														
<i>Tolypothrix tenuis</i> f. <i>lanata</i> (WARTM.) KOSSINSK.					+														
P Y R R O P H Y T A																			
<i>Gleodinium</i> sp.																		+	
<i>Peridinium cinctum</i> EHR.										+									
<i>Peridinium palustre</i> (LIND.) LEFR.																		+	
<i>Peridinium villei</i> (HUITF.) KASS.																		+	
C H R Y S O P H Y T A																			
<i>Chrysopyxis</i> sp.										+									
<i>Hydrurus phoetidus</i> (VILL.) TREV.																		+	
B A C I L L A R I O P H Y T A																			
<i>Achnanthes coarctata</i> BRÉB.	+	+	+	+	+	+	+												
<i>Achnanthes lanceolata</i> (BREB.) GRUN.										+	+	+							
<i>Achnanthes lanceolata</i> f. <i>capitata</i> O. MÜLL.										+									
<i>Achnanthes lanceolata</i> f. <i>ventricosa</i> HUST.										+									
<i>Achnanthes lanceolata</i> var. <i>rostrata</i> (ØSTR.) HUST.										+									
<i>Achnanthes laterostrata</i> HUST.																			
<i>Achnanthes minutissima</i> var. <i>cryptocephyla</i> KTZ.																			
<i>Achnanthes trinodis</i> (W. SM.) GRUN.										+++									
<i>Amphora ovalis</i> KTZ.	+		+							++				++					
<i>Amphora ovalis</i> var. <i>pediculus</i> KTZ.																			
<i>Amphora veneta</i> KTZ.																			
<i>Amphora</i> sp.																			
<i>Amphora</i> sp.																			
<i>Anomoeoneis seriana</i> var. <i>brachysira</i> (BRÉB.) HUST.										+									
<i>Anomoeoneis styriaca</i> (GRUN.) HUST.										+									
<i>Anomoeoneis zellensis</i> (GRUN.) CL.	+	+	+																
<i>Caloneis alpestris</i> (GRUN.) CL.	+	+								++									
<i>Caloneis bacillum</i> (GRUN.) MER.	+									++	+								
<i>Caloneis silicula</i> (EHR.) CL.	+	+	+	+	+	+	+	+	+				+	+					
<i>Caloneis silicula</i> var. <i>alpina</i> CL.	+	+	+	+															
<i>Caloneis silicula</i> var. <i>major</i> GRUN.														+	+				
<i>Caloneis silicula</i> var. <i>longissima</i> SCHIRSCHOW.																+			
<i>Caloneis silicula</i> var. <i>ventricosa</i> (EHR.) DONK.																+			

Species	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Caloneis sp.															+				
Ceratoneis arcus (EHR.) KTZ.	+	+	+	+	+	+								+		+	+	+	
Ceratoneis arcus var.																			
amphyxoxys (EHR.) DONK.															+				
Ceratoneis arcus var. linearis																			
HOLOMBOE.	+	+	+	+	+	+										+	+	+	
Coccconeis placentula EHR.	+																		
Coccconeis placentula var.																			
euglypta (EHR.) CL.	+															+	+	+	
Coccconeis placentula var.																			
intermedia (HERIB. et PERAGE) CL.																			+
Coccconeis pediculus EHR.															+				
Coscinodiscus rothii (EHR.) GRUN.					+	+													
Coscinodiscus sp.															+				
Cyclotella bodanica EULENST.															+	+	+	+	+
Cyclotella comta (EHR.) KTZ.															+		+		
Cyclotella ocellata PANT.															+	+			
Cyclotella sp.																			+
Cyclotella sp.																			
Cymatopleura solea (BRÉB.) W. SM.															+	+		+	
Cymatopleura solea var. gracilis GRUN.															+				
Cymbella aequalis W. SM.															+	+			
Cymbella affinis KTZ.	..	+	+	+	+										+	+			
Cymbella amphycephala NAG.																			
Cymbella aspera (EHR.) CL.	+	+													+	+	+	+	+
Cymbella cistula (HEMP.) GRUN.	+														+	+	+	+	+
Cymbella cistula var. gibbosa GRUN.																			
Cymbella cuspidata KTZ.																			
Cymbella cymbiformis (AG. ?KTZ.) V. H.																			
Cymbella ehrenbergii KTZ.																			
Cymbella gracilis (RABENH.) CL.	++	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Cymbella hebridica (GREG.) GRUN.															+	+			
Cymbella helvetica KTZ.																			
Cymbella helvetica var. curta CL.															+				
Cymbella heteropleura EHR.																	+		
Cymbella heteropleura var. minor CL.																			+
Cymbella inaequalis EHR.																			+
Cymbella lanceolata (EHR.) V. H.	+														+	+	+	+	+
Cymbella laevis AG.																			+
Cymbella leptoceros (EHR.) GRUN.	+	+																	
Cymbella naviculiformis AUERSW.	+	+													+	+	+	+	+
Cymbella parva (W. SM.) CL.															+				
Cymbella prostrata (BERKELEY) CL.															+				
Cymbella prostrata var.																			
auerswaldii (RABENH.) REIN.															+				
Cymbella sinuata GREG.	+														+				+
Cymbella tumidula GRUN.															+	+	+		
Cymbella turgida (GREG.) CL.																			+
Cymbella ventricosa KTZ.	++	++	++	++	++	++	++	++	++	++	++	++	++	++	+	+	+	+	+
Cymbella sp.																			
Denticula tenuis KTZ.																			+
Denticula tenuis var. crassula CL.															+				

Species	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Gomphonema subtile EHR.														+					
Gomphonema subtile var. sagittum (SCHUM.) CL.														+					
Gomphonema sp.														+					
Gomphonema sp.														+					
Gyrosigma scalpoides (RABENH.) CL.																			+
Gyrosigma sp.														+					
Hantzschia amphioxys var. major GRUN.														+					
Hantzschia amphioxy f. capitata														+					
O. MULL.														+					
Hantzschia major GRUN.														+					
Hantzschia virgata (ROPER) GRUN.														+					+
Melosira granulata (EHR.) RALFS.					+									+					
Melosira islandica O. MULL.														+					
Melosira italicica var. valida (GRUN.) HUST.																			+
Melosira reesiana RABENH.														+					
Melosira sp.														+					
Meridion circulare AG.														+					+
Meridion circulare var. constrictum (RALFS.) V.H.														+					+
Navicula bacillum EHR.														+					+
Navicula contenta GRUN.														+					
Navicula contenta f. biceps ARN.														+					
Navicula contenta f. paralella																			
BOYE P.														+					
Navicula cryptocephala KTZ.																			+
Navicula cuspidata KTZ.														+					+
Navicula cuspidata f. primigena DIPP.														+					
Navicula dicephala (EHR.) W. SM.														+					
Navicula dismutica KRASSKE														+					
Navicula gracilis EHR.														+					
Navicula mutica KTZ.																			
Navicula mutica f. lanceolata																			
GRUN																			
Navicula menisculus SCHUM.														+					+
Navicula perpusilla GRUN.														+					+
Navicula pseudogracilis SKV.														+					+
Navicula pseudoscutiformis HUST.														+					
Navicula pupula KTZ.														+					
Navicula pupula var. elliptica HUST.																			+
Navicula pupula var. capitata HUST.																			+
Navicula pergarina (EHR.) KTZ.																			+
Navicula radiosa KTZ.														+					+
Navicula rhynchocephala KTZ.														+					
Navicula rotaeana (RABENH.) GRUN.														+					
Navicula tackei HUST.														+					
Navicula viridula KUTZ.																			+
Navicula sp.																			
Neidium affine var. amphirhynchus (EHR.) CL.														+					
Neidium bisulcatum (LAG.) CL.														+					
Neidium dubium (EHR.) CL.														+					+

Species	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
<i>Pinnularia viridis</i> var. rupestris (HANTZSCH.) CL.										+						+	+		
<i>Pinnularia viridis</i> var. sudetica (HILSE) HUST.							+				+								
<i>Pinnularia viridis</i> var. intermedia CL.												+							
<i>Pinnularia</i> sp.							+												
<i>Pinnularia</i> sp.												+							
<i>Rhizogalenia longiseta</i> ZACHARIS													+						
<i>Rhopalodia gibba</i> (EHR.) O.MULL.														+		+	+	+	
<i>Stauroneis acuta</i> W.SM.		+	+	+	+	+	+	+	+						+				
<i>Stauroneis anceps</i> EHR.		+	+	+	+	+	+	+	+					+	+				
<i>Stauroneis anceps</i> f. <i>gracilis</i> (EHR.) CL.															+				
<i>Stauroneis obtusa</i> LAGERST.				+															
<i>Stauroneis phoenicenteron</i> EHR.		+		+				+	+					+	+	+	+	+	
<i>Stauroneis smithii</i> GRUN.			+					+	+								+	+	
<i>Stauroneis smithi</i> var. <i>incisia</i> PANT.										+									
<i>Surirella angustata</i> KTZ.			+	+															
<i>Surirella biserata</i> BRÉB.														+			+		
<i>Surirella biserata</i> var. <i>constricta</i> GRUN.																			
<i>Surirella didyma</i> var. <i>minor</i> SKV.							+												
<i>Surirella linearis</i> var. <i>constricta</i> (EHR.) GRUN.															+				
<i>Surirella linearis</i> var. <i>helvetica</i> EHR.										+					+				
<i>Surirella ovata</i> KTZ.															+				
<i>Surirella ovata</i> var. <i>pinnata</i> (W.SM.) HUST.															+				
<i>Surirella robusta</i> var. <i>splendida</i> EHR.					+									+					
<i>Surirella</i> sp.					+														
<i>Surirella</i> sp.						+													
<i>Synedra acus</i> KTZ.														+	+				
<i>Synedra acus</i> var. <i>radians</i> (KTZ.) HUST.														+					
<i>Synedra ulna</i> (NITZ.) EHR.						+													
<i>Synedra ulna</i> var. <i>aequalis</i> (KTZ.) HUST.														+	+				
<i>Synedra ulna</i> var. <i>biceps</i> (KTZ.) CHÜNF.														+					
<i>Synedra ulna</i> var. <i>amphirhynchus</i> (EHR.) GRUN.																+	+		
<i>Synedra</i> sp.														+					
<i>Tabellaria flocculosa</i> (ROTH.) KÜTZ.					+									+	+	+	+	+	
<i>Tabellaria fenestacea</i> (LYNGB.) KÜTZ.																		+	
<i>Tetracyclus rupestris</i> (A.BR.) GRUN.																		+	
X A N T H O P H Y T A																			
Tribonema sp.																		+	
E U G L E N O P H Y T A																			
<i>Euglena megalitos</i> SKUYA														+					
<i>Euglena pisciformis</i> KLEBS														+	+				

Species	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Xanthidium antilopaenum var.																			
oligacanum SCHMIDLE																			+
Zygnema sp.					+														
Zygnema sp.							+												
Zygnema sp.								+											
Zygnema sp.									+										
Zygnema sp.																	+		
Zygnema sp.																		+	

The glacial lakes researched were located at the highest altitude (2,187 m/a/s/l average), had rocky bottoms and shores. Waters from cold mountain creeks, precipitation, snow and ice melting supply these lakes.

Nival lakes, compared to glacial lakes, are somewhat lower located (1,912 m/a/s/l average). Higher plant vegetation occupies the lakeshores; rocks, slime and moss cover their bottoms. These are filled with waters from ground creeks, snow melting and precipitation.

Solifluctional lakes covered with the alga research are located at the lowest gradient (1,575-m/a/s/l average). The lake shores are covered with higher plant vegetation, while the bottoms are covered with macrophyte vegetation and slime. Surrounding creeks, snow melting and precipitation provide the lakes with water.

The diversity of the conditions gave different picture of periphyton micro-flora.

The glacial lakes' periphyton base is made of the Bacillariophyta representatives, being present from 51.7 to 95.5%. Among the glacial lakes, Srednje Defsko Lake was distinguished as per domination of the Chlorophyta representatives, being present to 57.2%.

The nival lakes' periphyton communities differed from those of the glacial lakes with regard to the domination of Chlorophyta representatives, whose presence ranged from 44.4 to 63.5%. The Chlorophyta and Euglenophyta representatives were equally present (26.3% each) in Mekus Bor nival lake.

Two solifluctional lakes, of which: Gornje Tupankamensko, among the glacial and nival lakes, was the only that, exclusively, had the representatives of the Bacillariophyta divisions (45 taxa, 100.0%). In Donje Tupankamensko Lake, the Bacillariophyta representatives dominated over other alga (69.0%), also had large number of the Cyanophyta representatives presented with 8 taxa, or 11.8% (Figure 2).

Within the overall composition of the lakes' micro-phyte communities, the Bacillariophyta division had the largest number of taxon (273) within 33 genera, as follows: Pinnularia - 36 taxa, Eunotia and Cybella - 28 taxa each, Navicula - 26 taxa, Gomphonema - 25 taxa, Surirella - 12 taxa. Certain taxa were only found in the frames of the genera, as follows: Didimosphenia, Rhizosplenium, Rhopalodia and Tetracyclus.

The Chlorophyta representatives, although less numerous (196 taxa), compared to Bacillariophyta, are

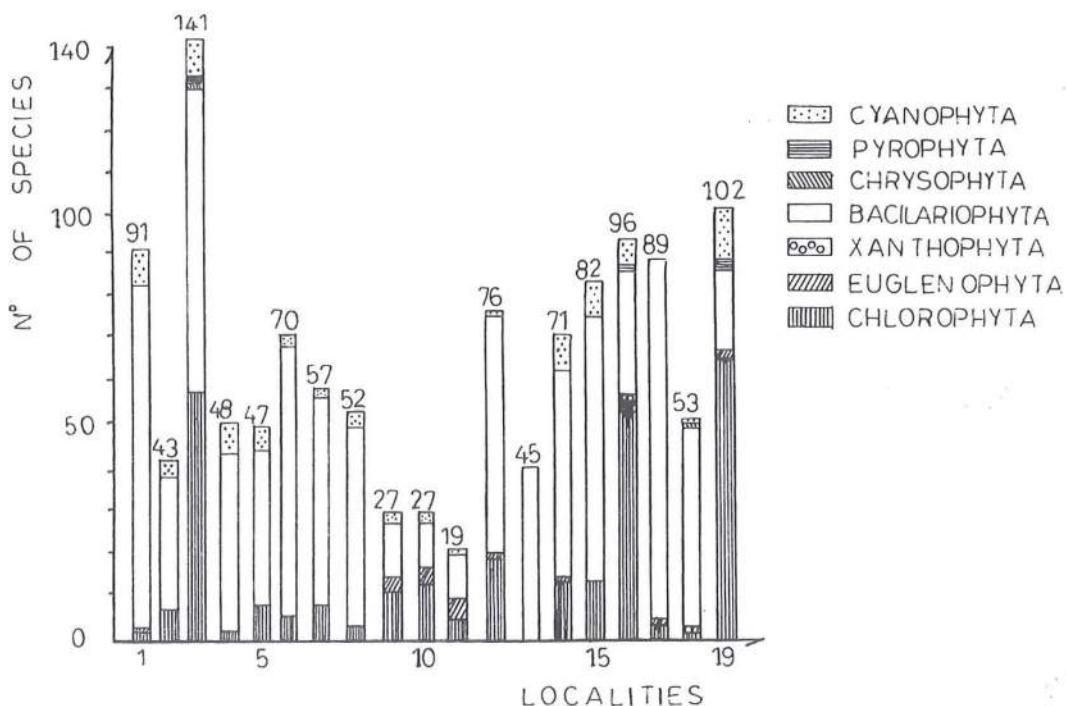


Figure 2.

characterized with more diverse affiliation to the taxa, with the following genera (45 genera): *Cosmarium* - 44, *Scenedesmus*, *Mougeotia*, *Closterum*, *Staurastrum* with 12 taxa each, etc.

Cyanophyta, according to the number of taxon (54), occupied third position. These have found the most favorable conditions for its development with 12 taxa in Gornje Veljinbesko nival lake.

Regarding the Sar-planina Mt. geologic characteristics, mentioned before, a conclusion was derived that, its geologic diverse composition produces the ground for the diverse community of micro-flora within each of the lakes researched (Figure 2). The respective means that, in addition to other factors, the geologic one, no doubt, plays great role too. The two species of *Cymbella ventricosa* and *Pinnularia distinguenda* were the residents in 13, of the 19 lakes researched.

No detailed research of Macedonian part of Sar-planina Mt. lakes was made, except in case of the following lakes: Malo Lake (2,180 m/a/s/l) and the peat bog below Malo Lake (2,160 m/a/s/l) with close gradients. Our distinguished colleague Stojanovic (1982) examined periphyton alga within the frame of *Bacillariophyta* division in these lakes. His research proved significant diversity of Macedonian and our lakes. All of the above mentioned contributes to the geologic, pedological, as well as climate factor of the environment.

REFERENCE

- Blazencic Jelena (Urednik), 1997. Vlasinsko jezero. Hidrobiolska studija. Bioloski fakultet Univerziteta u Beogradu, Beograd.
- Stojanov P., 1982. Dijatomeje vodenih ekosistema nacionalnog parka Pelister. Biosistematika, 8(1): 1-17, Beograd.
- Urosevic Violeta, 1994. Alge visokoplaninskih jezera Sirinicke strane Sar-planine. Monografija. Univerzitet u Pristini, pp.: 1-95, Pristina.
- Urosevic V., 1994. Peryphyton algae of glacial Lividicko lake of Sar-mountain. Univerzitsetska misao - prirodne nauke, 2: 13-19, Pristina.
- Urosevic V., 1997a. Obrastajne alge Gornjeg i Donnjeg Tupankamenskog jezera na Sar-planini. Fizickogeografski procesi na Kosovu i Metohiji. II(2): 49-58. Odsek za Geografiju, PMF, Univerzitet u Pristini. Pristina.
- Urosevic V., 1997. b. Peryphyton Algae in two small lakes on the springs Branch of Crnkamenska reka river on Sar-planina mt. University Thought, Nat. Sci., IV(1). Pristina.

Urosevic V., 1997. c. The Ginevodno lakes Algae on Sar-planina. University Thought, Nat. Sci., IV(2): 79-87, Pristina.

Urosevic V., 1998. Obrastajne alge Gornjeg veljinbeskog jezera na Sutmanu (Sar-planina). Zbornik radova sa V simpozijuma o flori Jugoistocne Srbije Zajecar. pp.: 8-18, Univerzitet u Nisu.

REZIME

PERIFITONSKIE ALGE U JEZERSKIM EKOSISTEMIMA JUGOSLOVENSKOG DELA ŠAR-PLANINE

Violeta UROŠEVIC vanredni profesor, Prirodno-matematički fakultet, Odsek za biologiju. Vidovdanska bb, 38000 Pristina, Jugoslavija.

Ispitivanja perifitonskih algi obavljana su u periodu od 1984. do 1998. godine na 19 jezera (glacijalnih - 13, nivacionih - 4 i soliflukcionih - 2) jugoslovenskog dela Šar-planine. U njima je utvrđeno ukupno 541 takson: Cyanophyta - 54, Pyrrophyta - 4, Chrysophyta - 2, Bacillariophyta - 273, Xanthophyta - 1, Euglenophyta - 11 i Chlorophyta - 196 (Tab. 1).

Raznovrsnost uslova ispitanih jezera (visinski položaj, snabdevanje vodom, obale i dno jezera, geološka i pedoloska podloga i dr.), dala su različitu sliku perifitonske mikroflore.

U glacijalnim i soliflukcionim jezerima okosnicu perifitonskih zajednica činili su predstavnici Bacillariophyta (51,7 do 100%). Glacijalno Srednje Defsko jezero izdvajalo se po dominaciji predstavnika Chlorophyta (57,2%).

U svim navedenim jezerima dominirali su predstavnici Chlorophyta (44,4 do 63,5%), osim jezera Mekuš Bor u kome su predstavnici Chlorophyta i Euglenophyta zajedno (sa po 26,3%) dominirali nad ostalim algama.

Raznovrsnost geoloskog sastava uzrokuje i raznovrsne zajednice mikroflore u okviru svakog ispitanih jezera (Fig. 2), što znači da pored ostalih faktora i ovaj geoloski svakako igra veliku ulogu. Samo su vrste *Cymbella ventricosa* i *Pinnularia distinguenda* (Bacillariophyta) odomaćene u 13 jezera od 19 ispitanih.

Received: November, 1998.

Accepted: December, 1998.

Fritillaria macedonica Bornm.- New species in Yugoslav flora

Amidzic Lidija¹, Krivosej Zoran², Stevanovic Vladimir³

¹Institute for Protection of Nature of Serbia, Faculty of Mathematics and Natural Sciences, University of Pristina

²Faculty of Mathematics and Natural Sciences, University of Pristina

³Institute of Botany and Botanical Garden, Faculty of Biology, University of Belgrade

Abstract

During the intensive Sar-Mountain field flora research in summer 1997, we came to the conclusion, although florally sufficiently researched, the massive still hiding species unreg-

istered up to now on it. Many from this interesting group present new species not only for Sar Mountain, but also for Serbia and Yugoslavia. The work gives presentation of a species.

Key words: *Fritillaria macedonica*, Sar-Mountain, Yugoslavia

INTRODUCTION

Five species of branch *Fritillaria* were described up to now in Yugoslavian flora (Diklic, 1975) (*F. meleagris* L., *F. degeneriana* L. Wagner, *F. montana* Hoppe, *F. gracilis* (Ebel) A. in G., *F. graeca* Boiss. et Sprn.). During the field research, we succeeded to register sixth species of the branch existing in Serbia. This is *Fritillaria macedonica* Bornm, representing the new species in flora of FR Yugoslavia.

MATERIAL AND METHODS

Herbal material collected during the high-mountain field research of northern slopes of Sar-mountain in June 1996 and 1997, was herbarized on the field. Determination of herbal material was made with assistance of numerous domestic and foreign literature.

RESULTS AND DISCUSSION

Fritillaria macedonica Bornm. belongs to *Eufritillaria* Boiss. section, including complex species *Fritillaria montana* Hoppe. The species was the most related with *Fritillaria epirotica* Tutil ex Rix.

Mentioned taxon is a perennial bulbous shaped plant whose bumpy stalk is of 7-20cm height. There are 5-6 leaves and a flower on a stalk. The leaves are bumpy, longish-lanced, width up to 16mm, length up to 8cm. The lowest leaves are opposite to one another, at the middle of a stalk they are in turns, and at the upper part are three in each vertebra. Perianth is wide-bell-like. Outer leaves are oval-lanced, dimension 30 x 11-16mm. Inner are wide and clogged on the edges, dimensions 12-16mm. Whole perianth is dark purple, tapeless, with rectangular shaped dots, arranged up like chess fields. Linear-longish nektarias grows up to 3mm. Filaments are smooth, with length to 10mm. Three-partial seal is 12mm long, and pestle pillar from 2-5mm. Shell is not winged.



Fig. 1. *Fritillaria macedonica* Bornm.

Fritillaria macedonica Bornm. was registered in vegetation of high-mountain soak lawns and meadows of southeastern Macedonia, east and central Albania. During the field research we found it on the Serbian side of Sar-Mountain within the glacial bend of Jazince Lake. In Bištra surroundings (2651m s.l.) in Jazince Lake area (2135m s.l.) its population covers northeast exposition on sea level around 2050-2250 m.

In conditions of severe peri-glacial, appears on humus-silicate ground accumulated on granite within *Jupiterus nana* - *Bruckenthalia spiculifolia* Horv. high-mountain association.

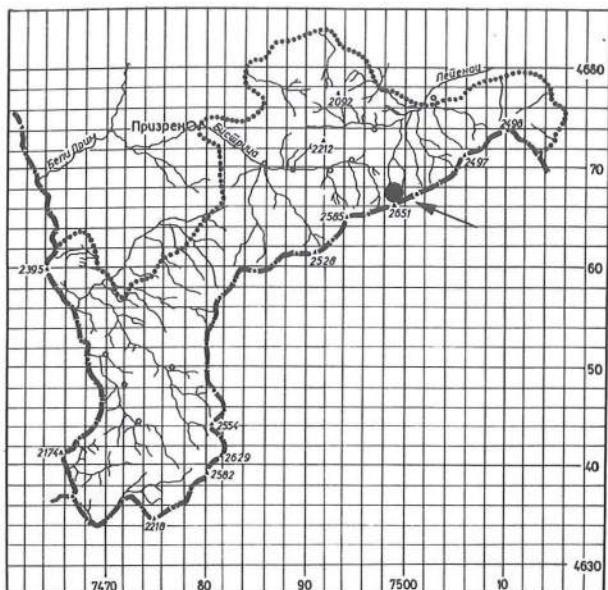


Fig. 2. Domicile of the *Fritillaria macedonica* Bornm. in the Sar Mountain National Park.

Sl. 2. Areal vrste *Fritillaria macedonica* Bornm. u Nacionalnom parku "Šarplanina"

Population of the South-European-mountain, precisely North-Scardino-Pindic endemic species, in Jazince glacial lake bend counts 300 examples. They are dispersively placed in groups of 10-30, mainly on snow long-lasting turfs. Period of blossoming starts during the second part of June, during the time of snow melting.

Taxon was clasified in R category of European red list for territory of Macedonia, or ex SFRY (ECCONNR-EC, 1983:136). As a rare, it is also mentioned for Albania (Vangjeli et al., 1994:95). After its evidencing and for flora of Serbia as well as for FR Yugoslavia, it was put in the list of the First Volume of Flora of Serbia Red Book (in print), as an extremely endangered (CR) considering its appearance only at Jazince glacial lake cove on the north slopes of Sar-Mountain.

CONCLUSION

Fritillaria macedonica Bornm. as an North-Scardo-Pindian endemism was described up to now only for flora of Macedonia and Albania. New finding of the species at Jazince glacial lake cove on the north slopes of Sar-Mountain, presents the most northern frontier of its areal. Considering the extremely endangered species (CR) on the territory of Serbia and Yugoslavia, legal preservation is necessary at the Sar-Mountain National Park.

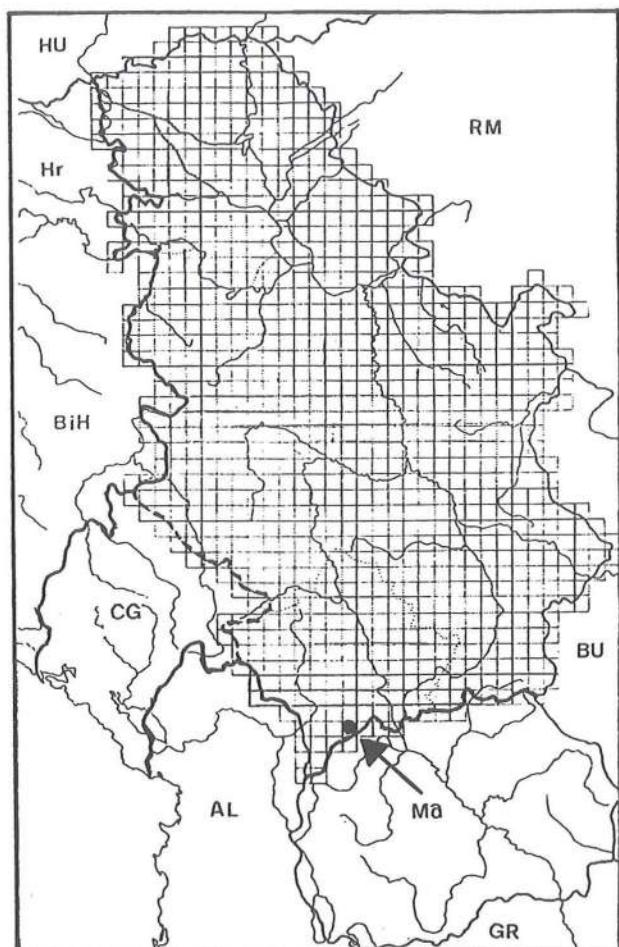


Fig. 3. Areal of the species *Fritillaria macedonica* Bornm. in Serbia

Sl. 3. Areal vrste *Fritillaria macedonica* Bornm. u Srbiji.

REFERENCES

- Amidžić, L. (1997) : High mountain vegetation of the Circues in Suvi Potok and Durlev potok Creek-Basins on the Sar-planina Mt. Northern Slopes. Univ. Thought., Nat. Sci, IV (1): 27-31. Pristina.
- Amidžić, L. et Belij, S. (1996) : Florističke i vegetacijske specifičnosti cirka Jažinačkog jezera na Šar-planini . Zbornik sažetaka sa 5. Kongresa ekologa Jugoslavije . Društvo ekologa Srbije. Beograd .
- Demiri , M. (1983) : Flora ekskursioniste e Shqipetarise . T. , "Shtep. Bot. e Librit Shkollor" . Tirane.
- Hayek, A (1927 - 1933) : Prodromus Florae Peninsulae Balcanicae . Berlin - Dahlem.
- Horvat, I. (1960): Planinska vegetacija Makedonije u svijetu suvremenih istraživanja . Acta Musei Macedonici Scientiarum Naturalium . Tom VI , 8 (60): 162-203. Skopje.
- Josifović, M. (ed.) (1970-1977) : Flora SR Srbije , VII . SANU , Odeljenje prirodno-matematičkih nauka . Beograd.
- Kamari, G. (1991): Fritillaria. In ed. Mountain Flora of Greece : 672-683.

Rajevski, L. 1974 (1990) : Fitocenološke karakteristike planinskih pašnjaka severnog dela Šar planine . Glas. Inst. za botaniku i Bot. bašte Univerziteta , IX . Beograd.

Rix, E.M. (1980): *Fritillaria*. In Tutin et al. (ed.) : Flora Europaea : 31-34. Cambridge University Press.

Šilić , Č. (1990) : Endemične biljke . "Svijetlost" Sarajevo , Zavod za udžbenike i nastavna sredstva , Beograd.

Rezime

FRITILLARIA MACEDONICA BORN.M. - NOVA VRSTA ZA FLORU JUGOSLAVIJE

Lidija Amidžić¹, Zoran Krivošej², Vladimir Stevanović³

¹Zavod za zaštitu prirode Srbije, Odsek za biologiju PMF-a Univerziteta u Prištini

²Odsek za biologiju PMF-a Univerziteta u Prištini

³Institut za botaniku i Botanička bašta Biološkog fakulteta Univerziteta u Beogradu

U flori Srbije je do sada opisano pet vrsta roda *Fritillaria* (*F. meleagris* L. , *F. degeniana* L. Wagner, *F. montana* Hoppe, *F. gracilis* (Ebel) A. u G., *F. graeca* Bois. et Sprun.). Tokom terenskih istraživanja 1996. i 1997. godine na Šar-planini smo registrovali i šestu vrstu ovog roda prisutnu u Srbiji. To je *Fritillaria macedonica* Bornm. koja istovremeno predstavlja i novu vrstu za floru Jugoslavije.

Fritillaria macedonica Bornm. pripada sekciji *Eufritillaria* Boiss. u okviru koje ulazi i kompleks vrste *Fritillaria montana* Hoppe. pokazujući istovremeno najbliže srodstvo sa vrstom *Fritillaria epirotica* Tuti ex Rix.

Ova višegodišnja lukovičasta, veoma dekorativna biljka je do sada bila registrovana u vegetaciji visoko-planinskih vlažnih pašnjaka i livada jugozapadne Makedonije, istočne i centralne Albanije. Na srpskoj strani Šar-planine smo je našli u cirku Jažinačkog jezera , u zaleđu Bistre (2651 m n.v.), uglavnom u okolini Jažinačkog jezera (2135 m n.v.). Na malom prostoru primerci ove južnoevropsko-planinske, odnosno, severoskardopindske endemične vrste, zauzimaju severoistočne ekspozicije na nadmorskoj visini od oko 2050 do 2250 m. U uslovima surove periglacialne klime , javlja se na humusno-silikatnom zemljištu akumuliranom na granitima u okviru visokoplaninske žbunaste asocijacije *Juniperus nana - Bruckenthalia spiculifolia Horv.*

Populacija vrste *Fritillaria macedonica* u Jažinačkom cirku broji oko 300 primeraka. Oni su disperzno raspoređeni u grupicama od 10-30, uglavnom na rudinama na kojima se dugo zadržava sneg. Period cvetanja počinje tek drugom polovinom juna, u vreme njegovog intenzivnijegtopljenja.

Takson je uvršten u evropsku crvenu listu u kategoriji R za teritoriju Makedonije, odnosno, bivše SFRJ (ECCONNR-EC, 1983: 136). Kao redak se navodi i za Albaniju (Vangjeli et all., 1994 : 95). Nakon njegovog evidentiranja i za floru Srbije, odnosno, SR Jugoslavije, stavljen je u spisak vrsta Toma 1 Crvene knjige flore Srbije (Srevanović, V., ed. 1999. - in press) kao krajnje ugrožen (CR).

Received: November, 1998.

Accepted: December, 1998.

Silene graefferi Guss. - new species for Yugoslav flora

¹Krivosej Zoran, ²Amidzic Lidija, ³Stevanovic Vladimir

¹Faculty of Mathematics and Natural Sciences, University of Pristina, ²Institute for Protection of Nature of Serbia, Faculty of Mathematics and Natural Sciences, University of Pristina, ³Institute of Botany and Botanical Garden, Faculty of Biology, the Belgrade University

ABSTRACT

During the intensive field research of Sar-Mountain flora, in the past several years we came to the conclusion the gorge, although florally researched sufficiently, has species that not are not yet noted. Many from this interesting group pres-

ent new species, not only for Sar-Mountain, but also for Serbia and Yugoslavia. The work gives presentation of a species that belong to the group.

Key words : Silene graefferi, Osljak, Ostrovica, Yugoslavia

INTRODUCTION

On lime stone and serpentine rocky ground and rocks in the region of Osljak and Ostrovica high-mountain zones, *Silene graeffery* Gußs. The species has not noted yet for Yugoslavian flora.

MATERIAL AND METHODS

Herb material collected in the field researches of Sar-Mountain and its slopes during 1996 was herbarized on the field. Determination of material was done with assistance of domestic and foreign literature.

RESULTS AND DISCUSSION

Silene graefferi Guss. is a perennial herbaceous, thickly bushed plant, wooded at the bottom of a tree. Numerous leaves trees of 5-30cm high, are covered with limb hair. Leaves of a bush are spear-spherical up to linear, over the edge lash-hairy. Cluster is dyhasium, composed of two to four flowers. Seldom, flowers can be single. Stems are visibly shorter from a cup, that is 10-20mm long, with ten intermingled nerves. A cluster is white or pink, longer than a cup, double filed deeply cut.

The species blossoming from July to September, depending on a sea level height. Populations on Osljak and Ostrovica blossoming from the beginning of July to the midst of August. It is to be pollinate by enthomophylia, and it carries its pod during September. It is reproduced by aside sprouts from the wooden bottom of a tree, forming thick turfs. It belongs to the vital form of turf hamefits (CH suff caesp-semipulv).

Silene graefferi was described in flora of central Apennine and Balkan Peninsula central and southern part mountains: in Macedonia (Sar-Mountain, Jakupica, Bistra, Pletvar-Kozjak), Bulgaria (Stara Mountain, Rila, Pirin, Alibitus), Greece (Olympia, Tzena, Pinovan, Menikon, Orvilos, Falakron). Finding on Sar-Mt. slopes, Osljak and Ostrovica presents the most northern point of its areal.



Fig. 1. Silene graefferi Guss. (in Flora na NR Blgarija)

The species is the only representative of sect. Fruticulosae in flora of Balkan Peninsula, presenting the remain of oro-Mediterranean of tertiary flora. According to flora-genetic belonging, *Silene graefferi* belongs to the South-European mountain or Apennine - Scardo - Pindic - West Balkan flora element.

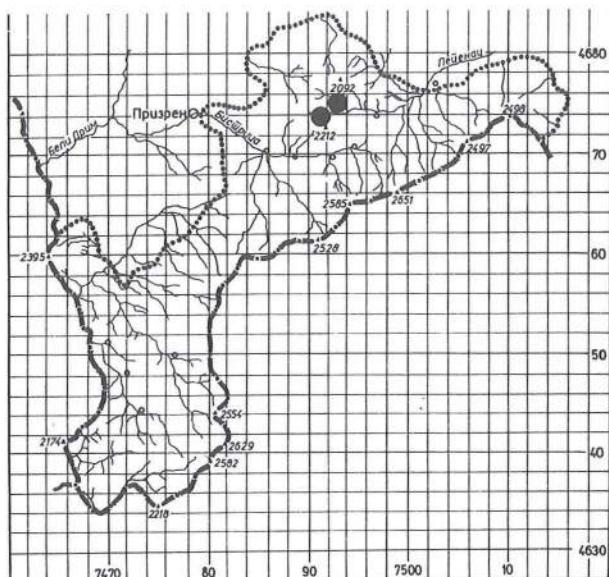


Fig. 2. Domicile of the *Silene graefferi* Guss. in the Sar Mountain National Park
Sl. 2. Areal vrste *Silene graefferi* Guss. u Nacionalnom parku "Šarplanina".

Population of the kind are small numbered, composed of several hundred examples. Regarding the species in the territory of Serbia and Yugoslavia is existing in the narrow zone of high-mountain region of Sar-Mt. slopes Ostrovica and Osljak, it is as extremely endangered (CR B1:B2c), is on the list of the First Chapter of Flora of Serbia Red Book (in print).

CONCLUSION

Silene graefferi Guss. relict, the remain that belong to the South-European mountain or Apennine - Scardo - Pindic - West Balkan flora element. Up to now, the taxon was described as a part of central Apennine, Macedonia, Bulgaria and Greece flora. Its new finding on Sar-Mt. slopes, Osljak and Ostrovica presents the most northern point of its areal. Regarding the species in the territory of Serbia (CR B1:B2c), its permanent legal preservation is necessary in future widened the Sar Mountain National Park.

REFERENCES

- Chater, A.O. et Walters, S.M. (1964): *Silene ciliata* in Tutin, T.G. et all. (eds.): *Flora Europaea* 1 : 172. Cambridge University Press.
 Fiori, A. (1921): *Iconographia florae Italicae*: 187. Firenze
 Jordanov, D. et Panov, P. (1966): Rod *Silene* L. in Jordanov, D. (ed.) : *Flora na NR Blgarija III* : 485-486. BAN. Sofija.

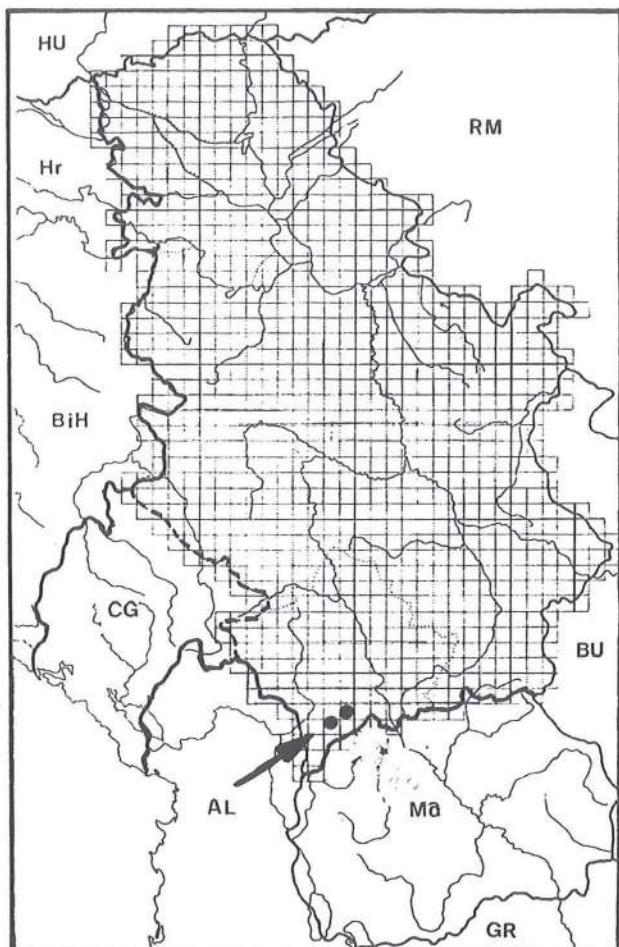


Fig. 3. Areal of the species *Silene graefferi* Guss. in Serbia
Sl. 3. Areal vrste *Silene graefferi* Guss. u Srbiji.

Micevski, K. (1993) : *Flora na Republika Makedonija*. Tom 1, Sv. 2 : 332. MANU. Skopje.

Stevanović, V., Niketić, M. (1998): *Silene* L. in Sarić, M. (ed.): *Flora Srbije* 2. SANU, Odeljenje prirodnno-matematičkih nauka. Beograd. (in press)

Stevanović, V. (ed.) (1999): *Crvena knjiga flore Srbije*. Tom 1. Biološki fakultet Univerziteta u Beogradu, Zavod za zaštitu prirode Srbije. Beograd. (in press)

REZIME

SILENE GRAEFFERI GUSS. - NOVA VRSTA ZA FLORU JUGOSLAVIJE

¹ Zoran Krivošej, ² Lidija Amidžić, ³ Vladimir Stevanović

¹ Odsek za biologiju PMF-a Univerziteta u Prištini

² Zavod za zaštitu Prirode Srbije, Odsek za biologiju PMF-a Univerziteta u Prištini ³ Institut za botaniku i Botanička bašta Biološkog fakulteta Univerziteta u Beogradu

Silene graefferi Guss. je višegodišnja zeljasta, gusto busenasta biljka, odrvenela u dnu delu stabla. Pripada životnoj formi busenastih hamefita (CH suff caesp-semipulv)

Do sada je *Silene graefferi* opisana u flori centralnih Apenina i planina centralnog i južnog dela Balkanskog poluostrva : u Makedoniji (Šar-planina, Jakupica, Bistra, Pletvar-Kozjak), Bugarskoj (Stara planina, Rila, Pirin, Alibituš) i Grčkoj (Olimpia, Tzena, Pinovan, Menikon, Orvilos, Falakron).

Tokom terenskih istraživawa 1996. godine vrsta je evidentirana na krečnjačkim i serpentinitskim kamenjarima i stenama u visokoplaninskoj zoni šarskih ogranača Ošljaka i Ostrovice. Ovo jedino nalazište u Srbiji, odnosno, Jugoslaviji, predstavlja najseverniju tačku njenog areala.

U flori Balkanskog poluostrva *Silene graefferi* je jedini predstavnik sect. *Fruticulosae* kao ostatak

oromediteranske tercijarne flore. Prema florogenetskoj pripadnosti, *Silene graefferi* pripada južnoevropsko planinskom, odnosno, apeninsko-skardo-pindsko-zapadnobalkanskom elementu flore.

Populacije ove vrste su malobrojne, sastavljene od nekoliko stotina primeraka. Pošto se radi o vrsti koja je na prostoru Srbije, odnosno Jugoslavije, prisutna samo u uskoj zoni visokoplaninske oblasti šarskih ogranača Ostrovice i Ošljaka, ona je kao krajnje ugrožena (CR B1:B2c), svrstana u spisak Toma 1 Crvene knjige flore Srbije (S t e v a n o v i ć, V. - ed., 1999 , in press).

Received: November, 1998.

Accepted: December, 1998.

Draba siliquosa Bieb. (D. carinthiaca Hoppe) - a new species of Flora of Yugoslavia

¹ AMIDZIC Lidija, ² STEVANOVIC Vladimir, ³ KRIVOSEJ Zoran

¹ Institute of Protection of Nature of Serbia, Faculty of Mathematics and Natural Sciences of Pristina

² Institute of Botany and Botanical Garden, Faculty of Biology, the Belgrade University

³ Faculty of Mathematics and natural Sciences of Pristina

ABSTRACT

During the intensive field research of Sar-Mountain flora, in the past several years we came to the conclusion the gorge, although florally researched sufficiently, has species that not are not yet noted. Many from this interesting group pres-

ent new species, not only for Sar-Mountain, but also for Serbia and Yugoslavia. The work gives presentation of a species that belong to the group.

Key words: Draba siliquosa, Crni vrh, Sara Mountain, Yugoslavia

INTRODUCTION

On silicate rocks and rocky ground of the north slopes of Sar-Mountain, underneath the very crest of Crni Vrh (2584m above the sea level) during the field research 1996, *Draba siliquosa* was noted. The species belong to the Cruciferae family was not registered up to now in the flora of Yugoslavia.

MATERIAL AND METHODS

Herbal material collected during the field researches in July 1996 from the northern slopes of Sar-Mountain was herbarised on the field. The determination of materials was conducted with assistance of domestic and foreign literature.

RESULTS AND DISCUSSION

Draba siliquosa Bieb. (*Draba carinthiaca* Hoppe) belongs to sect. Leucodraba with only one representative in the flora of Yugoslavia-the endemic Balkan species *Draba corabensis* spreads over the southwest and east Serbian Mountains (Sar-Mt., Prokletije and Stara Mountains), north and northeast Albanian and west Bulgarian mountains. Within the sect. Leucodraba the species of *Draba silicuosa* is the most related to the Pirineas -Alpine species of *Draba dubia* Suter.

This glacial relict is a small turf plant of a height between 1-8cm, but the samples from Sar-Mountain never grow higher than 2cm. Stalk is bare or covered with rare star like hair at the base. There are no leaves at the base or only two can be found. The leaves of rosettes are longish-oval-lash like. But, they can be also bare, variable. They are usually covered with branchy, branchless and star like hair. Clusters are composed from 2-12 leaves. Clusters leaves are white, from 2-5mm long, up to 4mm wide. Shell is elliptic and smooth, without pillar. If there is one, it is up to 0,5mm long.



Fig. 1. *Draba siliquosa* Bieb.

The species blossoming by the end of July. It is being reproduced by the seed. Kariotype of species was studied on Alps and accordingly it is $2n + 16$. It belongs to the hamefit midget turf life form (Ch suff caesp).

Draba silicuosa is described up to now in flora of Middle Europe Mountains, from Pirineas via Alps, Sudets, Tatra, on east to Carpathians. The lowest part of

its areal was known until Rila and Pirin in Bulgaria up to now. Its new finding on Sara Mountain represents another mountain disjunct of the orofit that belongs to Middle Europe mountain element (Pirinean-Alpic-Carpathian-Balkan-NorthScardopian).

Population noted directly beneath the crest of Crni Vrh, within the Sara National Park is small numbered, consists only few tenths of examples. Since this narrow area of Alpian zone of Sara Mountain its only finding, *Draba siliquosa* was noted into the First Volume of Flora of Serbia Red Book (in press), as an extremely endangered (CR B1) according to the IUCN category of endanger in Serbia.

CONCLUSION

Draba siliquosa Bieb (*D. carinthiaca* Hoppe) as an Middle-European orofit and glacial relict, has been described up to now as a flora of Middle-European and Bulgarian mountains. Its new finding directly beneath the crest part of Crni Vrh presents significant contribution of flora diversity, not only of Sar-mountain, but also Yugoslavia. Regarding the extremely endangered species (CR B1) existing in Yugoslavia with several examples only, within the Sara Mountain National Park, a responsibility about its legal preservation in the area of Serbia is necessary.

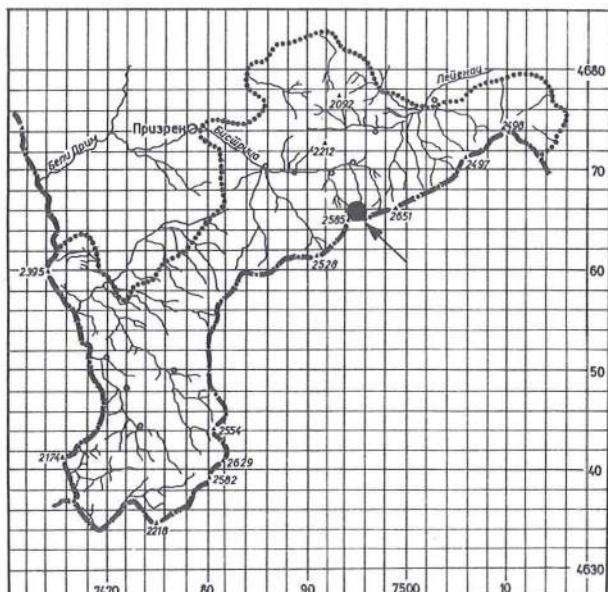


Fig. 2. Domicile of the *Draba siliquosa* Bieb. in the Sara Mountain National Park
Sl. 2. Areal vrste *Draba siliquosa* Bieb. u Nacionalnom parku "Šarplanina"

REFERENCES

Stevanović, V. (ed.) (1999) :Crvena knjiga flore Srbije. Tom 1. (in press). Biološki fakultet Univerziteta u Beogradu, Zavod za zaštitu prirode Srbije. Beograd.

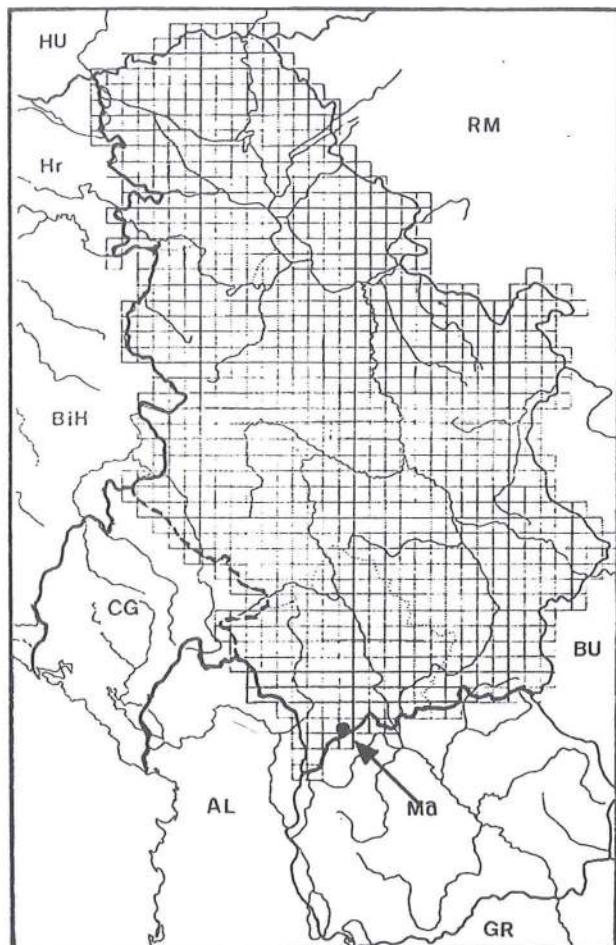


Fig. 3. Areal of the species *Draba siliquosa* Bieb. in Serbia
Sl. 2. Areal vrste *Draba siliquosa* Bieb. u Srbiji.

Tutin,T.G., Heywood,V.H., Burges, N.A., Moore,D.M., Valentine, D.H., Walters, S.M. & Webb, D.A. (eds.)(1964): *Draba carinthiaca* Hoppe, Flora Europaea 1: 311. Cambridge University Press.

Velčev, V. (ed.)(1984): Červena kniga na NR Blgarija. Tom I. BAN. Sofija.

Vlev, ST. (1970): Rod Rupa-*Draba* L. In Jordanov, D. (ed.): Flora na NR Blgarija, IV: 523-530. BAN, Sofija.

REZIME

DRABA SILIQUOSA BIEB. (DRABA CARINTHIACA HOPPE) - NOVA VRSTA ZA FLORU JUGOSLAVIJE

¹Lidija Amidžić, ²Vladimir Stevanović, ³Zoran Krivošej

¹Zavod za zaštitu prirode Srbije, Odsek za biologiju PMF-a Univerziteta u Prištini ²Institut za botaniku i Botanička bašta Biološkog fakulteta Univerziteta u Beogradu ³Odsek za biologiju PMF-a Univerziteta u Prištini

Draba siliquosa Bieb. (*Draba carinthiaca* Hoppe) je glacijalni relikt do sada opisan u visokoplanskoj flori srednje Evrope, od Pirineja, preko Alpa, Sudeta, Tatri, pa do Pirina i Rile na Balkanskom poluoselu.

Tokom terenskih istraživanja 1996. godine, ovaj smo takson pronašli i u Srbiji ispod samog grebena Crnog vrha (2581 m n.v.), na silikatnim stenama i kamenjarima alpijske zone severnih padina Šar-planine. Novo nalazište predstavlja još jedan planinski disjunkt ove orofite koja ulazi u grupu srednjeevropskih planinskih elemenata flore (pirinejsko-alpsko-karpatsko-balkansko-severnoskardopindskih).

Draba siliquosa Bieb. pripada sekciji *Leucodraba* koja je u flori Jugoslavije do sada imala samo jednog predstavnika - endemičnu balkansku vrstu *Draba korabensis* Kumm. et Deg., rasprostranjenu na planinama jugozapadne i istočne Srbije (Šar-planina, Prokletije, Stara planina), zapadne Bugarske i severne i severo-istočne Albanije. Poput vrste *Draba korabensis*,

i *Draba siliquosa* je mala biljčica (1-8 cm) koja na Šar-planini ne premašuje visinu od 2 cm. Pripada životnoj formi patuljastih busenastih hamefita (*Ch suff caesp.*).

Populacija ove vrste na grebenskom delu Crnog vrha u granicama Nacionalnog parka "Šarplanina", je malobrojna, sastavljena od nekoliko desetina prime-raka. Pošto je to do sada njena jedina registrovana populacija ne samo u Srbiji, nego i u Jugoslaviji, *Draba siliquosa* se nalazi na spisku Toma 1 Crvene knjige flore Srbije (S t e v a n o v i ć, V. ed., 1999, in press), kao krajnje ugrožena (CR B1) prema IUCN kategoriji ugroženosti u Srbiji.

Received: November, 1998.

Accepted: December, 1998.



DISTRIBUTION OF BUTTERFLY COMMUNITIES (Lepidoptera: Hesperioidea & Papilioidea) IN PLANT COMMUNITIES OVER THE JAZINACKO JEZERO LAKE REGION ON SAR-PLANINA MT.

Predrag JAKŠIĆ

Doc. dr Predrag Jakšić, Faculty of Natural Sciences and Mathematics, Vidovdanska Str., bb,
YU-38 000 Pristina, Yugoslavia

ABSTRACT

Existence of zoocenotic complex of some species of butterflies in plant communities (alliance and their association) on Šar-planina Mt. has been examined. Field investigations have been done on the vertical profil of Šar-planina Mt., from the River Lepenac (390 m), through Brezovica (900 m) and the Jažinačko jezero Lake (2180 m) to the highest peak Peskovi (2651 m) on

the crest (= bilo) of Šar-planina Mt. It has been established presence of specific community of butterflies in each plant community. Analogy at vertical disposition of butterflies on Šar-planina Mt. and horizontal disposition in Europe has been discussed analyzing the fauna elements in particular plant communities.

KEY WORDS: zoocenotic analyzis, butterflies, Šar-planina Mt.

INTRODUCTION

Plant communities located on the Šar-planina Mt. are the subjects for intensive research for most scientist for years. Rexhepi (1994) gave the survey of the alliances and their associations. However, it is also very important to define fauna elements in some of the vegetative regions together with phytocenological separation of Šar-planina Mt.

Matvejev (1961) and Matvejev & Puncer (1989) have given global concept of analitical discussion about the connection between plant communities and their animal species. They have cited the specific elements of fauna, mostly grasshoppers, reptile, birds and mammals. On the other hand, connection of some butterflies' species to some biome has been widely discussed in scientific papers of the most lepidopterologist. Lattin G. de (1952, 1957), Kostrowicki (1969) and Varga (1977) gave summary review of these researches. The distribution of butterflies in plant communities in the region of former Yugoslavia is still incomplete, thus it can be found only in a few texts about fauna in individual regions. There are a large number of studies on plant communities, but the studies on communities of individual butterflies' species are still at the beginning. Only fragmentary data show that two or more butterflies' species meet together. This has encouraged us to pay more attention on this specific category of corelations during our field examination. So, in the following we would like to present the distribution of individual butterflies species in some plant communities, and also to point out the reciprocal connection between them. We will try to explain the factors that indicate such connections.

MATERIAL AND METHODS

We have explored the north slopes of the Šar-planina Mt., from the river Lepenac near the place called Deneral Janković (390 m), via Brezovica (900 m) and Jažinačko jezero Lake (2180 m), up to the highest peaks of Peskovi massive (2651 m). The difference in altitude between the highest and the lowest point of this profile is 2261 m that indicate climazonal, oroclimatic and pedoclimatic separation of vegetation. There are many different systems of classification and nomination of plant communities, but we have decided to accept the classification of basic types of vegetation in this specific profile according to Stevanović et al (1995).

During our field research, we have registered butterfly' species in several different biotopes and in several vegetative zones. Some of these species, which are very mobile, could be found through whole vertical profile of explored region. We have cited specific biotope for each species. Specific biotope is the place where female finds oviposition plants and where the adult nectar plants are present. One of the indicators for specific biotope is the frequency in presence in concerned vegetative zone. We have also considered the fact that each species is characterized with specific dynamics of population' numerously. We have included some specific cases of deviation, for example inversion of fauna which is present in gorges and canyons, as well as the appearance of fauna azonality which could be found along the mountain riversides. From 147 established species of butterflies on Šar-planina Mt. we have reviewed 61, and they are involved in formation of 8 zoocenoses.

Taxonomy and nomenclature of butterflies has been given according to Kudrna (1986).

We have been doing zoocenotic analysis of butterflies (Lepidoptera: Hesperioidae & Papilioidea) in this region for over 20 years (1976 - 1997). Our field exploration have been supported by several resources. One of them is Academie Serbe des Sciences et des Arts, their Foundation for fauna of Serbia and the Department for environmental protection of Serbia. University of Priština was also involved. I am using this opportunity to express my gratitude.

RESULTS

1. The lowest point on vertical profile of Šar-planina Mt. is the riverbed of river Lepenac (390 m). In this part the main type is the vegetation of floatable, marshy and higrophile ivy and popular forest of Salicion albae and Populion albae. Typical association of these forests is Ass. Salici-Populeum nigrae, and basic creators of this community are plants from Salix and Populus genus.

In the following we are citing specific species of butterflies for this community, the names of food plants of their caterpillars are given in brackets:

Carcharodus floccifera (Zeller, 1847) (*Stachys* sp.),

Everes alcetas (Hoffmannsegg, 1804) (*Leguminosae*),

Apatura iris Linnaeus, 1758 (*Salix caprea*, *S. aurata* & *S. cinerea*),

Apatura ilia D. und S., 1775 (*Populus tremula* & *P. nigra*) and

Limenitis populi Linnaeus, 1758 (*Populus tremula*).

Obvious connection between these five species caused by food plants and their caterpillars. All five species could be found at the same time by the rule. They are sympatric and synchroic. We have found them from General Janković (390 m) to Brezovica (900 m), near the Muržička reka River, about 900 m.

Zerynthia species (*Z. polyxena* D. und S., 1775 and *Z. cerisyi* Godart, 1822) is also connected to community of floatable, marshy and higrophile ivy and popular forests. Food plant for its caterpillars are planites from Aristolochia genus, and butterflies appear in the spring. This species was present on several localities along Lepenac river, Muržica river and Prizrenksa Bistrica river, but it is not synchroic with previous species.

Five cited species had been found together on several other localities: near Pećka Bistrica river and Dečanska Bistrica river (Jakšić, 1997, unpublished); near river Tara (Sijarić et al., 1984) and other.

2. In the foothil of Šar-planina Mt. crest main vegetative entirety consist of different communities of xerophile and xeromesophile hilly region of oak forest Quercion frainetto Ht., 1954. Typical association of these forests is *Quercetum frainetto cerris scardicum* Krasnić, 1968. This community is located on the edge of Sirinićka župa district. Basic creators of this community are plants from genus of *Quercus*, *Pirus*, *Sorbus*,

Crataegus, *Acer*, *Cornus*, *Rosa*, *Malus*, *Lathyrus*, *Stachys*, *Dactylis* et cet. In the following we are citing specific species of butterflies for this community:

Aporia crataegi Linnaeus, 1758 (*Prunus*, *Crataegus*, *Spiraea*),

Anthocharis cardamines Linnaeus, 1758 (*Cardamine*, *Sisymbrium*),

Pontia daplidice Linnaeus, 1758 (*Arabis*, *Reseda*, *Sinapis*),

Pieris brassicae Linnaeus, 1758 (*Cruciferae*, especially *Brassica* and *Tropaeolum*),

Pieris napi Linnaeus, 1758 (*Cruciferae*),

Leptidea sinapis Linnaeus, 1758 (*Leguminosae*),
Satyrium spini D. und S., 1775 (*Rhamnus*, *Prunus*, etc.),

Quercusia quercus Linnaeus, 1758 (*Quercus*),

Melitaea phoebe Goeze, 1779 (*Centaurea*, *Cirsium*, *Serratula*),

Argynnis paphia Linnaeus, 1758 (*Viola*, *Rubus*).

Homogenosity of this community is expressed through their presence in fauna of butterflies in almost all European countries. Areals of these species generally match with areal of diffusion of oak forests. Analyzing fauna of butterflies Tien Schan and Altai (Zhdanko, 1983) we can notice that all of cited species are present in deciduous forests. Almost all of the species from this group are arboreal fauna elements in zoogeographic sense and have Palaearctic distribution.

3. In the region of deciduous forests the communities of hilly meadows, pastures and stony grounds of alliance of *Chrysopogono-Danthonion alpinae* Kojć, 1957 could be found. Typical association of this alliance for Brezovica region is Ass. *Centaureo-Trifolietum velenovskyi* Rexhepi, 1978. On these xerophile meadows we can find the community of following species:

Pyrgus alveus (Hbner, 1803) (*Potentilla*, *Althaea*, *Malva*, *Centaurea*),

Erynnis tages Linnaeus, 1758 (*Lotus*, *Coronilla*, *Medicago*),

Polyommatus icarus Rott., 1775 (*Trifolium*, *Ononis*, *Genista*),

Lycaeides idas Linnaeus, 1761 (*Leguminosae*),

Cyaniris semiargus Rott., 1775 (*Anthyllus*, *Trifolium*, *Melilotus*, *Genista*),

Maculinea arion Linnaeus, 1758 (*Thymus*),

Hyponephele lycaon K(hn, 1774 (*Poa*, *Aira*),

Melanargia galathea Linnaeus, 1758 (*Pbleum*, *Holcus*, *Bromus*),

Coenonympha pamphilus Linnaeus, 1758 (*Cynosurus*, *Poa*, *Anthoxanthum*).

This community is present in the south region but in the higher parts lake the region of Gini vode waters and Mekuš bor - 1500 m.

All these species belong to arboreal fauna elements and have eurosiberian areal type.

4. Above oak forest region there are the mesophyle continental hilly - mountain beech forests alliances of *Fagion moesiaceae* Blečić et Lakušić, 1970, with two suballiances and each has one association typical for Šar-planina Mt. from Brezovica (900 m) re-

gion to Prevalac pass (1500 m): Ass. *Fagetum moesiaceae* montanum Blečić et Lakušić, 1970; and *Abieti-Fagetum moesiaceae* Blečić et Lakušić, 1970.

In these associations we have found the community of the following species of butterflies:

Pyrgus malvae Linnaeus, 1758 (*Fragaria*, *Rubus*, *Coronilla*),

Papilio machaon Linnaeus, 1758 (*Umbelliferae*, *Rutaceae*),

Gonepteryx rhamni Linnaeus, 1758 (*Rhamnus*),
Lycaena virgaureae Linnaeus, 1758 (*Rumex*),
Celastrina argiolus Linnaeus, 1758 (*Rhamnus*, *Calluna*),

Polyommatus thersites Cantener, 1834 (*Onobrychis*),

Argynnis adippe Linnaeus, 1767 (*Viola*),
Argynnis niobe Linnaeus, 1758 (*Viola*),
Limenitis reducta Staudinger, 1901 (*Lonicera*),
Nymphalis polychloros Linnaeus, 1758 (*Cerasus*, *Ulmus*, *Prunus*),

Coenonympha arcania Linnaeus, 1761 (*Brachypodium*, *Melica*).

These species are of the same type as previous.

5. Subalpic forests of Munika pine in the limestone and serpentine alliance of *Pinion heldreichi* Ht., 1946 present on Šar-planina Mt. in the region of Gine voda waters (1400 - 1600 m) with association *Seslerio autumnalis* - *Pinetum heldreichii* Janković et Bogojević, 1962. Munika pine forest are light, warm and dry (Janković et al., 1981). Munika pine itself as tertiary relict is typical representative of oromediterranean, and Trinajstić (1985) marked this region as Balcanian province.

Typical community of butterflies established in the region of this particular plant community consist of the following species of butterflies:

Cupido osiris Meigen, 1829 (*Onobrychis*, *Lathyrus*),

Lycaena candens H.-S., 1844,
Polyommatus coridon Poda, 1761 (*Hippocrepis*),
Polyommatus belargus Rott., 1775 (*Hippocrepis*),
Erebia ottomana H.-S., 1847,
Erebia melas Herbst, 1796,
Coenonympha rhodopensis Elwes, 1900.

All of them are typical representatives for oromediterranean.

6. Subalpic forests of Molika pine on the silicate alliances of *Pinion peucis typicum* M. Janković, are also located on Šar-planina Mt. in the region of Gine vode waters, exposed toward Nort - West, well developed on 1700 meters. This alliance is represented by association *Ajugo pyramidalis* - *Pinetum peucis* Janković et Bogojević, 1962 in this locality. Below jažinačko jezero lake, in the river basin of Suvi potok Creek, and little further from the region of Jažinačko jezero lake near Stojkova kuća (1850 m) there is another important community of Molika pine: *Rhododendro ferruginei* - *Pinetum peucis* Janković et Bogojević, 1962. Molika pine forest are dark and moist (Janković et al., 1981).

Typical community of butterflies established in the region of this particular plant community consist of the following species:

Boloria graeca Staudinger, 1870

Erebia rhodopensis Nicholl, 1900,
Erebia gorge Hübner, 1804.

These three species have been found together in most localities of Rila Mt., Šar-planina Mt. and Prokletije Mt. They can also be found in the next vegetative zone of Juniper tree community, which is similar to Molika pine community. This butterflies species appeared there during glacial period.

They belong to oreal fauna elements group and to subgroup of euroalpic fauna elements.

7. Over the zone of Molika and Munika pine forests there is a zone of coniferous and bushes vegetation alliance of *Juniperion sibiricae*, its typical association is *Bruckenthalio* - *Juniperetum* Ht., 1938. Amidžić (1997) has been studying this area and divided it into two subassociations: 1. *Juniperus nana* - *bruckenthalia spiculifolia* Horv., subass. *Vaccinetosum uliginosi* L. Raj. in the area of Devedenica and Gornja šija; 2. *Juniperus nana* - *bruckenthalia spiculifolia* Horv., subass. *Rhododendrosum ferruginei* L. Raj. in the area of Jažinačko jezero lake, Suvi potok and Virovi.

Typical community for this region consist of the following butterflies species:

Boloria pales D. und S., 1775,

Erebia pandrose Bork., 1788 (*Festuca*, *Poa*),

Erebia cassioides Reiner & Hoh., 1792 (*Nardus strictus*).

They belong to oreal fauna elements from the group of oreotundral species.

8. The highest zone of Šar-planina Mt. massive is the zone of forest free alpine grass vegetation. It is located on the crest of Bistra Mt. with its peak Peskovi (2651 m) and Jažinačka Čuka (2586 m). It is the alliance of *Ranunculion crenati* Lakušić, 1966 with typical association *Ranunculatum crenati scardicum* Rexhepi et Randjelović, 1980. In this same region we can also find alliance *Seslerion comosae* Simon, 1957 with one association which has been differently marked by many various authors: *Jasioni-caricetum curvulae* Ht., 1937 (= *Seslerietum comosae* s. Lat.), (named by Rexhepi, 1994), and *Carex curvula-Sesleria comosa* Horv. (named by Amidžić, 1997). There is one more alliance *Sileneon lerchenfeldiana* Ht., 1960, with its association *Potentillo doerfleri* - *Juncetum trifidi* Stevanović et al., 1989.

This region could be considered as ecoton because of the presence of three different alliances. Unique combination of plant species and several different types of fauna elements

characterize this area.

Such natural resources indicate rich fauna of butterflies. We will cite most common:

Pyrgus andromedae Wall., 1853; *Thymelicus aceteon* Rott., 1775; *Carcharodus flocifera* Zeller, 1847; *Erynnis tages* Linnaeus, 1758; *Parnassius mnemosyne* Linnaeus, 1758; *P. apollo* Linnaeus, 1758; *Scolitanides orion* Pallas, 1771; *Polyommatus icarus* Rott., 1775; *Aglais urticae* Linnaeus, 1758; *Clossiana euphrosyne* Linnaeus, 1758; *Boloria graeca* Stgr., 1758; *Boloria graeca* Stgr., 1870; *Erebia rhodopensis* Nicholl, 1900; *E. gorge* Hbn., 1804; *E. pandrose* Borkh., 1788; *Lasiommata petropolitana* F., 1787; and others.

According to this list it is obvious that the region of Šar-planina Mt. crest is also characterized by fauna conglomerate of different fauna elements and of different origin and genesis (preglacial, glacial and postglacial). Thorough analysis would probably show that in this region there are no food plants for caterpillars of certain butterflies species and that they are present because of nectar. But it is certain that two species (*Pyrus andromedae* Wall., and *Erebia pandrose* Borkh.) have optimal ecological condition for presence of their adults in this region. All species, without exception, have only one generation per one year. But, the species in the lower zones have two or more generation (except those with one generation). Some species of genus *Pieris*, *Polyommatus*, *Coenonympha* etc in the region of Lepenac river can form four generation per one year.

DISCUSSION

The fact that allochone species of Šar-planina Mt. crest have different origin, genesis and age impose the question when have they come to this region. Movable of this insects is one of the answers. But, it explains only the presence of the species which do not take oviposition. To solve this we have to compare the data on their distribution together with data on historical geology. Lindroth (1949) discovered, using the example of Fenoskandinavija insects, that many species have adapted to hills which have not been covered with ice, and on this places they are distributed very local. In that narrow refuges they could survive negative conditions. The same must have happened to preglacial coniferous Molika and Munika pine. They have spread their areal into today's boundaires during the postglacial period. Glacial species which prefer cold climate, after withdrawing if ice, could remain only on the peak of north exposition. Such examples on this part of Šar-planina Mt. are: *Pyrus andromedae* Wallengren, 1853; *Vacciniina optilete* Knoch, 1781, *Boloria pales* D. und S., 1775; *Erebia pandrose* Borkhausen, 1788, etcet.

We have to point out on the presence of some aggressive migratory elements of butterflies fauna which does not belong at all to palaeartic species, for example palaeotropic species *Colias crocea* Geoffron in Fourcroy (fam. *Pieridae*), which came from eumediterranean. The other species from this group is *Vanessa cardui* Linnaeus, 1758 (*Nymphalidae*) which has inartic origin. Both species do not have diapause in any developing stadium on the entire profile of Šar-planina Mt.

Disposition of some fauna elements in vegetative zones of explored part of Šar-planina Mt. are shown on Fig. 1.

This figure show that in vertical distribution of butterflies fauna on explored profile of Šar-planina Mt. exist the same legitimization which can be noticed when analyzing fauna structure from south toward the north European land.

Fig. 1.: Disposition of some elements of butterflies fauna in vegetative zones on vertical profile of Šar-planina Mt. in the section Lepenac - Peskovi.

VEGETATIVE ZONES	THE FAUNA ELEMENTS OF BUTTERFLIES
Salicion albae & Popilion albae	Palaeartic Siberian Mediterranean East Mediterranean
Quercion frainetto	Palaeartic Siberian Mediterranean
Chrysopogono-Danthonion alpinae	Palaeartic Siberian Mediterranean East Mediterranean
Fagion moesiaceae	Siberian Mediterranean East Mediterranean North and Pontic Mediterranean
Pinion heldreichii	East Mediterranean Oromediterranean
Pinion peucis	Oromediterranean European Alpine
Juniperion sibiricae	European Alpine Oreotundral
Ranunculion crenati & Seslerion comosae	Siberian Mediterranean
	East Mediterranean Oromediterranean European Alpine Oreotundral Boreal

CONCLUSION

Our exploration have proved the existence of butterflies communities on vertical profile of Šar-planina Mt., from river Lepenac to Peskovi Mt.

The existence of 8 vegetative zones in the range of alliances has been established. The presence of specific zoocenotic combinations of butterflies species has been established for each zone. From 147 established species 61 is involved in creation of 8 zoocenoses.

This combinations are caused by ecological factor effects, like the existence of food plants for caterpillars and other.

This fact has been established by having insight into literature, and her existence in many different areas of Palaeartic region. Zoogeographical analysis has showed that for each vegetative zone there specific presence of certain fauna elements. Vertical distribution on Šar-planina Mt. matches the horizontal distribution on European land, toward north - south.

Azonal arrangement in distribution is registered along narrow zone of riverbanks, as well as in the area of Šar-planina Mt. crest.

REFERENCES

- Adamović L., 1909. Die Vegetationsverhältnisse der Balkanlanderer. Leipzig.
- Amidžić Lidija, 1997. High-mountain Vegetation of the Circues in Suvi and Durlov Potok Creek-Basins on the Šar-planina Northern Slopes. University Thought, Nat. Sci., IV(1): 27-31, Priština.
- Em H., 1931. Karta šuma po vrsti drveća i karta šuma po vrsti uzgoja Južne Srbije., 1: 100.000. Ministarstvo šuma i rudnika, Beograd.
- Horvat I., 1935-39. Istraživanje vegetacije planina Vardarske banovine. Ljetopis Jugoslavenske Akademije, 47-51, Zagreb.
- Horvat I., 1960. Planinska vegetacija makedonije u svijetu suvremenih istraživanja. Acta Musei Macedonici, Sci. Nat., VI(8): 163-204, Skopje.
- Jakšić P., 1997. Dnevni leptiri Prokletija (Lepidoptera: Hesperioidea & Papilioidea). Manuscript, In print.
- Janković M.M. i Bogojević R., 1974. Pinetum mughi-Ptilotricho-Bruckenthalietum spiculifoliae, nova asocijacija planinskog bora krivulja (*Pinus mugo*) na serpentinskih masivima Ostrovice (Šar-planina, SR Srbija). Ekologija, 9(2): 153-156, Beograd.
- Janković M.M., Bogojević R., Živanović Ž. i Blaženčić Jelena, 1981. Rezultati uporednih proučavanja mikroklimatskih uslova u različitim visinskim šumskim pojasevima Šarplanine. Ekologija, 16(1): 57-78, Beograd.
- Kostrowicki A.S., 1969. Geography of the Palearctic Papilioidea (Lepidoptera). PWN, Krakow.
- Kudrna O., 1986. The Butterflies of Europe. Aula Verlag, Wiesbaden.
- Latin G. De, 1952. Zur Evolution der westpal(arktischen) Lepidopterenfauna. Decheniana, 105-106: 115-164.
- Latin G. De, 1957. Die Ausbreitungszentren der holarktischen Landtierwelt. Verh. Dtsch. Zool. Ges. Hamburg, 380-410.
- Matvejev S.D., 1961. Biogeografija Jugoslavije. Biološki institut NR Srbije, Beograd.
- Matvejev S.D. i Puncer I., 1989. Karta bioma. Preddeli Jugoslavije i njihova zaštita. Prirodnački muzej u Beogradu, Beograd.
- Rexhepi F., 1994. Vegjetacioni i Kosovës. Prishtinë.
- Sijarić R., Lorković Z., Cornelutti J. i Jakšić P., 1984. Fauna Durmitora: Rhopalocera (Insecta, Lepidoptera). Fauna Durmitora, I: 95-184, CANU, Titograd.
- Stevanović V., Jovanović S. i Lakušić D., 1995. Diverzitet vegetacije Jugoslavije. U: Stevanović V., Vasić V., eds. (1995) Biodiverzitet Jugoslavije sa pregledom vrsta od medjunarodnog značaja. Biološki fakultet i Ecolibri, Beograd.
- Trinajstić I., 1985. Oromediterranska fitogeografska regija. Biosistematika, 11(2): 83-89, Beograd.
- Varga Z., 1977. Das Prinzip der areal-analytischen Methode in der Zoogeographie und die Faunelemente-Einteilung der europäischen Tagschmetterlinge (Lepidoptera: Diurna). Acta Biologica debrecina, 14: 223-285.
- Zhdanko A.B., 1983. Altitudinal distribution of the butterflies (Lepidoptera: Papilioidea) in the mountains of northern Tien Schain and southern Altai. Revue d' Entomologie de l' URSS, LXII(4): 716-727, Leningrad.

REZIME

DISTRIBUCIJA ZAJEDNICA DNEVNIH LEPTIRA (Lepidoptera: Hesperioidea & Papilioidea) U BILJNIM ZAJEDNICAMA NA ŠIREM PODRUČJU JAŽINAČKOG JEZERA NA ŠAR-PLANINI

JAKŠIĆ Predrag, Univerzitet u Prištini, PMF, Odsek za biologiju, Vidovdanska bb, 38000 Priština

Na vertikalnom profilu Šar-planine od reke Lepe-nac (390 m), preko Brezovice (900 m) i Jažinačkog jezera (2180 m) do najvišeg vrha Peskovi (2651 m) vršili smo istraživanje zoocenološkog kompleksa dnevnih leptira. Raščlanjenje tog vertikalnog profila uradili smo prema postojećim vegetacijskim pojasevima (8 sveza). Za svaki pojaz smo utvrdili postojanje specifične zoocenoze dnevnih leptira. Vezanost datih vrsta za određeni vegetacijski pojaz uslovljena je ekološkim faktorima, najpre postojanjem prehrambenih biljki gusenica. Analizirali smo faunističku pripadnost vrsta tipičnih za date pojaseve. Utvrđili smo postojanje pravilne smene tih elemenata. Izuzetak je azonalni raspored duž reka i azonalni raspored na samom planinskom bilu (Fig. 1). Smena faunističkih elemenata na vertikalnom profilu Šar-planine analogna je smeni faune na horizontalnom profilu Evrope, idući od juga ka severu.

Received: September, 1998.

Accepted: October, 1998.

ALTITUDINAL DISTRIBUTION AND BIOGEOGRAPHICAL DIVISION OF THE BUTTERFLIES OF BALKAN PENINSULA (Lepidoptera: Hesperioidae & Papilionoidea)

Doc. dr Predrag JAKŠIĆ, University of Pristina, Faculty of Natural Sciences and Mathematics,
Department of Biology, Vidovdanska bb, 38000 Pristina

ABSTRACT

Altitudinal distribution of 285 butterflies species of the Balkan peninsula, which is based on our own results obtained through field work and also on the basis of information from literature, have been presented in this work.

Biogeographical division of butterflies of the Balkan peninsula have been revised by analyzing altitudinal and horizontal distribution, as well as general biological features of species. They have

been classified into 20 biogeographical units, according to their distribution, origin and genesis. Thus, fauna is formed of seventeen Palaearctic biogeographical regions, two Palaeotropic regions and one Nearctic region. Each butterfly species has been classified into appropriate biome.

Some expositions, have been given for offered results through certain examples.

KEY WORDS: Butterflies, Altitudinal distribution, Biogeographical division, The Balkan peninsula.

INTRODUCTION

There is a fact that species are not completely distributed in their areals. This is confirmed through analysis of distribution maps of butterflies of the Balkan peninsula. The areal territory is unhomogenous because of variable ecological factors. The most important cause for this unhomogeneity on the Balkan peninsula is the orographic factor. At the same time it is also very important factor for fauna resources. On the other side, the species itself are incapable of living in each part of their areals because of their biological characteristics (ecological restrictions). Effects caused by orographic factors are closely related to geological characteristics. There are several great geological entities on the Balkan peninsula. They differ in their geological constitution, history of forming, tectonic and in other features. Orographic factors are closely related with microclimatic factors, especially with temperature. It is known that temperature is falling with higher altitudes, for example on each 140 - 195 m temperature is falling for 1°C. Herein, this temperature value is areal altitude factor, it has an influence over its altitudinal zonality.

The matter of altitudinal distribution of butterflies of Balkan peninsula still has not been considered as integral form. This matter is brought up in some faunistic papers about smaller or bigger geographical entities. However, analysis of the rules of distribution and integral syntheses are still missing.

The aim of our work was to present and analyze altitudinal distribution of butterflies of Balkan peninsula. We have also tried to establish a correlation between distribution and disposition of altitudinal zones in the mountains of Balkan peninsula. That is how we have attained a prerequisite for analysis of biogeographical appurtenance of butterflies of the Balkan peninsula.

METHOD

According to our own results obtained through field work and litterature data, we have shown in tabular form altitudinal distribution of butterflies of Balkan peninsula. We have determined 10 altitudinal zones. Among abiotic ecological factors the most important are geologic-historical factors and climatic factors:

1. Para-Tethys Coastline during the Neogene period was spreded up to about 450 m.
2. The level of the ancient Aegean sea during the Neogene period was 600-800 m.
3. Aegean lake coast during the Pliocene period was on 760 m.
4. The level of prae-lake valley in Macedonia during the Miocene period was on 1000-1200 m.
5. Lower border of glacial coastline during the Diluvium period was up to 1600 m.
6. Lower border of fluvio-denudational surface was up to 1800-2000 m.

Among biotic factors, a phenomen of vegetative zones highly influenced the development of altitudinal zones. The most important borders of zones are:

7. In the zone of 0-300 m, Mediterranean province and subprovince of Pannonian-Dakian steppes.
8. In the zone of 300-450 m, Sub-Mediterranean province, whose representative is upper border of forests of Sessile Oak and Hornbeam (Quercus-Carpinetum HT, 1938 s. lat.).
9. In the zone of 450-600 m there is a climatogene community of Pubescent Oak forests and Eastern forests (Quercus-Carpinetum orientalis H-JČ, 1939 s. lat.). There is also Moesian Forest and Hungarian Oak region (Quercetum frainetto moesiacum B. Jov., 1975), together with the lower border of Macedonian Oak Forests [Quercetum trajanae EM et HT (1950) 1959 s. lat.].

10. In the zone of 600-800 m, a subprovince of Balkanian-Middle European forests. This zone is characterized by the following communities:

- Upper border of Macedonian Oak Forest (*Quercetum trajanae* EM),
- Moesian Forest of Turkey Oak (*Quercetum ceris moesiacum* E.Vuk. 1966 s. lat.),
- Lower border of Eastern Hornbeam and Balkan Yam forests (*Dioscoreo-Carpinetum orientalis* BLEČ. et LAKŠĆ, 1966),
- Lower forest border of Beech and Common Silver Fir forest (*Abieti-Fagetum* (HT. 1938) TREG. 1957 s. lat.).

11. Altitudinal zone of 800-1000 m is characterized by the following zones:

- Upper forest border of Subprovince of Submediterranean-Balkanian forest.
- Upper border of Epi-Mediterranean zone of Mediterranean-Montane vegetative zone of Mediterranean-Montane vegetative zone of Mediterranean region, and
- Lower border of Subprovince of Balkanian-Middle European forests in the South-Eastern part of areal.

The following plant communities are typical for this altitudinal zone:

- Upper border of Pubescent Oak and European Hornbeam forests [*Ostryo-Quercetum pubescens* (HT. 1950) TRINAJ. 1974],
- Upper forest border of Macedonian forest of Steppe Common Oak [*Quercetum pedunculliflorae macedonicum* EM. 1965].
- Upper forest border of Sessile Oak forest [*Quercetum petrae* (B. JOV. 1948) ČER. et B. JOV., 1953 s. lat.].

12. Altitudinal zone located between 1000-1200 m is characterized by the following zones:

- Upper border of Subprovince of Aegean-Anatolic semideserts and
- Lower forest border of Eastern-Mediterranean Coastal forests.

The following plant communities are typical for this altitudinal zone:

- Lower border of Subalpine Beech forest (*Fagetum subalpinum* HT. 1938 s. lat.),

- Lower border of Mountain forests of Norway Spruce [*Piceetum abietis montanum* HT (1938, 1950, 1962) 1967 s. lat.].

13. Altitude zone located between 1200-1400 m is characterized by the presence of two communities:

- Lower border of Heldreich's Pine Forests (*Pinetum heldreichii* BLEČ. 1959 s. lat.), and
- Lower border of Mountain-Pine forests (*Pinetum mugo* HT. 1938 s. lat.).

14. In lower altitude zone located between 1600-1800 m there is a lower border of biome of rocky grounds and pastures. This typical afforested altitude zone is characterized by the following communities:

- Lower border of Beech and Common Silver Fir forest [*Abieti-Fagetum* (HT. 1938) TREG. 1957 s. lat.],
- Upper border of Mountain forests of Norway Spruce [*Piceetum abietis montanum* HT. (1938, 1950, 1962) 1967. s. lat.].
- Upper border of Heldreich's Pine forests (*Pinetum heldreichii* BLEČ. 1959 s. lat.)

15. Altitude zones located between 1800-2000 m is the upper border of Mediterranean Coastline forests. It is characterized by the following plant communities:

- Upper border of Rhododendron community (*Rhododendron-Pinetum peucis* M. JANK.)
- Upper border of Subalpine Beech forests (*Fagetum subalpinum* B.JOV. 1976 s. lat.).

16. Altitude zone located between 2000-2200 m is defined by the presence of upper border of

Subprovince European forests of the taiga type, and lower border of Subprovince European high mountain rocky tundra. Two communities are present:

- Upper border of Macedonian Pine forests (*Pinetum peuce* HT. 1930 s. lat.), and
- Upper border of Mountain Pine forest (*Pinetum mugo* HT. 1938 s. lat.).

17. Altitude zone located between 2200-2925 m is defined by a zone of Subprovince European high mountain rocky tundra.

This altitudinal distribution on Balkan peninsula mountains (0-2925 m) have its equivalent in vegetative distribution on horizontal profile of Europe, in a direction toward North - South. This equivalency have been presented by Gorodkov (1984), and it is shown in Fig. 1.

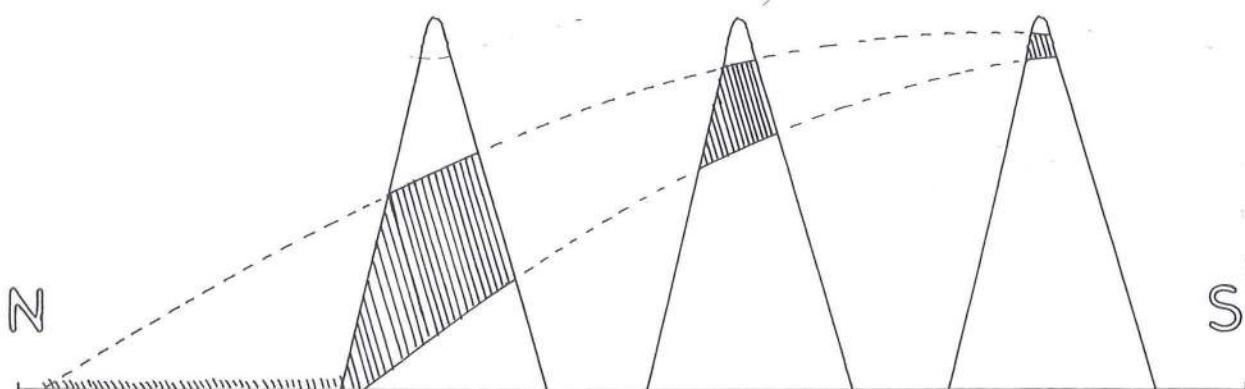


Fig. 1. The equivalent relationship between the horizontal area of Europe (North - South direction) and altitudinal area of the Balkan peninsula mountains. (According to Gorodkov, 1984. Modified)

Biological consequences of this phenomenon have been summarized in the fact that 8 zonobiomes and orobiomes are present on the balkan peninsula.

Having in mind these stated principles and biological features of species, we have analyzed appurtenance of butterflies of Balkan peninsula. It is based on principles which had been given by several authors: Varga (1977), for butterflies and Matvejev (1961), Matvejev & Puncer (1989) and Lopatin & Matvejev (1995) for general biological principles. That is how we have connected each species of butterflies of balkan peninsula with specific biome. The biome represent theirs historical issue. Biogeographic division that has been presented in this paper was deducted from division of flora on planet Earth according to Diels (1928) and Engler (1936). This was excepted by many contemporary authors of today like Magdefrau und Ehrendorfer (1971), Janković (1985) and many others.

Apiled classification and nomenclature of butterflies are given according to Karsholt & Razowski (1996).

RESULTS

The results of altitudinal distribution analysis of butterflies of Balkan peninsula are shown in Table 1 (columns 1 - 10). The results obtained through analysis of biogeographic appurtenance of these species are shown in Table 1 (column 11). The key for explanation of applied biogeographic classification is shown in Table 2. This key contain the connection between 20 biogeographic units and biomes typical for these units in Palaearctic.

The biomes in Palaearctic: A. (1, 2 & 3)Biomes of Alpine and High Nordic rock-grounds, pastures and snow patches, B.(4) Biome of European, mostly coniferous boreal type woodlands, C. (5 & 6) Biome of South European, Mostly deciduous woodlands, D. (7, 8, 9 & 10) Biome of steppes and woodland steppe, E. (11) Biome of Irano-Turanian semideserts, F. (13) Biome of Submediterranean mostly Oak woodlands, G. (14) Biome of evergreen Mediterranean maritime woodlands and maquis, H. (15) Biome of rocky grounds, pastures and (Pinion peucis HT. 1950 and Pinion heldreichii HT. 1946) woodlands on rocky grounds of (oro) Mediterranean mountains, I. (17) Biomes of deserts and semideserts.

DISCUSSION

Using the information in Table 1 it is possible to analyze a connection between sympatry and alopatri of some faunistical components. In the very beginning we can separate species that are impassable stenotopic. There are two groups of species: the first group are those found in a zone between 0-450 m (1. and 2. column on Table 1). This group has 8 species: 7, 35, 89, 101, 120, 214, 229 and 235. This species are located in South Greece and on the East-Mediterranean islands. The Faunistical ones mostly belong to Irano-Turanian

and Saharo-Eremial groups. The second clearly separated group are those species found in a zone between 1800-2925 m (7 - 10 column on Table 1). There are 22 species: 16, 17, 85, 87, 125, 127, 128, 129, 130, 144, 185, 241, 246, 247, 248, 249, 251, 257, 258, 278, 281 and 284. We can divide this group into two subgroups: the first subgroup are thermophile (Oro)Mediterranean species of high mountains in the southern part of Balkan peninsula (no. 15 on Table 2). The second subgroup are frigofuge glacial relict species of Northern mountains of Balkan peninsula (columns 1, 2, 3 and 4 on Table 2). The rest 255 species are mostly equally distributed on vertical profile of Balkan peninsula. This is caused by increased mobility of butterflies as groups of organisms, including favorable ecological circumstances of Balkan peninsula as entity. Species find their ecological optimum in one altitudinal zone where larval oviposition plants, adult nectar plants and roosting - sites are. However, we can find species out of altitudinal zone of ecological optimum, only the frequency in presence is lesser. In order to achieve complex relation in alopatri it is necessary to combine it with horizontal distribution and asynchrony in the appearing period for the species during the season.

The main material constituent for butterfly communities in Balkan peninsula are Pontis-Mediterranean fauna elements with 48 species, and Middle-European fauna elements with 45 species, as shown on Table 1. (Oro)Mediterranean element with 31 species also take an important part. Middle-European fauna elements are not dominant on Balkan peninsula, not even in the community with two remnant components of European-Siberian group [Boreal (4) and European-montane (5)]. These three components take part in fauna of Balkan peninsula with 61 species, which are only 21% of the species.

A better explanation for this phenomena has been given through horizontal distribution analysis. European-Siberian species are mostly distributed in the North-West region of Balkan peninsula. In this region, mostly localized species are the glacial relict species. The range Prokletije Mt. - Šar-planina Mt. - Rila Mt. represent distinct border zone between two fauna types. Fauna of Mediterranean basin and Pontic basin is typical for Macedonian mountains, South-Bulgarian mountains and Greek mountains. During Cretaceous period, the eastern part of Balkan peninsula had been partially inundated by Paratetis. During the Alpic orogeny period in Mesozoic this part of the peninsula had been completely connected with land. This land had a direct contact with Ponto-Caspian valley. During the Pliocene period, Aegeida had been connected to Asia. All these had an important influence over long term communication and exchanges of fauna of these areas. However, the southern part of Balkan peninsula had not been under the influence of glaciation. For this reason, there are 100 species from these biogeographical units (10 - 16, Table 2), which makes 36% of butterflies' fauna on Balkan peninsula. Among them, there is a great number of species that represent endemes and relicts of Ancient Mediterranean.

Tab. 1. Altitudinal distribution and biographical division of the butterflies (*Lepidoptera: Hesperioidae & Papilioidea*) on the Balkan peninsula.

1-10 = altitudinal zones (1=0-300 m, 2=300-450 m, 3=450-600 m, 4=600-1.000 m, 5=1.000-1.200 m, 6=1.200-1.500 m, 7=1.500-1.800 m, 8=1.800-2.000 m, 9=2.000-2.200 m, and 10=2.200-2.925 m); 11=biogeographical division (1-20) according to Tab. 2.



I. PALAEARCTIC

Arctic

Arctic-Alpine	Arctic-Alpine s. str.	1
Sub-Arctic	East-Alpine	2
	Sub-Alpine	3 A

European-Siberian

Boreal	4 B
European-Mountain.....	5
Middle-European.....	6 C

Central-Asian

South-Siberian.....	Subpontic (Sarmat).....	7
Pontic.....	Pontic-Panonian.....	8
	Pontic-Centr.-Asian.....	9
	Pontic-Mediterranean.....	10 D

Irano-Turanian	11 E
----------------------	------

Mediterranean

East-Mediterranean	Euxinus	12
	Sub-Mediterranean	13 F
	Eu-Mediterranean.....	14 G
	(Oro)Mediterranean	15 H
West-Mediterranean ...	Sub-Atlantic-Submediterranean	16

North-African

Saharo-Eremial	17 I
----------------------	------

II. PALAEOTROPIC

Afrotropic	18
Oriental	19

III. NEARCTIC

Central-American	20
------------------------	----

Table 2. Biogeographical division of the butterflies (*Lepid.: Hesperioidae & Papilioidea*) on the Balkan peninsula.

The biomes in Palaeartic: A. (1, 2 & 3)Biomes of Alpine and High Nordic rock-grounds, pastures and snow patches, B.(4) Biome of European, mostly coniferous boreal type woodlands, C. (5 & 6) Biome of South European, Mostly deciduous woodlands, D. (7, 8, 9 & 10) Biome of steppes and woodland steppe, E. (11) Biome of Irano-Turanien semideserts, F. (13) Biome of Submediterranean mostly Oak woodlands, G. (14) Biome of evergreen Mediterranean maritime woodlands and maquis, H. (15) Biome of rocky grounds, pastures and (Pinion peucis HT. 1950 and Pinion heldreichii HT. 1946) woodlands on rocky grounds of (oro) Mediterranean mountains, I. (17) Biomes of deserts and semideserts.

	1	2	3	4	5	6	7	8	9	10	11
HESPERIOIDEA											
HESPERIIDAE											
1. <i>Erynnis tages</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+			6
2. <i>Erynnis marloyi</i> (Boisduval, 1834)	+	+	+	+	+	+	+	+			10
3. <i>Carcharodus alceae</i> (Esper, 1780)	+	+	+	+	+	+	+	+			13
4. <i>Carcharodus lavatherae</i> (Esper, 1783)	+	+	+	+	+	+	+				14
5. <i>Carcharodus floccifera</i> (Zeller, 1847)	+	+	+	+	+	+	+	+			13
6. <i>Carcharodus orientalis</i> Reverdin, 1913	+	+	+	+	+	+	+	+			10
7. <i>Carcharodus stauderi</i> Reverdin, 1913	+										11
8. <i>Spialia phlomidis</i> (Herrich-Schäffer, 1845)	+	+	+	+	+	+	+	+			10
9. <i>Spialia sertorius</i> (Hoffmannsegg, 1804)			+	+	+	+					16
10. <i>Spialia orbifer</i> (Hübner, 1823)	+	+	+	+	+	+	+				10
11. <i>Muschampia proto</i> (Ochsenheimer, 1808)	+	+	+	+	+	+	+				14
12. <i>Muschampia tessellum</i> (Hübner, 1803)	+	+	+	+							14
13. <i>Muschampia cribrellum</i> (Eversmann, 1841)				+							9
14. <i>Pyrgus carthami</i> (Hübner, 1813)			+	+	+	+	+				6
15. <i>Pyrgus sidae</i> (Esper, 1784)	+	+	+	+	+	+	+	+			10
16. <i>Pyrgus andromedae</i> (Wallengren, 1853)								+	+	+	4
17. <i>Pyrgus cacaliae</i> (Rambur, 1839)							+	+	+	+	4
18. <i>Pyrgus malvae</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+		6
19. <i>Pyrgus malvoides</i> (Elwes & Edwards, 1897)	+	+	+	+	+	+					16
20. <i>Pyrgus serratulae</i> (Rambur, 1839)	+	+	+	+	+	+	+	+	+		6
21. <i>Pyrgus onopordi</i> (Rambur, 1839)			+	+	+	+					16
22. <i>Pyrgus cinarae</i> (Rambur, 1839)	+	+	+	+	+	+	+				10
23. <i>Pyrgus armoricanus</i> (Oberthür, 1910)	+	+	+	+	+	+	+	+			13
24. <i>Pyrgus alveus</i> (Hübner, 1803)	+	+	+	+	+	+	+	+	+		6
25. <i>Heteropterus morpheus</i> (Pallas, 1771)	+	+	+								6
26. <i>Carterocephalus palaemon</i> (Pallas, 1771)			+	+	+	+					6
27. <i>Thymelicus lineola</i> (Ochsenheimer, 1808)	+	+	+	+	+	+	+	+			13
28. <i>Thymelicus sylvestris</i> (Poda, 1761)	+	+	+	+	+	+	+	+			13
29. <i>Thymelicus acteon</i> (Rottemburg, 1775)	+	+	+	+	+	+	+	+			10
30. <i>Thymelicus hyrax</i> (Lederer, 1861)	+	+									14
31. <i>Hesperia comma</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+		13
32. <i>Ochlodes venata</i> (Bremer & Grey, 1853)	+	+	+	+	+	+	+	+			5
33. <i>Gegenes pumilio</i> (Hoffmannsegg, 1804)	+	+	+	+	+	+					17
34. <i>Gegenes nostrodamus</i> (Fabricius, 1793)	+	+	+	+							14
35. <i>Pelopidas thrax</i> (Hübner, 1821)	+	+									17
PAPILIONOIDEA											
PAPILIONIDAE											
36. <i>Zerynthia polyxena</i> (Denis & Schiffermüller, 1775)	+	+	+	+	+						10
37. <i>Allancastria cerisy</i> (Godart, 1824)	+	+	+	+							12

	1	2	3	4	5	6	7	8	9	10	
38. <i>Allancastria cretica</i> (Rebel, 1904)	+	+	+	+	+						15
39. <i>Archon apollinus</i> (Herbst, 1798)	+	+	+	+	+	+					12
40. <i>Parnassius mnemosyne</i> (Linnaeus, 1758)			+	+	+	+	+	+	+		10
41. <i>Parnassius apollo</i> (Linnaeus, 1758)			+	+	+	+	+	+	+		5
42. <i>Iphiclidess podalirius</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+			10
43. <i>Papilio machaon</i> Linnaeus, 1758	+	+	+	+	+	+	+	+	+		13
44. <i>Papilio alexanor</i> Esper, 1800	+	+	+	+	+	+	+	+			15
PIERIDAE											
45. <i>Leptidea sinapis</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+			7
46. <i>Leptidea reali</i> Reissinger, 1989	+	+	+	+	+	+					6
47. <i>Leptidea duponcheli</i> (Staudinger, 1871)	+	+	+	+							12
48. <i>Leptidea morsei</i> Fenton, 1881	+	+	+								9
49. <i>Anthocharis cardamines</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+		6
50. <i>Anthocharis damone</i> Boisduval, 1836				+							12
51. <i>Anthocharis gruneri</i> Herrich-Schäffer, 1851	+	+	+	+	+	+	+	+			12
52. <i>Euchloe ausonia</i> (Hübner, 1804)	+	+	+	+	+	+					10
53. <i>Elphinstonia penia</i> (Freyer, 1851)	+	+	+	+	+	+	+	+	+		17
54. <i>Aporia crataegi</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+		6
55. <i>Pieris brassicae</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+		13
56. <i>Pieris krueperi</i> Staudinger, 1860	+	+	+	+	+						10
57. <i>Pieris mannii</i> (Mayer, 1851)	+	+	+	+	+	+	+	+			10
58. <i>Pieris rapae</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+		13
59. <i>Pieris ergane</i> (Geyer, 1828)	+	+	+	+	+	+	+	+			10
60. <i>Pieris napi</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+			6
61. <i>Pieris bryoniae</i> (Hübner, 1806)				+	+	+	+				4
62. <i>Pieris balcana</i> Lorković, 1970				+	+	+	+	+	+		6
63. <i>Pontia callidice</i> (Hübner, 1800)								+	+		1
64. <i>Pontia daplidice</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+			13
65. <i>Pontia chloridice</i> (Hübner, 1813)	+	+	+	+	+	+	+				8
66. <i>Colias erate</i> (Esper, 1805)		+	+	+	+						8
67. <i>Colias croceus</i> (Fourcroy, 1785)	+	+	+	+	+	+	+	+	+		18
68. <i>Colias myrmidone</i> (Esper, 1780)	+	+	+								10
69. <i>Colias chrysostheme</i> (Esper, 1781)	+	+	+	+							8
70. <i>Colias aurorina</i> Herrich-Schäffer, 1850							+	+	+	+	11
71. <i>Colias caucasica</i> Staudinger, 1871						+	+	+	+		15
72. <i>Colias hyale</i> (Linnaeus, 1758)					+	+	+	+			7
73. <i>Colias alfaciensis</i> Ribbe, 1905	+	+	+	+	+	+	+				7
74. <i>Gonepteryx rhamni</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+		13
75. <i>Gonepteryx farinosa</i> (Zeller, 1847)	+	+	+	+	+	+	+	+	+		12
76. <i>Gonepteryx cleopatra</i> (Linnaeus, 1767)	+	+	+	+	+						10
LYCAENIDAE											
77. <i>Hamearis lucina</i> (Linnaeus, 1758)		+	+	+	+	+					7
78. <i>Lycaena phlaeas</i> (Linnaeus, 1761)	+	+	+	+	+	+	+	+			13
79. <i>Lycaena dispar</i> (Haworth, 1802)	+	+	+	+							9
80. <i>Lycaena virgaureae</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+			5
81. <i>Lycaena ottomanus</i> (Lefebvre, 1830)	+	+	+	+	+	+	+	+	+		12
82. <i>Lycaena tityrus</i> (Poda, 1761)	+	+	+	+	+	+	+	+			6
83. <i>Lycaena alciphron</i> (Rottemburg, 1775)	+	+	+	+	+	+	+	+	+		6
84. <i>Lycaena hippothoe</i> (Linnaeus, 1767)		+	+	+	+	+					7

85. <i>Lycaena candens</i> (Herrich-Schäffer, 1844)							+ + +			15
86. <i>Lycaena thersamon</i> (Esper, 1784)	+	+	+	+	+	+				10
87. <i>Lycaena thetis</i> Klug, 1834							+ +			12
88. <i>Thecla betulae</i> (Linnaeus, 1758)		+	+	+	+	+				7
89. <i>Apharitis acamas</i> (Klug, 1834)		+	+							17
90. <i>Neozephyrus quercus</i> (Linnaeus, 1758)		+	+	+	+	+	+	+	+	10
91. <i>Callophrys rubi</i> (Linnaeus, 1758)		+	+	+	+	+				6
92. <i>Satyrium w-album</i> (Knoch, 1782)		+	+	+						6
93. <i>Satyrium pruni</i> (Linnaeus, 1758)					+	+	+			6
94. <i>Satyrium spinii</i> (Denis & Schiffmüller, 1775)			+	+	+	+	+	+	+	10
95. <i>Satyrium ilicis</i> (Esper, 1779)		+	+	+	+	+				10
96. <i>Satyrium acaciae</i> (Fabricius, 1787)		+	+	+	+	+	+	+		10
97. <i>Satyrium ledereri</i> (Boisduval, 1848)										11
98. <i>Lampides boeticus</i> (Linnaeus, 1767)		+	+	+	+	+	+	+		19
99. <i>Leptotes pirithous</i> (Linnaeus, 1767)		+	+	+	+	+	+	+		18
100. <i>Tarucus balkanica</i> (Freyer, 1844)		+	+	+	+	+				10
101. <i>Zizeeria karsandra</i> (Moore, 1865)		+	+							19
102. <i>Cupido minimus</i> (Fuessly, 1775)		+	+	+	+	+	+	+	+	5
103. <i>Cupido osiris</i> (Meigen, 1829)				+	+	+	+	+		15
104. <i>Everes argiades</i> (Pallas, 1771)		+	+	+	+	+	+	+		6
105. <i>Everes decolorata</i> (Staudinger, 1886)		+	+	+	+					10
106. <i>Everes alcetas</i> (Hoffmannsegg, 1804)		+	+	+	+	+				9
107. <i>Celastrina argiolus</i> (Linnaeus, 1758)		+	+	+	+	+				6
108. <i>Pseudophilotes vicrama</i> (Moore, 1865)		+	+	+	+	+	+	+	+	10
109. <i>Pseudophilotes bavius</i> (Eversmann, 1832)					+	+	+			16
110. <i>Scolitantides orion</i> (Pallas, 1771)		+	+	+	+	+	+			9
111. <i>Glaucopsyche alexis</i> (Poda, 1761)		+	+	+	+	+	+			6
112. <i>Glaucopsyche paphos</i> Chapman, 1920					+	+				15
113. <i>Iolana iolas</i> (Ochsenheimer, 1816)		+	+	+	+	+				10
114. <i>Maculinea arion</i> (Linnaeus, 1758)		+	+	+	+	+	+	+		6
115. <i>Maculinea teleius</i> (Bergsträsser, 1779)					+	+	+	+	+	9
116. <i>Maculinea nausithous</i> (Bergsträsser, 1779)				+	+	+				9
117. <i>Maculinea rebeli</i> (Hirschke, 1904)				+	+	+	+	+		9
118. <i>Turanana endymion</i> (Freyer, 1850)					+	+	+	+	+	11
119. <i>Chilades trochylus</i> (Freyer, 1845)		+	+	+	+					19
120. <i>Chilades galba</i> Lederer, 1855		+								11
121. <i>Plebeius pylaon</i> (Fischer v. Waldheim, 1832)			+	+	+	+	+	+	+	16
122. <i>Plebeius argus</i> (Linnaeus, 1758)		+	+	+	+	+	+	+		6
123. <i>Plebeius idas</i> (Linnaeus, 1761)			+	+	+	+	+	+		6
124. <i>Plebeius argyrognomon</i> (Bergsträsser, 1779)			+	+	+	+	+	+		9
125. <i>Vacciniina optilete</i> (Knoch, 1781)							+	+	+	4
126. <i>Plebejidea loewii</i> (Zeller, 1847)		+	+	+						11
127. <i>Kretania eurypilus</i> (Freyer, 1851)							+			11
128. <i>Kretania psylorita</i> (Freyer, 1845)							+			15
129. <i>Agriades pyrenaica</i> (Boisduval, 1840)							+	+	+	15

	1	2	3	4	5	6	7	8	9	10	
163. <i>Brenthis ino</i> (Rottemburg, 1775)				+	+	+					7
164. <i>Brenthis daphne</i> (Denis & Schiffermüller, 1775)	+	+	+	+	+	+	+				6
165. <i>Brenthis hecate</i> (Denis & Schiffermüller, 1775)	+	+	+	+	+	+	+				6
166. <i>Boloria eunomia</i> (Esper, 1799)	+	+	+	+	+						7
167. <i>Clossiana euphrosyne</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+		5
168. <i>Clossiana titania</i> (Esper, 1793)				+	+	+	+				4
169. <i>Clossiana selene</i> (Denis & Schiffermüller, 1775)				+	+	+	+				7
170. <i>Clossiana dia</i> (Linnaeus, 1767)	+	+	+	+	+	+	+				6
171. <i>Clossiana thore</i> (Hübner, 1803)				+	+						1
172. <i>Boloria pales</i> (Denis & Schiffermüller, 1775)							+	+	+		3
173. <i>Boloria graeca</i> (Staudinger, 1870)							+	+	+		15
174. <i>Vanessa atalanta</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+			13
175. <i>Vanessa cardui</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+			20
176. <i>Inachis io</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+		6
177. <i>Aglais urticae</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+		6
178. <i>Polygonia c-album</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+			6
179. <i>Polygonia egea</i> (Cramer, 1775)	+	+	+	+	+	+	+				12
180. <i>Araschnia levana</i> (Linnaeus, 1758)	+	+	+	+	+						7
181. <i>Nymphalis antiopa</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+		6
182. <i>Nymphalis polychloros</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+		6
183. <i>Nymphalis xanthomelas</i> (Esper, 1781)				+	+	+					7
184. <i>Nymphalis vaualbum</i> (Denis & Schiffermüller, 1775)						+					9
185. <i>Euphydryas cynthia</i> (Denis & Schiffermüller, 1775)									+	+	3
186. <i>Euphydryas intermedia</i> (Ménétriés, 1859)						+	+				2
187. <i>Euphydryas maturna</i> (Linnaeus, 1758)			+	+							9
188. <i>Euphydryas aurinia</i> (Rottemburg, 1775)			+	+	+	+					6
189. <i>Melitaea cinxia</i> (Linnaeus, 1758)	+	+	+	+	+	+	+				6
190. <i>Melitaea phoebe</i> (Denis & Schiffermüller, 1775)	+	+	+	+	+	+	+				6
191. <i>Melitaea arduinna</i> (Esper, 1783)				+	+						9
192. <i>Melitaea trivia</i> (Denis & Schiffermüller, 1775)	+	+	+	+	+	+	+	+			10
193. <i>Melitaea didyma</i> (Esper, 1778)	+	+	+	+	+	+	+				10
194. <i>Melitaea diamina</i> (Lang, 1789)				+	+	+					7
195. <i>Melitaea aurelia</i> Nickerl, 1850				+	+	+					6
196. <i>Melitaea britomartis</i> Assmann, 1847		+	+	+	+						9
197. <i>Melitaea athalia</i> (Rottemburg, 1775)	+	+	+	+	+	+	+				6
198. <i>Limenitis populi</i> (Linnaeus, 1758)	+	+	+	+	+	+					7
199. <i>Limenitis camilla</i> (Linnaeus, 1764)	+	+	+	+							6
200. <i>Limenitis reducta</i> Staudinger, 1901	+	+	+	+	+						19
201. <i>Neptis sappho</i> (Pallas, 1771)	+	+	+	+							9
202. <i>Neptis rivularis</i> (Scopoli, 1763)		+	+	+	+	+					9
203. <i>Charaxes jasius</i> (Linnaeus, 1767)	+	+	+	+	+						18

	1	2	3	4	5	6	7	8	9	10	
204. <i>Apatura metis</i> Freyer, 1829	+	+									8
205. <i>Apatura ilia</i> (Denis & Schiffermüller, 1775)	+	+	+	+	+						6
206. <i>Apatura iris</i> (Linnaeus, 1758)	+	+	+	+	+	+					6
207. <i>Kirinia roxelana</i> (Cramer, 1777)	+	+	+	+	+	+					12
208. <i>Esperarge climene</i> (Esper, 1783)	+	+	+	+	+						9
209. <i>Pararge aegeria</i> (Linnaeus, 1758)	+	+	+	+	+	+	+				13
210. <i>Lasiommata megera</i> (Linnaeus, 1767)	+	+	+	+	+	+	+	+	+		13
211. <i>Lasiommata petropolitana</i> (Fabricius, 1787)	+	+	+	+	+	+	+	+	+		4
212. <i>Lasiommata maera</i> (Linnaeus, 1758)					+	+	+	+	+		10
213. <i>Lopinga achine</i> (Scopoli, 1763)		+	+	+							9
214. <i>Yphima asterope</i> (Klug, 1832)	+										17
215. <i>Coenonympha tullia</i> (Müller, 1764)					+	+					5
216. <i>Coenonympha oedipus</i> (Fabricius, 1787)					+	+					9
217. <i>Coenonympha rhodopensis</i> Elwes, 1900					+	+	+	+	+	+	15
218. <i>Coenonympha arcania</i> (Linnaeus, 1761)	+	+	+	+	+	+	+				7
219. <i>Coenonympha glycerion</i> (Borkhausen, 1788)					+	+	+				7
220. <i>Coenonympha gardetta</i> (Prunner, 1798)					+	+	+	+	+		5
221. <i>Coenonympha leander</i> (Esper, 1784)					+	+	+	+			10
222. <i>Coenonympha pamphilus</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+		13
223. <i>Coenonympha thrysus</i> (Freyer, 1845)	+	+	+	+	+	+	+				15
224. <i>Pyronia tithonus</i> (Linnaeus, 1767)	+	+	+	+	+	+					7
225. <i>Pyronia cecilia</i> (Vallantin, 1894)	+	+	+	+	+						10
226. <i>Aphantopus hyperantus</i> (Linnaeus, 1758)	+	+	+	+	+	+					7
227. <i>Maniola telmessia</i> (Zeller, 1847)	+	+	+	+	+	+					11
228. <i>Maniola cypricola</i> Graves, 1928	+	+	+	+	+	+					15
229. <i>Maniola halicarnassus</i> Thomson, 1990	+										11
230. <i>Maniola chia</i> Thomson, 1987	+	+	+								15
231. <i>Maniola jurtina</i> (Linnaeus, 1758)	+	+	+	+	+	+	+				10
232. <i>Maniola megalia</i> (Oberthür, 1909)	+	+	+	+							11
233. <i>Hyponephele lycaon</i> (Rottemburg, 1775)					+	+	+	+			10
234. <i>Hyponephele lupinus</i> (O. Costa, 1836)	+	+	+	+	+	+	+				10
235. <i>Proterebia afra</i> (Fabricius, 1787)	+										9
236. <i>Erebia ligea</i> (Linnaeus, 1758)		+	+	+	+	+	+	+			7
237. <i>Erebia euryale</i> (Esper, 1805)					+	+	+	+			3
238. <i>Erebia manto</i> (Denis & Schiffermüller, 1775)					+	+	+	+			3
239. <i>Erebia epiphron</i> (Knoch, 1783)					+	+	+	+	+	+	3
240. <i>Erebia orientalis</i> Elwes, 1909						+					15
241. <i>Erebia pharte</i> (Hübner, 1804)								+	+	+	3
242. <i>Erebia aethiops</i> (Esper, 1777)	+	+	+	+	+	+	+				7
243. <i>Erebia triaria</i> (Prunner, 1798)					+	+	+	+	+	+	15
244. <i>Erebia medusa</i> (Denis & Schiffermüller, 1775)					+	+	+	+	+		7

Table 2. Biogeographical division of the butterflies (*Lepid.: Hesperioidea & Papilionoidea*) on the Balkan peninsula.

	1	2	3	4	5	6	7	8	9	10
245. <i>Erebia alberganus</i> (Prunner, 1798)			+	+	+	+				15
246. <i>Erebia pluto</i> (Prunner, 1798)					+	+	+	+	+	3
247. <i>Erebia gorge</i> (Hübner, 1804)					+	+	+	+		15
248. <i>Erebia rhodopensis</i> Nicholl, 1900					+	+	+			15
249. <i>Erebia ottomana</i> Herrich-Schäffer, 1847					+	+	+			15
250. <i>Erebia calcaria</i> Lorković, 1949					+	+				2
251. <i>Erebia cassiooides</i> (Reiner & Hochenwarth, 1792)						+	+	+	+	3
252. <i>Erebia pronoe</i> (Esper, 1780)					+	+	+	+	+	3
253. <i>Erebia stirus</i> (Godart, 1824)					+	+	+			2
254. <i>Erebia styx</i> (Freyer, 1834)						+	+			3
255. <i>Erebia melas</i> (Herbst, 1796)	+	+	+	+	+	+	+	+		15
256. <i>Erebia oeme</i> (Hübner, 1804)					+	+	+	+	+	3
257. <i>Erebia pandrose</i> (Borkhausen, 1788)						+	+	+		1
258. <i>Melanargia russiae</i> (Esper, 1783)							+	+		15
259. <i>Melanargia galathea</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+		10
260. <i>Melanargia larissa</i> (Geyer, 1828)	+	+	+	+	+	+	+	+	+	12
261. <i>Satyrus ferula</i> (Fabricius, 1793)	+	+	+	+	+	+	+	+		10
262. <i>Minois dryas</i> (Scopoli, 1763)	+	+	+	+	+					9
263. <i>Hipparchia fagi</i> (Scopoli, 1763)	+	+	+	+	+	+	+	+	+	10
264. <i>Hipparchia syriaca</i> (Staudinger, 1871)	+	+	+	+	+	+				12
265. <i>Hipparchia aristaeus</i> (Bonelli, 1826)	+	+	+	+	+					14
266. <i>Hipparchia cretica</i> (Rebel, 1916)	+	+	+	+	+	+				15
267. <i>Hipparchia semele</i> (Linnaeus, 1758)	+	+	+	+	+	+	+	+	+	6
268. <i>Hipparchia mersina</i> (Staudinger, 1871)	+	+	+	+						11
269. <i>Hipparchia volgensis</i> (Mazochin-Porshnjakov, 1952)			+	+	+	+	+	+	+	13
270. <i>Hipparchia christensei</i> Kudrna, 1977	+	+	+							15
271. <i>Hipparchia pellucida</i> (Stauder, 1924)			+	+	+	+	+			11
272. <i>Hipparchia statilinus</i> (Hufnagel, 1766)	+	+	+	+	+	+	+			10
273. <i>Hipparchia fatua</i> (Freyer, 1844)	+	+	+	+	+	+				12
274. <i>Arethusana arethusa</i> (Denis & Schiffermüller, 1775)				+	+	+	+			16
275. <i>Brintesia circe</i> (Fabricius, 1775)	+	+	+	+	+	+	+			10
276. <i>Chazara briseis</i> (Linnaeus, 1764)	+	+	+	+	+	+	+	+	+	13
277. <i>Pseudochazara geyeri</i> (Herrich-Schäffer, 1846)					+	+	+			12
278. <i>Pseudochazara graeca</i> (Staudinger, 1870)							+	+	+	15
279. <i>Pseudochazara amymone</i> Brown, 1976			+	+	+	+				15
280. <i>Pseudochazara orestes</i> De Prins & Poorten, 1981	+	+	+	+	+	+	+	+		11
281. <i>Pseudochazara mniszechii</i> (Herrich-Schäffer, 1851)							+	+	+	15
282. <i>Pseudochazara cingovskii</i> Gross, 1973				+	+	+	+			13
283. <i>Pseudochazara anthelea</i> (Hübner, 1824)			+	+	+	+	+			12
284. <i>Oeneis glacialis</i> (Moll, 1783)							+	+	+	2
285. <i>Danaus chrysippus</i> (Linnaeus, 1758)	+	+	+	+	+					18

CONCLUSION

Based on literary data and our own results, the altitudinal distribution of all 285 butterflies species of Balkan peninsula has been presented for the first time.

Vertical profile of the Balkan peninsula is divided into 10 altitudinal zones, according to geological, historical, climate and phytogeographic features. Each species is present in one or more zones except for palearctic migrant *Colias croceus* that is present in all 10 altitudinal zones.

Two groups of species are narrow stenotopic and they are: species in the zone located between 0-450 m and species in the zone located between 1800-2925 m.

Complex biogeographic discontinuity between different faunistic groups is achieved through combining discontinuity in altitudinal distribution, horizontal distribution and in appearing period.

Biogeographic classification of Balkan peninsula butterflies has also been carried away (Table 2). Total 20 biogeographic regions had been identified, and each species was classified into one of these regions (Table 1, column 11).

The main material constituents of butterflies' community on the Balkan peninsula are Pontic-Mediterranean species (48), Middle-European species (45) and (Oro)Mediterranean species (31).

REFERENCES

- | VERTIKALNA
BIOGEOGRAFSKA
LEPTIRA BALKANSKOG
POLUOSTRVA | DISTRIBUCIJA
PRIPADNOST
DNEVNIH
(Lepidoptera: Hesperioidea & Papilionoidea) | I |
|---|--|---|
| Predrag JAKŠIĆ, Univerzitet u Prištini, PMF, Odsek za biologiju, Vidovdanska bb, 38000 Priština | | |
| U biogeografiji je poznato da je teritorija areala jedne vrste nehomogeno naseljena zbog variranja ekoloških faktora. Najvačniji uzrok te nehomogenosti na Balkanskem poluostrvu, kod dnevnih leptira, je orografski faktor. Ovaj faktor je, u kombinaciji sa geološkim i klimatskim faktorom, glavni uzrok bogatstva faune Balkanskog poluostrva. Iako je fauna dnevnih leptira Balkanskog poluostrva relativno dobro proučena pitanje njene vertikalne distribucije još nije razmatrano integralno. Posebno smo želeli da analiziramo stepen korelacije između pojASNOSTI vegetacije i rasporeda faune dnevnih leptira u tim pojasevima. Rezultate te analize smo prikazali na tabeli 1 (kolone 1 - 10). Odabrali smo 10 pojaseva na vertikalnom profilu Balkanskog poluostrva (0 - 2.925 m) nabazi istorijsko-geoloških faktora, istorijskih i savremenih klimatskih prilika i na bazi rasporeda vegetacionih pojaseva na planinama. | | |
| Istovremeno, u ovom radu je po prvi put prikazana analiza biogeografske pripadnosti 285 vrsta dnevnih leptira balkanskog poluostrva (tabela 1, kolona 11; tabela 2). Utvrđeno je postojanje 20 biogeografskih jedinica - 17 jedinica je iz okrila Palaearctica, 2 jedinice potiču iz Palearctika i jedna jedinica potiče iz Nearctica. Palaearktičke jedinice su u korespondenciji sa biomima, što je prikazano na tabeli 2 (Matvejev i Puncer, 1989; Lopatin i Matvejev, 1995). Na taj način je 285 vrsta dnevnih leptira Balkanskog poluostrva svrstano u svoje ishodne biome. | | |
- Bondev I., 1991. The Vegetation of Bulgaria. Map 1: 600 000 with explanatory text. St. Kliment Ohridski University Press, Sofia.
- Diels L., 1928. Kontinentalverschiebung u. Pflanzengeographie. Ber. d.d. Botan. Gesel., XLVI.
- Jakšić P., 1988. Provisional distribution maps of the butterflies of Yugoslavia (Lepidoptera: Rhopalocera). Societas entomologica Jugoslavica, Edit. separ., 1: 1-214, Zagreb.
- Janković M.M., 1985. Fitogeografija. Prirodno matematički fakultet Univerziteta u Beogradu i Jugoslovenski zavod za produktivnost rada i informacione sisteme. Beograd.
- Jovanović B., Rajna Jovanović and Zupančič M., 1986. Natural potential vegetation of Yugoslavia. Commentary to the map 1: 1,000.000 & Vegetation Map of Yugoslavia. Scientific Council of Vegetation Map of Yugoslavia, Ljubljana.
- Karsholt O. & Razowski J., 1996. The Lepidoptera of Europe. A Distributional Checklist. Apollo Books, Stenstrup.
- Kostrowicki A.S., 1969. Geography of the Palearctic Papilionoidea (Lepidoptera). Zakład zoologii systematycznej polskiej akademii nauk. Państwowe wydawnictwo naukowe. Krakow.
- Leestmans R. et Arheilger T., 1987. Les Lépidoptères du massif du Chelmos (Péloponèse, Grèce): inventaire et considérations zoogéographiques (première partie). Linneana Belgica, XI(4): 150-192, Vilvoorde.
- Lopatin I.K., 1995. Zoogeografija (Prevod sa ruskog Snejana Pešić), Zim-Prom, Kragujevac.
- Lopatin I.K. i Matvejev S.D., 1995. Kratka zoogeografija sa osnovama biogeografije i ekologije bioma Balkanskog poluostrva. Izdavač: dr. Sergej D. Matvejev, Ljubljana.
- Mägdefrau K. i Ehrendorfer F., 1988. Udzbenik botanike za visoke škole. Sistematika, evolucija i geobotanika. Školska knjiga, Zagreb.
- Manil L., 1990. Les Rhopalocères de Chypre. Linneana Belgica, XII (8): 313-391. Vilvoorde.
- Matvejev S., 1961. Biogeography of Yugoslavia. Biološki institut NR Srbije, Monographies, Vol. 9, Beograd.
- Matvejev S.D. and Puncer I.J., 1989. Map of Biomes Landscapes of Yugoslavia and their protection. Natural History Museum in Belgrade. Beograd.
- Pamperis L., 1997. The Butterflies of Greece. Bastas-Plessas, Athens.
- Varga Z., 1977. Das Prinzip der areal-analytischen Methode in der Zoogeographie und die Faunelemente-Einteilung der europäischen Tagschmetterlinge (Lepidoptera: Diurna). Acta Biologica Debrecina, 14: 223-285, Debrecen.

Received: September, 1998.
Accepted: October, 1998.

DISTRIBUTION OF SOME MICROELEMENTS IN MUSCULAR TISSUE AND ORGANS OF THE CHUBS (*Leuciscus cephalus*) CAUGHT IN THE IBAR RIVER

Mr Marija VUKAŠINOVIC¹, Dr Randjel MIHAJLOVIC², Nina PAVLIĆEVIĆ³

¹Veterinary Specialistic Institute "Kraljevo", 36000 Kraljevo, Yugoslavia, ²Faculty of chemistri, 34000 Kragujevac, Yugoslavia, ³Spec.tox.chem, Veterinary Specialistic Institute "Kraljevo", 36000 Kraljevo, Yugoslavia

ABSTRACT

The contents of copper (Cu), zinc (Zn), lead (Pb) and cadmium (Cd) in the muscular tissue, skin, gills, liver and kidneys of the chubs (*Leuciscus cephalus*) caught from January the 23 th to August the 15 th in 1995 in the Ibar river near Mataruška Spa, were estimated by atomic absorption spectrophotometry (AAS). A total of nine specimens were analised, one specimen being caught each month.

The presence of all investigated elements was detected in the muscular tissue, skin, gills, liver and kidneys.

The average copper concentrations were as follows: in the muscular tissue 1.75, skin 3.07, gills 6.32, liver 22.64 and kidneys 15.02 mg/kg.

The average zinc concentrations were: in the muscular tissue 3.70, skin 22.71, gills 28.03, liver 14.10 and kidneys 30.81 mg/kg.

The average lead concentrations were: in the muscular tissue 0.27, skin 0.81, gills 1.41, liver 2.47 and kidneys 3.20 mg/kg.

The average cadmium concentrations were: in the muscular tissue 0.02, skin 0.20, gills 0.14, liver 0.30 and kidneys 1.14 mg/kg.

Key words: Heavy metals, AAS, Tissues, *Leuciscus cephalus*.

INTRODUCTION

From Novembar 1986 to April 1987 permanently and since then from time to time there were detected increased amount of copper, zinc, lead and cadmium in the waters of the Ibar (1).

Earlier works have shown that microelements introduced with food and water accumulate in the inner fish organs (4).

As fishes, in contrast to other organisms, satisfy their need for mineral matter not only from food but also from water, we have put a task to investigate the contents of Cu, Zn, Pb and Cd in the muscular tissue and organs (skin, gills, liver and kidneys) of fishes caught in the Ibar.

The aim of the present work was to establish the distribution of introduced microelements within the muscular fish tissue and different fish organs.

EXPERIMENTAL

Reagents

All chemicals used were of analytical grade from Merck and Fluka.

1. Stock standard solution of cadmium: Dissolve 1.000 g of cadmium metal in a minimum volume of (1+1) HCl. Dilute to 1 L with % (v/v) HCl.

2. Stock standard solution of copper: Dissolve 1.000 g of copper metal in a minimum volume of (1+1) HNO₃.

3. Stock standard solution of lead: Dissolve 1.598 g of lead nitrate, Pb(NO₃)₂, in 1% (v/v) HNO₃ and dilute to 1 L with 1% (v/v) HNO₃.

4. Stock standard solution of zinc: Dissolve 1.000 g of zinc metal in a minimum volume of (1+1) HCl and dilute to 1 L with 1% (v/v) HCl.

Work standard solution for cadmium (0.5-2 µg/mL), copper (0.5-5 µg/mL), lead (1-10 µg/mL) and zinc (0.5-1 µg/mL) were prepared immediately before the determination these elements in samples.

Apparatus

All the experiments were preformed on a Perkin Elmer 3 300 double- beam atomic absorption spectrometer.

Sample preparation

Weight 2.5 g of sample into a 600 mL beaker. Add 25 mL of concentrated HNO₃, coker with a watch glass, and boil gently for 30- 40 minutes to oxidize all the easily oxidizable material. Cool the solution and slowly add 10 mL of 70% HClO₄. Boil very gently until the solution is nearly colorless. Do not allow the solution to go dryness. Cool, add deionized water, filter and dilute to 50 mL with deionized water. This solution is aspirated intro the atomic absorption spectrometer and the absorbance due to Pb, Cu, Cd and Zn is measured.

RESULTS AND DISCUSSION

The results obtained on the contents of copper, zinc, lead and cadmium in the muscular tissue of the

chubs are shown in the Table 1. Graphic representations of the distribution of investigated microelements are given in Charts 1, 2, 3 and 4.

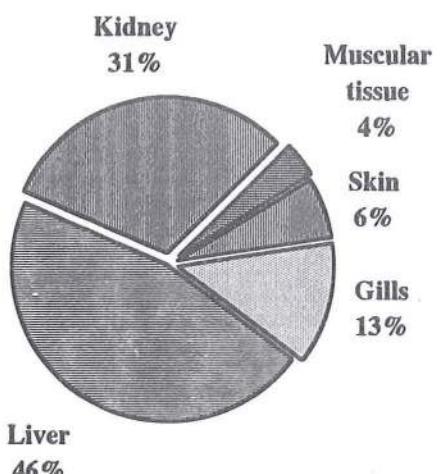


Chart 1. Distribution of copper

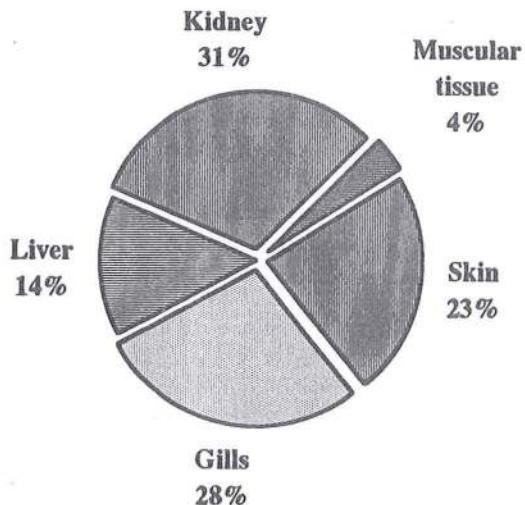


Chart 2. Distribution of zinc

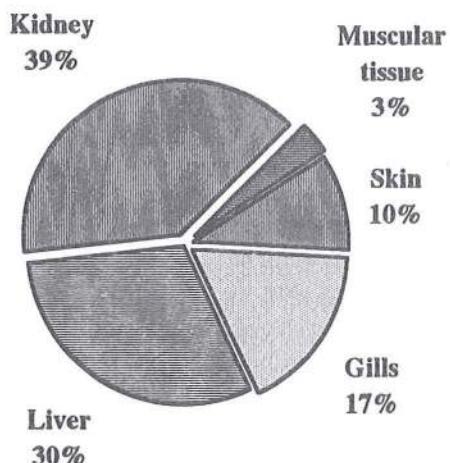


Chart 3. Distribution of lead

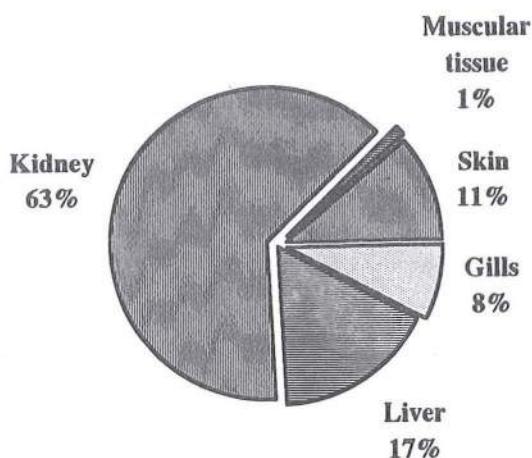


Chart 4. Distribution of cadmium

As seen from Table 1 the average zinc concentration in the muscular tissue of the chubs was 3.70 mg/kg, with variation range 0.23- 12.68 mg/kg; in skin 22.71 mg/kg with variation range 4.41- 69.25 mg/kg; in gills 28.03 mg/kg with a variation range 11.73- 65.13 mg/kg; in liver 14.10 mg/kg with a variation range 2.26- 33.72 mg/kg; in kidneys 30.81 mg/kg with a variation range 7.64- 60.45 mg/kg.

The content of zinc in muscular tissue was similar to that established by Brown and Chow (1977) which amounted 3- 9 mg/kg and Materna (1977) which was 7.7 mg/kg. Winikour et al. (1980) have reported that zinc concentration in the muscular tissue of trouts ranged within 100- 109 mg/kg of dry matter. In fishes caught in the Danube, Wacsh (1982) found zinc concentrations in the muscular tissue 2.5- 23.5 mg/kg; in liver 44.5 mg/kg; kidneys 75.4 mg/kg.

The average copper concentration in the muscular tissue was 1.75, skin 3.07, gills 6.23, liver 22.64 and kidneys 15.02 mg/kg; the variation range was 0.12- 3.40 for the muscular tissue, skin 0.50- 6.39; gills 1.14- 14.12; liver 2.01- 43.23 and kidneys 4.27- 34.73 mg/kg.

The copper content in the muscular tissue was similar to that established by Wacsh (1982) in the muscular tissue of fishes caught in the Danube (0.1- 1.9 mg/kg) but the content of copper was considerably lower in liver (4.0 mg/kg) and kidneys (1.1 mg/kg).

Our earlear investigations (Marija Vukašinović, Isidor Rajić, 1989) have shown that copper content in the muscular tissue of trouts bred in fish ponds ranged from 0.10 to 16.94 mg/kg. If fishes spend 12 weeks in water with 70 µg/L copper (Buckley and all., 1982), fish gills were contained 5.6 - 0.8 µg/kg Cu, kidneys 9.01+1.4 µg/kg Cu and liver 700+63 µg/kg Cu. At a copper concentration of 140 µg/L, after 12 weeks, it was founded 9.8+1.8 in fish gills, kidneys 13+4.0 and liver 718+25 µg/kg Cu. These data provide evidence that copper accumulates in the liver which is also confirmed by our investigations.

The average lead concentration in the muscular tissue of the chubs was 0.27, skin 0.81, gills 1.41, liver 2.47 and kidnyes 3.2 mg/kg.

Table 1. Average concentration of zinc, copper, lead and cadmium in the muscular tissue and organs of the chubs (*Leuciscus cephalus*), in mg/kg.

Variaton	Muscular tissue	Skin	Gills	Liver	Kidney
Zn					
x	3.70	22.71	28.03	14.10	30.81
Sd	3.79	21.55	20.06	11.21	21.62
Cv	102.53	94.90	71.55	79.48	70.18
Iv	0.23-12.60	4.40-69.20	11.70-65.10	2.30-33.70	7.60-60.40
Cu					
x	1.75	3.07	6.32	22.64	15.02
Sd	1.28	1.97	4.28	14.61	9.65
Cv	72.85	64.19	67.80	64.52	64.25
Iv	0.10-3.40	0.50-6.40	1.10-14.10	2.10-43.20	4.30-34.70
Pb					
x	0.27	0.81	1.41	2.47	3.20
Sd	0.14	0.61	0.88	1.47	2.32
Cv	52.85	75.21	62.16	59.44	72.55
Iv	0.00-0.40	0.10-1.80	0.20-2.50	0.40-5.20	0.40-7.90
Cd					
x	0.02	0.20	0.14	0.30	1.14
Sd	0.018	0.385	0.100	0.275	0.278
Cv	94.72	194.13	71.79	90.79	63.79
Iv	0.00-0.05	0.02-0.20	0.02-0.30	0.09-0.60	0.26-2.50

Materna (1977) has established that the muscular tissue of fishes contain lead in a concentration of 141 µg/kg. Ray (1978) has reported in Canada fishes contain lead in the muscular tissue in a concentration of 1.35 mg/kg, in liver 5.67 and in kidneys 6.82 mg/kg. Hegi and Geiger (1979) were founded that content of lead in muscle tissue of fishes was 0.048 mg/kg and in liver 0.067 mg/kg. Wong et al. (1981) have published that in fishes lead is first deposited in the fat tissue, skin and gills. Book of regulations on the amount of pesticides and other toxic materials (12) allows the presence of lead in fresh muscular tissue in a amount of 1 mg/kg.

The average cadmium concentration in the muscular tissue of the chubs was 0.02, in skin 0.20, gills 0.14, liver 0.30 and kidneys 1.41 mg/kg with a variation range for the muscular tissue from 0.00 to 0.05, skin from 0.02 to 1.22, gills 0.02 to 0.29, liver 0.02 to 0.69 and kidneys 0.26 to 2.54 mg/kg.

Badsha and Gainsbury (1977) have established that muscular fish tissue contain cadmium in an amount of 2.5 mg/kg (Severn river) and from 1.3 to 1.4 mg/kg (in rivers of the Southern England). Edgeren and Notter (1980) have found that cadmium is primarily deposited in the inner fish organs and only than in the muscular fish tissue. Book of Regulations of the amounts of pesticides and other toxic materials (12) allows the presence of cadmium in an amount of 0.1 mg/kg in fresh muscular fish tissue.

CONCLUSIONS

On the basic of the result obtained the following may be concluded:

1. The lowest levels of zinc, copper, lead and cadmium were found in the muscular tissue of the chubs (*Leuciscus cephalus*); these findings confirm earlier observations that metals accumulate in the liver, kidneys, skin and gills.

2. In chubs zinc is accumulated in the kidneys and gills, copper in the liver and kidneys, cadmium in the kidneys and liver.

3. From the standpoint of the content of toxic metals (Cd and Pb), the muscular tissue of the chubs that live in the Ibar river may be used in human diet.

REFERENCES

1. Badsha K.S., Sainsbury M., (1977): Uptake of zinc, lead, and cadmium by young whiting in the Severn estuary. Marine Pollution Bulletin 8, 164-168.
2. Brown J.C.R., Chrow L.Y., (1977): Heavy metal concentrations in Ontario fish. ZBulletin of Environmental Contamination and Toxicology 17, 190-195.
3. Edgern M., Notter M., (1989): Cadmium uptake by fingerlings of perc (*perca fluviatilis*) studied by aCd- 115 m at two different temperatures. Bulletin of Environmental Contamination and Toxicology 24, 647-651.
4. Hegi V.H.R., Geiger W., (1979): Schwermetalle (Hg, Cd, Cu, Pb, Zn) in Lebern und musculatur des Fussbarsches (*Perca fluviatilis* aus Bielersee und Walensee. Schweizerische Zeitschrift fur Hydrologie 41, 94- 107.

5. Materna V. (1977): Über den Blei -, cadmium - und Zinkhit in Fishen oboerserrchishert Gewasser (Dissertation), W.T.M. 64, 134.

6. Ray S. (1978): Bioaccumulation of lead in Atlantic salmon *Salmo salar*. Bulletin of Environmental Contamination and Toxicology 19, 631- 636.

7. Von Zbodo Wacsh, (1982): Schwermetallgehalt von Fishen aus der Donau. Z. Wasser Abwaser Forsch. 15, Nr.2, 43- 49.

8. Winikour W.S., Goldstain R.M., Anderson R.V., (1980): Bioconcentration patterns of zinc, copper, cadmium and lead in selected fish species from Tox River, Illinois. Bulletin of Environmental Contamination and toxicology 24, 727- 734.

9. Buckley J.T., Roch M., Mc Carter J.A., Randell C.A., Matheson A.T. (1982): Chronic exposure of cono salmon to sublethal copper concentrations- I Effect on growth, accumulation and distribution of copper tolerance. Comp. Biochem. Physiol. Vol 72 C, No 1, 15- 19.

10. Marija Vukašinović, R. Mihajlović, (1990): Investigation on the quality of water of the Ibar river during 1987., 1988. and 1989., Water protection, bulletin 85- 86, 8- 15.

11. Marija Vukašinović, I.Rajić, (1989): Investigation on the quality and contents of some microelements in the muscular tissue of trouts, Technology of meat 2, 61- 64.

12. Book of regulations (1983) on amounts of pesticides and other Toxic Matters, Hormons, Antibiotics and mycotoxins which may be present in the food.

REZIME

DISTRIBUCIJA NEKIH MIKROELEMENTA U MIŠIĆNOM TKIVU I ORGANIMA RIBA (*Leuciscus cephalus*) ULOVLJENIH U IBRU

Mr VUKAŠINOVIC Marija , Veterinarski specijalistički institut "Kraljevo", 36000 Kraljevo, Jugoslavija

Dr MIHAJLOVIĆ Randjel, Prirodno matematički fakultet, 34000 Kragujevac, Jugoslavija

PAVLIČEVIĆ Nina, Spec.toks.hem., veterinarski specijalistički institut "Kraljevo", 36000 Kraljevo, Jugoslavija

Praćen je sadržaj bakra(Cu), cinka (Zn), olova (Pb) i kadmijuma (Cd) u mišićnom tkivu, koži, škrigama i bubregu riba (*Leuciscus cephalis*) ulovljenih u Ibru kod Mataruške Banje od 23.01.1995. godine do 15.08.1995. godine po jedan uzorak mesečno. Ukupno je obradjeno devet uzoraka.

U mišićnom tkivu, koži, škrigama, jetri i buregu utvrđeno je prisustvo svih ispitivanih elemenata.

Prosečna koncentracija Cu bila je u mišićnom tkivu 1.75; koži 3.07; škrigama 6.32; jetri 22.64 i bubregu 15.02 mg/kg.

Prosečna koncentracija Zn bila je: u mišićnom tkivu 3.70; koži 22.71; škrigama 28.03; jetri 14.10 i bubregu 30.81 mg/kg.

Prosečna koncentracija Pb iznosila je: u mišićnom tkivu 0.27; koži 0.81; škrigama 1.41; jetri 2.47 i u bubregu 3.20 mg/kg.

Prosečna koncentracija kadmijuma bila je: u mišićnom tkivu 0.02; koži 0.20; škrigama 0.14; jetri 0.30 i bubregu 1.14 mg/kg.

Raspodela bakra (Slika 1) ukazuje na depozovanje ovog elementa u jetri gde je zastupljen sa 46%, bubregu 31%; škrigama 13%, koži 6% i mišićnom tkivu 4%.

Najviše vrednosti cinka utvrđene su u škrigama 28%, bubregu 31%, koži 23%, jetri 14% i mišićnom tkivu 4% (Slika 2).

Raspodela olova (Slika 3) izgleda ovako: 39% depozovano u bubregu, 30% u jetri, 17% u škrigama, 10% u koži i 3% u mišićnom tkivu.

Kadmijum je kao i ostali elementi utvrđen u najnižim koncentracijama u mišićnom tkivu 1%, škrigama 8%, koži 11%, jetri 17% i bubregu 63%. 1.

Naši rezultati ukazuju da se u mišićnom tkivu najmanje akumuliraju ispitivani elementi.

Received: November, 1998.

Accepted: December, 1998.

DEMOGRAPHIC AND ETHNIC PROBLEMS IN KOSOVO AND METOHIJA

Dedicated to the memory of Professor Radomir ILIC, Ph.D.

Professor Petar GOLUBOVIC, Ph.D., Assistant Suzana MARKOVIC Krstic
The Faculty of Philosophy

A B S T R A C T

The paper presents a number of historical and demographic facts of Serbian people and their endeavors to live and survive on their own land of Kosovo and Metohija.

The general appearance of Kosovo had been deeply changed in V and VI century when the Serbs settled this area and transformed it into an essentially Serbian country. In the Middle Ages Kosovo became the heart of spiritual and cultural growth of the Serbs. However, an extensive demographic shift was later induced by the immigration of the Albanians converted to Islam, the settlement of whom was highly favored by the Ottoman Empire. The territorial expansionism of Albania, found in 1913, arose the viewpoint according to which Kosovo and Metohija were to become a part of the newly established

state. The Albanian political aspirations to annex this territory persisted during the Italian and German occupation and after World War II; consequently, a considerable part of local Serbian population was forced or induced to leave.

The amendment of the Constitution of Serbia in 1989 influenced the political state of affairs of Kosovo and Metohija positively, for the Republic of Serbia assumed legal control of the province.

At present, the Serbs and members of other ethnic communities who do not support the Albanian territorial expansionism are being terrorized again. It has finally become clear that the Serbian Government must decisively defend the indisputable right of Serbia to the territory of Kosovo and Metohija.

KEY WORDS : Kosovo and Metohija, Serbs, Albanians, Charter of Decani, conversion to Islam, Serbia...

Deep sense of sacred duty to our people inclined us to open and highlight certain historical, demographic, social, and cultural problems of Kosovo and Metohija. Our task is to present the truth about the Serbian population of this area. Thus we intend to contribute to the rightful understanding of the efforts of Serbian people to stay in Kosovo which is their native soil and fatherland; at the same time we will try to prove that the Serbs have never been the conquerors, but honest and gentle folk.

Rich in fertile soil and minerals, the region of Kosovo had been exposed to a massive demographic turbulence in V and VI century when the Serbs reached these parts and made them densely populated and utterly indigenous by naming places, rivers, and hills¹. Due to the multitude of their people, conversion to Christianity, and, later, their political organization, the Serbs soon dominated the remainder of aboriginal population.

The name of Kosovo had never been mentioned in the old Serbian documents prior to XIV century. It firstly emerged in 1389, at the time of the Battle of Kosovo, and it was applied to places that formerly bore

other names. In several letters in Latin dated to this year Kosovo is referred to as Campus turdorum (thrush forest) or Campus merularum (blackbird forest). So, an opinion gained ground that the etymology of this place-name should, among other possibilities, be explained by the name of the blackbird (Serbian : kos). We believe this etymology to be the most probable and therefore accept it. Nevertheless, people believe that this name is derived from the verb to mow (Serbian : kosit), for Kosovo is "a true meadow of God", vast and covered with marvelous grass. Others claim that the name appeared as the result of numerous battles of many nations, for "many a dragon mowed and fought each other on its ground."² Its Slavonic origin is confirmed by the fact that this name is common to other areas inhabited by the Serbs, such as the village of Kosovac by the river of Drina and in Macva, the village of Kosovica near Užice, the hamlet of Kosovo in the mountain of Rudnik, which are all in Serbia. Located at latitude 42° to 43° northeast and at longitude 18° to 19° east, Kosovo borders the Kingdom of Serbia in the northeast, the region of Šara in the east, Metohija in the northwest, and the Sandzak of Novi Pazar, which lies beyond the mountains of Rožaje, in the north.³

¹ Branislav Nušić, Kosovo, Prosveta, Beograd, 1986, p. 9.

² Ibid., p. 10.

³ Ibid., p. 12.

When the Serbs settled this area in V and VI century they did not name it Kosovo because they distributed over the region according to their tribal structure establishing counties, some of which were named after rivers, hills, or settlements, such as Lab, by the river of Lab, or Lipljan nearby the famous Roman town of Ulpiana ; other names, however, like Sitnica or Drenica, were brought from the original Serbian homeland.⁴

Joined to other Slavic tribal territories, Kosovo was also exposed to frequent attempts of its neighbors to dominate it. In the middle of IX century, at the time of Bulgarian expansion, Serbia turned into a battleground of the Byzantine Empire and Bulgaria. Conversion to Christianity of the principal Serbian families was an important political success of the Empire. This led to the massive conversion of commoners followed by strong Byzantine political and cultural influence, the consequence of which upon development of the Serbs was to be felt much later. In the meantime the Empire weakened; its ultimate triumph was the conquest of Hungary and the surrounding Serbian territories under the Emperor Manojlo Komnin (1143 - 1180). This campaign, however, exhausted the sources of the Empire so the death of the Emperor was followed by a long period of crisis. The weakness of the Empire gave the Great Zupan of Serbia, Stefan Nemanja (1166 - 1196), an opportunity to enlarge his territory and to comprise the valleys of the Southern and the Great Morava, the present-day Kosovo, the plains around the Lake of Skadar, and the Adriatic coastal towns from Kotor to Skadar. This enlargement altered the denominational structure of his subjects, for the coastal towns were inhabited by Roman-Catholics, while the Greek Orthodox population was concentrated in the diocese of the Archbishop of Ohrid, including the dioceses of the bishops of Ras, Lipljan, and Prizren.

Thus the revival of culture in this region was distinctively marked by the progress of the Kingdom of Serbia and Serbian Orthodox Church. The cult of canonized monarchs glorified the authority of the dynasty and the State incorporated a specific Serbian tradition into the general Christian civilization.

The dynastic conflict between Stefan Dragutin (1276 - 1282, died in 1316) and Stefan Uroš II Milutin (1282 - 1321) at the beginning of XIV century jeopardized the achievement of the previous period. Therefore, weakening of the State and loss of certain territories marked the beginning of reign of Milutin's son Stefan Uroš II Decanski (1321 - 1331). The Charters of Decani, which appeared by the year 1330, contain surveys of monastic properties and settlements as well as censuses which prove that the inhabitants, including some Vlachs, bore Slavic names. "These Charters are solemn documents signed by the founder and sponsor of the monastery and they consist of a solemn part in which the sponsor denotes his own place in the history of his people and, optionally, as it is the case with two of the Charters, of the survey of his lands and possessions including people, and the list of other commodities which he presented as a gift to the monastery he spon-

sored; when the sponsor in question was a monarch, namely the king Stefan Decanski, the documents also contained his unalienable and indisputable rights."⁵

Three of these Charters were made while the monastery of Visoki Decani was being built and one of them is an eighteen century copy made in Baja, Vojvodina. They enable us to investigate the name of Metohija and give us an opportunity to learn about the medieval Serbia and its social conditions. The word metohion is of Greek origin and denotes the monastic property. The name was applied to the region between Pec and Decani, Djakovica and Prizren, and it confirms that even after seven hundred years of Turkish domination this region is still an essentially Serbian soil.

According to the data provided by these Charters, the Serbs of Orthodox denomination made 98 % of the population of Kosovo and Metohija in XI, XII and XIII century. Certain remote villages in the mountains west of Decani, such as the village of Mete, once completely Serbian and now of biethnic population, half Albanian and half Serbian, still remind us that this land once upon a time was a monastic property.

The specimens of fine architecture characterized by high artistic value witness the existence of the Serbs in this area over the centuries. Stefan Nemanja invested considerable financial means and labor into foundation of churches and monasteries in order to affirm the authority of the State which at that time became an important partner to the neighboring countries since it had comprised both coastal and continental regions. Sponsorship appeared to be an important act of medieval ruler's independence on all levels of authority and at the same time a major cultural event.

Among lots of monuments the following should particularly be mentioned : the monastery of Studenica Hvostanska from XIII cent., the Patriarchy of Pec built during XIII and XIV cent., the monastery of Gracanica sponsored by king Milutin, the foundation stone being laid in 1313, the church of the diocese of Lipljan beneath the present-day Gracanica, the church in Banjska, the church of St Archangel, and many others (see the map below). These most famous monuments of Serbian spirit and architecture point out that here was the heart of Serbian people and state.

Large stone-built fortresses of great strategic importance were distinguished elements of the image of medieval Serbia. White stone walls encircled towns, houses of the gentry, royal courts, monasteries, and military bases. Byzantine emperor and writer Constantine Porphyrogenit (mid X cent.) is the author of the oldest documents about fortified Serbian towns. Apart from towns in western parts of the country, he mentioned the town of Dostnik, present-day Drsnik in Metohija, as being the southernmost.⁶

The Turkish conquest of the Balkans, which was preceded and followed by migrations of the Serbs, stayed the entire progress of medieval Serbian culture. Unwilling to live under Turkish domination, the Serbs migrated and inhabited the waste frontiers. The Turks themselves forced some of the submitted Serbs to settle the devastated borders of the Ottoman Empire.

⁴ Ibid., p. 9.

⁵ Obeležja, Priština XII(1), 1982, Dr Dragutin Mićović, Imena metohijskih naselja, p. 154.

⁶ Istorija srpske kulture, Decije novine-Gornji Milanovac, Udruzenje izdavaca i novinara Jugoslavije, Beograd, 1994, p. 90.

After the conquest of Metohija, it took a century and a half for the Turks to submit the remainder of the Serbian State. From the middle of XV century until the early XIX century a large part of the oppressed Serbian population left their native soil and thus weakened the medieval nucleus of Serbian nation. Successive migrations took place in XVI and XVII century, best known

being the Great Migration of 1690. People remember another important migration of somewhat lesser intensity - the one from the year 1737. Both of these migrations were marked by the fact that the people were led by their Patriarchs Arsenije III and Arsenije IV. During the Great Migration of the Serbs about 37 000 families crossed the Sava and the Danube and settled as far as

Addition no. 1.

(source : Politika, October 7, 1998.)

MAP OF MONUMENTS OF SERBIAN CULTURE AND HISTORY IN KOSOVO AND МЕТОХИЈА



The fact that at least 300 monuments were left out of this map for the sake of legibility strongly confirms the presence of the Serbs in this region throughout the centuries.

the city of Buda, Hungary. In return, the Turks settled the Albanians from Malesija and from the highlands of Dukadjini all over now semi-populated Kosovo and Metohija; these settlers converted to Islam thus gaining numerous privileges in regard to Christian Serbs.

These newly converted Muslims joined the Turks in the attempt to reduce the Serbs and other Christians into serfdom. Highlanders from northern Albania who came to Metohija and converted to Islam were favored by the Turks more than Christian Serbs. Being an important resource of Turkish military power, guardians of northern and northwestern Turkish borders, and the "gendarmes" for the submitted nations of the Balkans, the Albanians became increasingly important for the Ottoman Empire.

The invasive immigration into Kosovo and Metohija lasted from XVII century on, and the Albanians of Metohija still keep their tribal names as well as the Serbian, i.e. Slavonic names of villages and towns in which they replaced the Serbs, phonetically adopted to the Albanian pronunciation, though.⁷

Conversion to Islam was never general, but it was perpetual and lasted until the beginning of XIX century in the north, i.e. the early XX century in the south. After the migration of 1690, The conversion was replaced by assimilation of the remainder Serbs in the boundary area between the two nations.

Dr. Milisav Lutovac⁸ discussed in detail the demographic movements in the area of Gora and Opolje. The inhabitants of Gora - the Gorans, present a Serbian oasis in the mountains of Šara and Koritnik since these parts had only partially been subdued to migrations. Relatively isolated population of these highlands was never directly exposed to the oppression and demographic movements typical for the lower country, so the Gorans remained Orthodox Christians longer than others.

They converted to Islam much later, due to the conversion in Ljuma and ethnic changes in the valley of the Drim and in Opolje.

The inhabitants of Opolje, on the other hand, belong to the Albanian-speaking community. They live in the ravine of Opolje and partially in the foothills of the mountain of Koritnik. Much flatter and richer in fertile soil than Gora, this region was attractive for the Turkish invaders - the fact that resulted in emigration of one, and conversion of the other part of local Serbian population. In time the natives amalgamated with the Albanian newcomers. The original homeland of these immigrants is shown in the Table 1.

As the survey shows, the clans immigrated from neighboring regions, mostly from Albania, Has, and Podrimlje. The time when this immigration began (mid XVIII cent.) and its intensity imply a considerable decrease in the local Serbian population caused by their previous migrations followed by anarchy that gave the

newcomers an opportunity not only to found new settlements, but also to occupy the existing ones which were already populated by the remaining Serbs.

Table 1. SURVEY OF THE IMMIGRANT CLANS ACCORDING TO THEIR NATIVE HOMELAND⁹

	CLANS	HOMES
Arbanija	18	283
Has & Podrimlje	9	150
Ljuma	5	58
Surroundings of Skoplje	2	45
Surroundings of Tetovo	2	28
Surroundings of Debar	1	13
Kačanik	1	2
Orson in Asia	1	20
Origin unknown	3	37
TOTAL	42	636

Although it is obvious that the Serbs had always been the native population of this region, they were quickly outnumbered by the Albanians and the converted and then assimilated Serbs.

In the war of 1876 - 1878 Serbia took possession of Toplica, Jablanica, and certain parts of Kosovo; the latest, however, had to be returned to Turkey according to the agreement made at the Congress of Berlin in June, 1878. Consequently, about 30 000 Albanians left Toplica and Jablanica and settled Kosovo; there they exposed the local Serbs to such terror and oppression that at least 150 000 of them emigrated from this region.¹⁰ This disturbed the ethnic balance that existed in Kosovo prior to 1878. Before this year the Serbs were still the majority; from 1878 to 1912 the two ethnic groups were equal in number, and after 1912 the ethnic structure changed in favor of the Albanians.

Spiridon Gopcevic, our famous countryman whose name is well known to any educated European, tried, as hard as any true patriot would, to present the truth about the Serbian people in the region of Old Serbia and Macedonia. Traveling through Old Serbia and Macedonia in 1888, Gopcevic had a burning desire to display the political, cultural and social state of affairs in our fatherland in order to accomplish the ultimate task : the union of all his compatriots within one single State of Great Serbia. He visited numerous villages and towns of this area and determined the exact number

⁷ Obeležja, pp. 158-159.

⁸ Dr Milisav Lutovac, Gora i Opolje, Beograd, 1995.

⁹ The Table taken from: Gora i Opolje, pp. 276-277.

¹⁰ Zbornik radova Filozofskog fakulteta 26 - 27 (1996 / 1997), Pritšina, 1997, pp. 112 - 113.

and ethnic structure of the inhabitants. He says : "Skoplje is a town of more than 20 000 souls. The population comprises 11 000 Serbs, 3 500 of whom being Muslim, 1 200 Jews, 150 Tzintzars, 400 Gypsies, 3 500 Albanians and 600 Turks. The Serbs speak Serbian pretty well, but many of them have been bulgarized due to the intensive propaganda."¹¹ He believes the majority of the present-day Albanians to be nothing else but assimilated Serbs. At the time of the Serbian Empire almost all of the Malisors and the people of the county of Elbasan were Serbian. The Serbian names of certain tribes and villages prove this. Over the centuries many of these names have been changed : Golobrdo to Koloparda, Belgrad to Berat, Sokol to Zogor, etc. The Malisors and the people of the Elbasan county still keep the memory of their Serbian origin, and many of them still honor their family Saints. Elbasan is full of Serbs 'under cover' who privately speak Serbian, honor their Saints and practice Christianity, but in public they declare themselves to be Muslim and speak Albanian."

Spiridon, who closely examined the history of Albania in XII, XIII, and XIV century, comes to the conclusion that it is not possible for the Shkipetars to have lived in Upper Albania, for Upper Albania has always been spoken of as a Serbian Country, governed by Serbian Zupans and Princes. The inhabitants of Upper Albania had always joined forces with the Serbs in every battle and war, so their destiny was always determined by the history of the Serbs - the history that never mentioned that the Shkipetars ever lived in Upper Albania. Dušan called himself "the Emperor of the Albanians" only after he submitted Lower Albania, Epyros, and Acarnania. "At those times Skenderbeg was called 'the Prince of Albania' and 'the Prince of Epyros' and the history knows him as the Albanian national hero. It must not be forgotten, though, that there is no Albanian nation as such, but there is only the geographical place-name of Albania. What we call the Albanians are in fact the Shkipetars."¹² Besides, the people of Upper Albania keep numerous expressions, festivities, and customs of Serbian origin - "therefore it is an obvious and indisputable truth that, in terms of ethnography, the population of Upper Albania does not belong to the Shkipetarian, but to the Serbian nation, and it has been so ever since the days of Skenderbeg."¹³

Prizren, once the capital town of the Kings of Serbia, had 12 000 homes and 60 000 inhabitants, the ethnic structure of which was as follows :

["] Turks	6 000
Catholic Albanians	1 200
Mohammedan Albanians	3 000
Christian Serbs	11 000

Mohammedan Serbs	36 000
Albanized Serbs	1 500
Tzintzars	700
Gypsies	800 " ¹⁴

Gopcevic also provides the data concerning Djakovica, which used to be a distinguished Serbian town, while now it is entirely albanized. "From 4 100 homes in Djakovica only 16 (!) are inhabited by the Serbs, 450 by the Gypsies, 130 by the Albanian Catholics, and the remainder are the Mohammedan Albanians - in fact all of them albanized Serbs ! who, as it usually is the case with renegades, are the greatest among the fanatics."¹⁵

The greatest changes of the ethnic structure in this part of Old Serbia took place between mid XVIII and mid XIX century, and between the Congress of Berlin in 1878 and the liberation from Turkey in 1912. This is confirmed by the numerous foreign authors, such as Joseph Muller who presented in 1838 the data concerning the ethnic and religious structure of the population of Pec, Prizren and Djakovica. "92 % of the population of Pec were the Serbs, 4 % the Albanians; 74 % of the population of Prizren were the Serbs, 17 % the Albanians; Djakovica, with 18 % of the Serbs, was the only town with the Albanian majority. Between 1876 and 1912 approximately 150 000 Greek Orthodox Serbs were forced to leave Old Serbia, called at the time the Vilajet of Kosovo."¹⁶

The League of Prizren was found in Kosovo and Metohija in June of 1878. This Albanian organization promoted the emigration of the Serbs in order to create a purely Albanian ethnic region and gain on that basis the autonomy within the Ottoman Empire. The notes of Russian lawyer and writer of travels Alexander Bashmacov, who traveled in 1908 through Montenegro, northern Albania and Old Serbia or Kosmet, witness the sufferings of the Serbs in Old Serbia. The panislamic propaganda worked out in detail, the pleaders of which appeared everywhere, and the intensified Austrian agitation incited the oppression upon the Orthodox population (banditism, etc.). The Albanians exterminated entire Serbian families, especially those of influential Christians distinguished by personal merits, power, or education. According to Bashmacov they killed 60 men in 11 villages. In the Nahija of Pec 180 Orthodox men were killed and 30 wounded during the following 14 years. The Nahija of Pec, settled in the western part of Metohija, had up to 3 000 Serbian homes with 15 000 people at the beginning of XIX century, while now there is approximately 3 000 ethnic Serbs in the area, and the town of Pec itself has only 490 Serbian homes with 2 500 inhabitants.¹⁷

¹¹ Spiridon Gopcevic, *Stara Srbija i Makedonija*, Parna štamparija Dimitrija Dimitrijevica, 1890, p. 189.

¹² Ibid., p. 208.

¹³ Ibid., p. 208.

¹⁴ Ibid., p. 210.

¹⁵ Ibid., p. 215.

¹⁶ Politika, 27. 08. 1998, p. 16.

¹⁷ Politika, 25. 07. 1998.

The national component of the problem became strongly emphasized after the Balkan War in 1912, when Serbia and Montenegro liberated Kosovo and Metohija from the Turks by joined military action and annexed these territories. The State of Albania was found in 1913, bordering Montenegro, Metohija and Macedonia. Henceforth the Albanian leaders intensified the politics of territorial expansionism in order to create "Great Albania". The factor of religion was also important, for the Islamic population traditionally averse Christian states and Muslims were the majority of the Albanian residents of Kosovo and Metohija; they could easily be engaged in combat for depriving the Serbs of their life space and for annexation of this region to the newly established State of Albania, itself dominated by Muslims.

While 497 000 people inhabited Kosovo and Metohija in 1912, in 1913, shortly after the liberation, this area was populated by 439 000 inhabitants, i.e. 58 000 people less than prior to the liberation, due to the emigration of Muslims to Turkey, the casualties of war, and the emigration of the Serbs during the Austrian occupation from 1916 to 1918. In 1931 Kosovo and Metohija were inhabited by 552 000 people, i.e. 113 000 people more than prior to 1921. 60 % of these people were the Albanians and the Turks, 32.7 % the Serbs and Montenegrins, and 7.3 % the remainder nations. In April of 1941, shortly before the World War II, approximately 666 000 people inhabited Kosovo and Metohija; the increase of 114 000 residents is explained by high birth-rate of the Albanians and the immigration between the Wars of 70 000 Serbs and Montenegrins, who now made 10.50 % of the total population.¹⁸

Immediately before the April War, and after the Italian occupation and annexation of Albania, the Comity of Kosovo, supported by Italy where it had been legalized, came to Albania and actively participated in the preparations for the future destructive actions in Yugoslavia, particularly in Kosovo and Metohija. Well known is the statement made by the Italian Count Cano according to whom the irredentism of the Albanians in Kosovo was "a knife pointed at the spine of Yugoslavia". The Count promised Great Albania and at the Beginning of the war both Kosovo and Metohija were joined to this fascist creation. Albanian nationalists and pleaders of territorial expansionism, as well as the Comity of Kosovo, overtook an extensive political activity in an attempt to popularize fascist Italy among the Albanian masses whose support they needed for the concept of Great Albania. Basically, they wanted to extend Albania in favor of Yugoslavia and to make new territories ethnically purely Albanian.

After the capitulation of Italy on September 8, 1943, Germany assumed control of the formerly Italian zone of occupation including Kosovo and Metohija. The Germans agreed with and supported the Albanian concept of dislocation of the Serbs and Montenegrins from Kosovo and Metohija. Between September of

1943 and April of 1944 the Serbs and Montenegrins were systematically forced or induced to leave Kosovo, and the Albanian attacks on Serbian villages became more frequent, more intensive, and more brutal. We lack the precise data concerning the number of Serbian refugees from Kosovo between 1941 and 1945, although it has been estimated at approximately 40 000 to 100 000. If prior to 1941 70 000 Serbs and Montenegrins settled in Kosovo, 20 000 of whom remained during the war, than at least 50 000 people left in this period. At the same time approximately 70 000 to 75 000 Albanians, former residents of Albania, immigrated to Kosovo between 1941 and 1944, and in that way significantly changed the ethnic structure of the population of Kosovo and Metohija in an attempt to establish an ethnically "clean" Albanian territory.¹⁹

In 1945 Kosovo and Metohija were given the administrative status of the Autonomous Region of Kosovo and Metohija within the People's Republic of Serbia. The principal goal of this autonomy was to insure legal rights for the Albanians and other ethnic minorities within Yugoslavia. Nevertheless, the administrative organs of the region comprised both the Albanian quislings and sympathizers of the National Liberation Movement, and they all formally declared the legal equality of all ethnic groups in the region.

In fact, they prevented the Serbian refugees from returning to Kosovo and misused the new laws concerning the ownership of land in favor of the Albanians, thus encouraging further emigration of the Serbs and Montenegrins. That was all a part of the plan for secession of Kosovo and Metohija from Yugoslavia.

On March 6, 1945, the Government of Yugoslavia decided to prohibit the return of the refugees to Kosovo and Metohija for the time being. This was induced by the political leaders of Kosovo and Metohija in order to avoid the presence of the refugees at the time when private property over land was to be revised. The Albanian secessionists got the benefit of this decision, for the decrease in Serbian and Montenegrin population made the existence of pure ethnic region more real and, in turn, increased the possibility of secession.

Due to this decision 2 450 families, or 10 300 individuals did not come back to Kosovo and Metohija. Between 1945 and 1946, 15 786 ha of arable land was expropriated from the Serbs and Montenegrins. About 10 300 people emigrated to Vojvodina while the immigration from Albania persisted, being supported by the political institutions of Kosovo and Metohija. According to the census of 1953, 816 000 people lived in Kosovo and Metohija, 816 000 i.e. 60 % of whom were the Albanians, which is 264 000 people more than the number of residents shown by the census of 1913. The increase of 525 000 people i.e. 64.34 % within the Albanian population in 22 years was the result of their high birthrate of 20 %, as well as of the immigration from Albania after the liberation. Serbian population decreased to 229 000 i.e. 29 % due to the exodus during

¹⁸ Zbornik radova Filozofskog fakulteta, Priština, p. 113.

¹⁹ Ibid., p. 116.

the war, casualties of war, the prohibition of returning of the refugees immediately after the war, and the emigration to Vojvodina in 1945 and 1946. The Turks 62 000 people i.e. 6.66 % of the total population.²⁰ It is obvious that the ethnic balance that existed prior to 1941 was disturbed in favor of the Albanians and that in regard to the total number of inhabitants the Serbian and Montenegrin population decreased while the increase of the Albanian population presents a permanent demographic characteristic of the area, as shown by the census of 1961 according to which the Albanian population increased from 64 % to 67 % and the Serbian and Montenegrin population decreased from 29 % to 27 %.

After the amendments of the Constitution between 1968 and 1971 Yugoslavia decentralized and Kosovo and Metohija became almost independent from the Republic of Serbia, so the perpetual oppression over the Serbs and Montenegrins increased in brutality while the immigration of the Albanians from Albania, Macedonia and Montenegro continued. Consequently, the census of 1971 showed that the Albanian population increased from 67 % to 74 % and the Serbian and Montenegrin population decreased from 27 % to 20 %. At the same time the Turkish population also decreased while the Gypsy population increased.

In 1974 the new partially confederate Constitution of Yugoslavia was established and the Province of Kosovo gained the prerogatives of the State, being joined to the Republic of Serbia only formally. Political leaders of Kosovo waited for an opportunity to formally decompose Yugoslavia and declare the Republic of Kosovo. The entire Serbian and Montenegrin population lived under permanent pressure, being continually forced or induced to immigrate, so 102 000 Serbs and Montenegrins left between 1961 and 1981. From 1974 on the financial means intended for subvention of the underdeveloped regions of Yugoslavia were constantly being invested in the future Albanian institutions and the purchase of Serbian land for the refugees from Albania was financed even from the funds of certain International Humanitarian Organizations. Thus the Albanian population of Kosovo and Metohija doubled between 1961 and 1981. According to the census of 1981 the population of Kosovo and Metohija numbered 1 585 000 people, 77.5 % i.e. 1 227 000 of whom were the Albanians (311 000 people more than a decade earlier) and 14.9 % i.e. 237 000 were the Serbs and Montenegrins (5.1 % less than a decade earlier). It is, however, important to emphasize that the data provided by the post-war censuses are not reliable because the data given by the Albanian residents were usually false.

The National Museum in Tirana found in 1980 contains a map of "the Albanian Territories" that had presumably been inhabited by the Illyrians, which include Kosovo and Metohija, a part of Montenegro, western part of Macedonia and the Greek province of

Chameria. According to the legend these territories were left "out of the homeland" in 1913. Contemporary Albanian leaders repeatedly stated that these territories must by all means be brought back to the "Mother Country". These territories have been the target of the Albanian territorial expansionism for centuries.²¹

The terror over the Serbian and Montenegrin population culminated in 1981, at the time of the Albanian separatist rebellion that lasted until 1989. Convincing that the time had come for the secession, the Albanians organized mass demonstrations in towns and villages and multiplied the pressure over the remainder Serbian population. Unprotected Serbs and Montenegrins immigrate so approximately 50 000 of them left Kosovo and Metohija between 1981 and 1990.

After the amendment of the Constitution of Serbia on March 28, 1989, the Republic of Serbia assumed legal control of Kosovo and Metohija. Some Albanians left their jobs, a part of the Faculty left the Albanian University and high schools, and the students followed them.

Since the Albanians boycotted the census of 1991 the contemporary statistical data concerning this ethnic minority, including the exact number of illegal immigrants, have never been determined. The data from the Press and certain publications are often subjective and approximate. Nevertheless, the number of the Albanian immigrants has certainly surpassed the number of the Serbian and Montenegrin emigrants so the ethnic structure of the Province endangers the integrity of its Serbian population.

At present, the Serbs and members of other ethnic communities who do not support the Albanian territorial expansionism are being terrorized again. The Serbs alone stay the progress of the Albanian territorial, political, and military aspirations. Attempting to reach these goals they use the fascist methods of mass destruction and torture (mass graves, massacres, cremation of men, women and even children). It has finally become clear that the Government of Serbia must decisively defend the indisputable right of Serbia to the territory of Kosovo and Metohija.

R E Z I M E

DEMOGRAFSKI I ETNICKI PROBLEMI KOSOVA I METOHIJE

Prof. dr GOLUBOVIC Petar, Asistent Suzana Markovic Krstic

Doseljavanjem srpskog stanovništva na prostore današnjeg Kosova, u V i VI veku, dolazi do znacajnih promena u ovoj oblasti. Naime, Srbi, koji su bili veoma brojni, pocinju da daju imena mestima, rekama, planinama, oblastima, donoseći u novu sredinu svoje navike i osobnosti, doprinoseći promeni ukupne fizičke ekonomije Kosova.

²⁰ Ibid., p. 127.

²¹ Politika, 06. 07. 1998.

Srednjovekovni duhovni i kulturni razvoj srpskog stanovništva biva ovekovecen u znamenitim spomenicima kulture (poput manastira, gradova), što samo dokazuje da je Kosovo bilo središte srpskog naroda.

Doseljavanje Albanaca i njihova afirmacija za vreme Turske Imperije i favorizovanje islamiziranih Albanaca kontinuirano je donelo niz demografskih i kulturnih promena na Kosovu.

Nastankom Albanije 1913. godine javlja se se ideja da Kosovo bude prikljuceno novonastaloj drzavi. Ta nastojanja se cesto opravdavaju tezom o ilirskom poreklu Albanaca i "oslobodenju" svih krajeva koji su naseljeni Albancima. U tom pravcu su išla mnoga nastojanja Albanaca tokom aprilskog rata pod italijanskim i nemackom okupacijom. Po oslobođenju Jugoslavije, obrazovanjem Autonomne Kosovske

Metohijske Oblasti u sastavu Republike Srbije stvaraju se uslovi za ostvarivanje "velikoalbanskih" ciljeva. Od tada Albanci smišljeno i planski proteruju Srbe a nasejavaju svoje sunarodnike iz Albanije.

U periodu izmedju 1981. i 1989. godine Albanci uporno pokušavaju da ostvare otcepljenje Kosova i Metohije putem ulicnih demonstracija i nemira. Republika Srbija 1989. godine preuzima državne prerogative na Kosovu i Metohiji, pa se situacija menja. Međutim, da pitanje Kosova i Metohije nije rešeno na zadovoljavajući i pravi nacin pokazuje stradanje i uništavanje Srba, danas na kraju XX veka.

Received: November, 1998.

Accepted: December, 1998.

BOOK REVIEWS - PRIKAZI

Zbornik radova V SIMPOZIJUM O FLORI JUGOISTOČNE SRBIJE, Zaječar '97. Univerzitet u Nišu, Tehnološki fakultet u Leskovcu, BD "Dr Sava Petrović" Niš i DD "Zdravlje" Leskovac, Niš, 1998.

U organizaciji tri navedene institucije i Biološkog društva "Dr Sava Petrović" iz Niša u Zaječaru je 1997. god. održan, sada već peti - tradicionalni, Simpozijum o flori jugoistočne Srbije. Radovi sa tog simpozijuma su publikovani u ovom Zborniku uz finansijsku podršku Ministarstva nauke Republike Srbije.

Na 362 strane Zbornika publikovan je 41 rad. Među njima jedan rad se odnosi na faunu Rotatoria, što po sadržaju i ne pripada ovome Zborniku. Dva rada su iz oblasti taksonomije i opšte problematike nižih biljaka a najveći broj ostalih (16) odnosi se na morfologiju, anatomiju, taksonomiju i floristiku vaskularne flore Srbije (i Makedonije). Dva rada tretiraju vegetaciju Zlatara i Stare planine. Ostali radovi pokrivaju različite

oblasti: biljnu etimologiju, primjenju fitofiziologiju i fitoekologiju i lekovita svojstva pojedinih vrsta naše flore. Radovi su pisani na srpskom i engleskom jeziku. Pojedini radovi pisani na srpskom jeziku imaju na kraju Rezime, dok drugi imaju Summary.

U prezentovanim radovima je izneta originalna naučna gradja, rezultirala iz terenskih i laboratorijskih istraživanja. Kao takva, bez obzira da li je u formi originalnog naučnog rada, ili u formi stručnog rada, ona će predstavljati dragoceni doprinos našoj botaničkoj nauci.

Organizatorima skupa upućujemo čestitke na uspešno obavljenom obimnom poslu. Takođe, upućujemo i sugestije da u narednoj svesci Zbornika radovi budu tematski razvrstani, da budu sadržajno uniformni, da se izvrši njihova UDK klasifikacija, kao i da Zbornik dobije ISBN oznaku.

P. Jakšić

Stanković S.M. (urednik), 1998.

ZBORNIK RADOVA EKOLOŠKA ISTINA. VI Naučno-stručni skup o prirodnim vrednostima i zaštiti životne sredine i XI Stručni sastanak preventivne medicine Timočke Krajine. Negotin, 27-30 maj 1998. Izdavač: Zavod za zaštitu zdravlja "Timok" Zaječar, Tehnički fakultet Bor, Društvo mladih istraživača Bor, SO Negotin, Centar za poljoprivredu i tehnološka istraživanja zaječar, RBN Bor, Ekološki pokret "Dubašnica" Bor. Bor.

U najnovijoj svesci ovog Zbornika na 490 stranica su prezentirani rezultati stručnjaka iz oblasti primenjenih i fundamentalnih geografskih i bioloških nauka, kao i zdravstvenih radnika angažovanih u domenu preventivne medicine. Ti su rezultati postignuti u proteklih godinu dana, u vremenu proteklom od prethodnog skupa "Naše ekološke istine". Ovo naglašavamo želeći da istaknemo činjenicu da TK i Bor posebno, u vremenu oskudice svake vrste, ulažu znatne napore i sredstva u one sfere naučne i stručne aktivnosti koje ne donose odmah, i ne tako vidno, korist.

Materija je u Zborniku podeljena na dva dela: plenarna predavanja i referate. Plenarnih predavanja ima tri i zbog značaja i interesa navodimo njihove autore i naslove: 1. Stanković S.M.: Geografska istraživanja

sistema čovek - životna sredina; 2. Ćurčić B.P.M., I.R. Savić, I.T. Radović i V.M. Jovanović: Biodiverzitet Jugoslavije: nastanak i istorijski razvoj, sa osvrtom na globalna shvatanja o njegovoj primenljivosti i vrednosti, i 3. Savić I.R., I.T. Radović, B.P.M. Ćurčić i A. Ćetković: Mogućnosti korišćenja biomonitoringa u funkciji očuvanja i zaštite biodiverziteta.

Drugi deo Zbornika čini 105 referata koji su tematski svrstani prema sledećim celinama: Naučnoistraživački projekti, Tehnologija i stanje životne sredine, Korišćenje i zaštita voda, Zaštita i očuvanje prirodnih vrednosti, Životna sredina i zdravlje, Ekološko vaspitanje, Ekološki menadžment, Socio-ekološki model zdravlja u teoriji i praksi, Mikrobi i ljudi, Demografski procesi u SR Jugoslaviji i Radovi naučnog podmladka.

Snalaženje u ovako obimnoj svesci Zbornika olakšava sadržaj i indeks autora. Prilozi su metodološki jednoobrazni, što je zasluga naučnog odbora i organizacionog odbora. Zamerke možemo uputiti jedino na vrlo sitna slova kojima je tekst štampan. Time je dobijeno na prostoru i uštedjeno na troškovima štampe, ali je pri čitanju potrebno naprezati oči.

P. Jakšić

PAMPERIS N. Lazaros, 1997.

THE BUTTERFLIES OF GREECE. Publications Bastas-Plessas & The J.F. Costopoulos (sponsor) foundation, pp. I-XII + 1-559, Athens.

ISBN: 960-7418-20-4

Ovo impresivno delo, formata A4, pored teksta sarži i brojne crteže, mape, dijagrame, tabele, karte rasprostranjenosti za 126 vrsta dnevnih leptira Grčke i 1.171 prekrasnih kolor fotografija adultnih leptira, njihovih razvojnih stadijuma i njihovih staništa. Sve ovo - tekst i likovni prilozi, je odštampano na najkvalitetnijem papiru i povezano tvrdim platnenim povezom. Tako ova knjiga, čija cena iznosi 100\$, ima i bibliofilsku vrednost.

U knjizi je prikazana fauna dnevnih leptira Grčke, koju čine 232 vrste, onako kako ju je višegodišnjim istraživačkim radom sagledao autor ove monografije. Te rezultate je autor prezentirao kroz poglavlja: Predgovor, Spoljne oznake dnevnih leptira, Staništa i životna sredina u Grčkoj, Detaljni opis utvrđenih vrsta, Ekologija dnevnih leptira, Rečnik pojmove, Bibliografija i Indeks.

Fauna dnevnih leptira Grčke je oduvek privlačila pažnju zbog svog bogatstva, naročito u tercijernim endemoreliktnim vrstama. Prvi opis leptira Grčke dao je još Aristotel (384 - 322). Temelje izučavanju ove faune uspostavio je Rebel (1910 - 1939) a posle II Svetskog rata Grčka je bila prava lepidopterološka Meka. Pamperisova monografija je kruna svih tih doprinosa i istinski ponos nacionalne faune.

U sadržajno najvažnijem delu knjige tekstrom i ilustracijama su predstavljene 232 vrste dnevnih leptira Grčke. Dat je dijagnostički opis, vreme leta, rasprostranjenje, osnovni podaci o ekologiji i stanje ugroženosti.

Ovaj tekst je propraćen sa ilustracijama. Za svaku vrstu je dat i dijagram koji prikazuje učestalost nalačenja u pojedinim visinskim zonama (0 - 3000 m) Grčke.

U poglavlju o ekologiji obradjena su pitanja životnog ciklusa, pronalaženja prehrambene biljke, predatora leptira, strategije preživljavanja, reprodukcije, specifičnosti prema staništima, retkosti, postanku i formiranju faune i aspektima njene zaštite. Koliko fascinantno izgleda bogatstvo faune dnevnih leptira celokupne Grčke, toliko iznenadjuje siromaštvo pojedinih regiona. Tako, jonska ostrva imaju samo 48 vrsta, Egejska ostrva 114, Peloponez 143 a Krit samo 45 vrsta. Ali, veliki broj lokalnih endema je nekako ravnomereno rasporedjen na celoj teritoriji Grčke pa je zbir vrsta impresivan. U poglavlju o poreklu dnevnih leptira Grčke autor ovo bogatstvo nije do kraja razjasnio - verovatno to zahteva zasebnu biogeografsku studiju.

Na brojnim dijagramima i tablama autor je dao mnoštvo korisnih informacija koje znatno upotpunjaju biološka znanja i služe kao izvrstan osnov za nove studije. Dosledno i argumentovano autor je diskutovao pitanje ugroženosti vrsta i dao je vrlo kvalitetno uradjenu listu od 109 vrsta koje su definisane kao ugrožene (E), ranjive (V) i retke (R). Izbor vrsta je zaista izvršen vrlo stručno, prema suštinskim kriterijumima koji su bitni za izbor. Ovo ističemo jer ima primera da se i u nacionalnim faunama pojedinih zemalja za zaštitu predlažu čak i vrste kojih uopšte nema u fauni tih zemalja. Poglavlje sa citiranim literaturom je pogrešno označeno kao Bibliography, a treba da stoji References, budući da su u njemu naznačeni samo oni radovi koje je autor koristio, a ne svi radovi o dnevним leptirima Grčke.

Sadržajno, vizuelno i stilski ova knjiga predstavlja izuzetnu celinu. Žalosna je činjenica da njenim pojavljivanjem Jugoslavija ostaje poslednja zemlja Evrope koja nema publikovanu svoju nacionalnu faunu ove grupe insekata. Uteha je da makar imamo uzor kako treba da je uradimo.

P. Jakšić

Vujić A., Šimić Smiljka, Milankov Vesna, Radović Dragana, Radišić P. i Radnović D., 1998.

FAUNA SYRPHIDAE (INSECTA: DIPTERA) OBEDSKE BARE. ZNAČAJ I POTREBA ZAŠTITE. Zavod za zaštitu prirode Srbije, Posebno izdanje br. 17, pp. 1 - 71, Beograd.

**YU ISSN - 0352-129
UDK - 595.773.1 (497.113)**

Publikovanje entomoloških monografija je kod nas prilično retko, zbog zapuštenosti entomološke nauke. Zato svako takvo novo delo zasluguje pažnju. U ovom delu su izneti rezultati originalnih naučnih istraživanja faune osolikih muva Obedske bare. Ova istraživanja su realizovana 90-tih godina, na 4 lokaliteta ovoga područja.

Rezultati pokazuju da na prostoru Obedske bare koegzistira 87 vrsta osolikih muva. To nije nimalo zanemarljiv broj vrsta, obzirom na monotonom staništu u kojima dominiraju zajednice šume topole i vrbe sa pratećim zajednicama močvarne i livadske vegetacije. Za utvrđene vrste su dati uobičajeni podaci: latinski naziv, rasprostranjenje (tip areala i rasprostranjenje na Balkanskom poluostrvu i u Srbiji), nalazi na području Obedske bare i ostala zapažanja. Jedna od utvrđenih vrsta je opisana kao nova za nauku. Dijagnoza i opis sa pratećim crtežima su potpuni ali novoopisana vrsta nije imenovana. Ovaj slučaj bi smo mogli da tretiramo kao NOMEN OBLITUM. Verovatno je to uradjeno zbog nalaza samo jednog primerka, mužjaka (koji predstavlja holotip). Na kraju rada je data zoogeografska analiza i istaknuta je potreba zaštite vrsta od značaja za područje Obedske bare.

Ukazali bi smo ovde i na odredjene nedoslednosti u tekstu. Zapaža se odsustvo biogeografski valjanog

koncepta tretiranja areala. Autori su podatke o arealima utvrđenih vrsta preuzeli od Peck-a (1988). Poznato je da je u praksi teško naći dve vrste čiji su areali identični. Tako su i ovde za 87 vrsta navedena 24 tipa areala. Očigledno je da nije primenjena biogeografski valjana koncepcija. Većina utvrđenih vrsta su, u stvari, palearktičkog raširenja, kako to i sami autori konstatuju na 53. strani, a među njima dominiraju srednjoevropske i submediteranske vrste. To je određeno samim geografskim položajem istraženog područja i tipom vegetacije. Potpuno ista situacija je ranije utvrđena i analizom faune dnevnih leptira Obedske bare (Rotschild, 1914; Tripković-Čubrilović, 1960). Prilikom razmatranja biogeografskih odlika područja

Obedske bare autori su citirali rad Jankovića (1984), ali su propustili da citiraju starije i potpunije rade Cincovića (1956) o tipovima livada Posavine i Brozove (1958) koja je prva opisala vegetaciju Obedske bare. Najzad, poglavlje "Larveno razviće" na 54. strani je trebalo uključiti u uvodnom tekstu na 8 - 9 strani, gde se govori o razviću.

Monografija ima 71 stranu teksta, od čega 61 stranu čini osnovni tekst, na jednoj strani je Summary a ostatak čine Pregled literature i Registar taksona. Monografija je publikovana u okviru proslave jubileja 50-to godišnjice Zavoda za zaštitu prirode Srbije.

P. Jakšić

ZAŠTITA PRIRODE, Broj 48-49 (za 1995-97) 1998., Str. 1-368. Zavod za zaštitu prirode Srbije, Beograd.

YU ISSN - 0514-5899

Najnovija sveska ovog časopisa u celosti je posvećena prezentaciji, valorizaciji i zaštiti geo-nasleđa Srbije. Zavod za zaštitu prirode Srbije se uključio u Evropsku asocijaciju za zaštitu geo-nasleđa (ProGEO). Rezultat toga uključenja i delovanja je organizacija naučno-stručnog skupa o geo-nasleđu Srbije (Novi Sad, 16-17. novembar 1995). Saopštenja izneta na tom skupu prezentirana su u ovoj svesci časopisa. Prema te-

matici raspoređena su po sledećim poglavljima: Ple-narni referati (10 saopštenja), Geokonzervacija - od inventara do zaštite (9 saopštenja), Važnost geostruktura za kulturno-istorijske spomenike i antropogeni uticaj (8 saopštenja) i Geo-objekti izuzetnih vrednosti na teritoriji Srbije (18 saopštenja). Na kraju je i usvojeni tekst deklaracije naučnog skupa "Geo-nasleđe Srbije".

Kako je istaknuto u uvodnoj reči urednika časopisa prezentirani radovi predstavljaju prvi korak u akciji očuvanja, uređenja i promocije geo-nasleđa Srbije.

P. Jakšić

Grubač B., 1998.

SURI ORAO - *Aquila chrysaetos* / GOLDEN EAGLE. Izdavač: Zavod za zaštitu prirode Srbije., Beograd.

ISBN 86-80877-01-8

Od Pančićeve knjige "Ptice u Srbiji" (1867.) do knjige "Ptice Srbije sa kartama distribucija" J. Rašajskog (1997) nižu se biseri srpske ornitološke literature. Ova monografija predstavlja perlu na toj niski. Monografija je reprezentativna: formata 30 cm, 128 strana, puni kunstdruk štamparije "Efekt" iz Beočina. Izdanje je realizovano povodom pedeset godina rada Zavoda za zaštitu prirode Srbije. Kolegi Grubaču je ovo druga monografija (prva je bila "Bradan - *Gypaetus barbatus*, 1990. g.) koja ga uvodi u krug naših najeminentnijih ornitologa.

U knjizi su sumirani rezultati dvadesetogodišnjeg istraživanja ove ugrožene vrste koja je stavljena na Crvenu listu faune Sveti, Evrope i Srbije. Zapažanja na terenu, vezana za brojne aspekte ekologije ove vrste, sistematično su prezentirana i stalno poređena sa podacima u domaćoj i inostranoj literaturi. Time je autor

na jedan suptilan način popunjavao mozaik znanja o ovoj vrsti a poređenjem sopstvenih zapažanja sa literaturnim podacima isticao osobenosti srpske (malobrojne) populacije surog orla. Detaljnim opisom staništa, ishrane, opštег ponašanja, gnezđenja, kretanja i odnosa čoveka prema ovoj ptici autor je razotkrio intimu ove vrste. To je bilo moguće samo velikim požrtvovanjem, često puta skopčanim i sa pitanjem lične bezbednosti.

Ovim delom je još jednom potvrđeno da je za biologe terenski rad najbolja laboratorija i da je jednostavna kineska izreka "Pođi do bora želiš li naučiti šta je to bor" ... velika mudrost. Priložene originalne fotografije su svedočanstva presudnih momenata u životu ove ptice a nastale su kao rezultat strpljenja i umeća. Preko 120 citiranih referenci ukazuje da je autor svestrano proučio biologiju ove vrste. Najzad, ova knjiga svojim sadržajem i tehničkim izgledom predstavlja međaš u domaćoj stručnoj literaturi jer buduće autore obavezuje na postignuti nivo, kolegu Grubača takođe. Najzad, moramo uputiti poljvale i Zavodu za zaštitu prirode Srbije koji je ovom knjigom i nizom drugih izdanja trajno obeležio jubilej na najbolji mogući način.

P. Jakšić

Kićović M.D., 1998.

TURIZMOLOŠKO EKOLOŠKI MOZAIK

Izdavač: Prirodno-matematički fakultet u Prištini; Studentski kulturni centar u Prištini i "Ecologica" u Beogradu. Priština.

ISBN 86-82697-06-8

Na 124 stranice teksta autor je sabrao radove koji su već publikovani u brojnim domaćim časopisima i zbornicima, tekstove prigodnih predavanja koji do sada nisu publikovani, kao i recenzije, uvodne reči i prikaze stručnih geografskih izdanja.

U ovome svojevrsnom zborniku - reprintu sakupljeno je 12 naučnih i stručnih radova. Kroz njih

provejava minuciozna autorova briga prema prirodi - kako da se ona zaštitи, unapredi i učini dostupnom čoveku a da ne bude narušena. Objekat autorovog interesa je severoistočna Crna Gora (Rožaje, Berane, Andrijevica, Plav). Dr Kićović je vrsni poznavalac toga prostora i pišeći o njemu on pokazuje ističani smisao da preko uočenog suptilnog detalja istakne suštinske pojave i procese u prirodi. Posebno ističe destruktivne ljudske delatnosti u prirodi.

Prezentirani tekstovi imaju saznajnu vrednost i naročito značajno didaktičko značenje. Knjiga će kao takva biti od koristi studentima geografije i brojnim drugim korisnicima. Primedbu stavljamo na kartu Crne Gore sa zastarem granicama iz perioda prethodne Jugoslavije.

P. Jakšić

DRUGI BALKANSKI SIMPOZIJUM RATARSKIH KULTURA

16 - 20 jun, Novi Sad, Jugoslavija

Razlog održavanja ovog Simpozijuma je prezentacija najnovijih dostignuća i radova iz oblasti ratarsko-povrtarske proizvodnje. Rad ovog Simpozijuma je podeljen u dve sekcije, i to:

Genetika i selekcija,

Ekologija i fiziologija ratarskih kultura.

Prezentacija radova na ovom Simpozijumu je podrazumevala usmena (uvodna) izlaganja i izlaganja putem postera.

Iz navedenih oblasti ukupno je bilo prezentovano 264 rada, od toga 68 usmenim putem i kao uvodna izlaganja od strane najeminentnijih kako naših tako i stranih stručnjaka iz svojih oblasti. Iz oblasti genetike i selekcije putem postera je bilo izloženo 103 naučna rada dok je iz oblasti ekologije i fiziologije bilja bilo izloženo 95 radova.

Na ovom simpozijumu učešće su uzeli i strani naučnici i to iz 15 zemalja sveta (Francuska, SAD, Rumunija, Bugarska, Ukrajina, Republika Češka, Kina, Makedonija i dr.).

Poljoprivredni i Prirodno-matematički fakultet u Prištini bili su aktivni po pitanju ovog Simpozijuma. Sa Poljoprivrednog fakulteta prezentovana su 4 rada iz oblasti ratarstva i povtarstva. Kao prvi autori radovima su se predstavili prof. dr Radomir Ognjanović, prof. dr Zoran Ilić, mr Milan Biberdžić i mr Nebojša Gudžić. Sa Prirodno-matematičkog fakulteta (fiziologija biljaka) učešće su uzeli prof. dr Miodrag Jablanović i doc. dr Radmila Filipović.

Prateći rad Simpozijuma moglo se zaključiti da su radovi bili savremeni i da je obradjivana problematika o najnovijim aktuelnostima i dostignućima iz oblasti genetike, selekcije, ekologije i fiziologije ratarsko-povrtarskih biljaka.

Na kraju je zaključeno da se nastavi sa istraživanjem, sa razmenom mišljenja naših i stranih naučnika, sa željom da na narednom Simpozijumu bude još više naučnih radova iz navedene problematike.

M. Biberdžić

I KONGRES LEKARA PREVENTIVNE MEDICINE
MAKEDONIJE SA MEDJUNARODNIM UČEŠĆEM

Ohrid, 6 - 10 oktobar 1998.

Na I Kongresu lekara preventivne medicine Makedonije pored domaćih učesnika prisutni su bili i naučni radnici iz Jugoslavije, Bugarske, Ukrajine, Belorusije ...

Na Kongresu je usmeno i putem postera predstavljeno 695 radova iz različitih oblasti, kao što su: epidemiološki i socijalno-medicinski aspekti malignih oboljenja, epidemiološki i socijalno-medicinski aspekti kardiovaskularnih i pulmoloških bolesti, alimentarne intoksikacije i drugi vidovi trovanja hranom - zdravstvena ispravnost životnih namirnica, ishrana - dije-

toterapija, zdravstveno-ekološki rizici u urbanim i radnim uslovima, edukacija u sistemu zdravstvene zaštite, zdravstveno-informativni sistem, primarna zdravstvena zaštita i reforme u zdravstvenom sistemu, primarna zdravstvena zaštita kod nekih specifičnih grupa stanovnika, životna sredina i zdravlje ljudi, zarazne bolesti kao epidemiološki problem, zoonoze, vakcinacija, mikrobiologija, zdravstveno-ekološki aspekti vode i vodosnabdevanje, epidemiološki i socijalno-medicinski aspekti nezaraznih bolesti i drugo narušavanje zdravlja.

Sa Univerziteta u Prištini prisutne su bile kolege sa Prirodno-matematičkog fakulteta i sa Poljoprivrednog fakulteta, kao i naučni radnici iz Zavoda za zaštitu zdravlja.

Z. Ilić

VII KONGRES TOKSIKOLOGA JUGOSLAVIJE SA
MEDJUNARODNIM UČEŠĆEM,

Igalo, 21 - 24 septembar 1998.

Ekspanzija novih hemijskih znanja, tehnika i instrumentalizacije postavila je pred toksikologe čitav spektar novih zadataka. Od njih se očekuje da vladaju novim analitičkim tehnikama kao i znatnim teoretskim znanjem iz srodnih oblasti, kako bi mogli kompetentno da interpretiraju rezultate kvalitativne i kvantitativne analize.

Oblast toksikologije je vrlo široka i na samom Kongresu obradjivani su problemi iz analitičke toksikologije sa 8 radova, toksikologije životne sredine sa 20 radova, eksperimentalne toksikologije sa 67 radova, toksikologije i obrazovanja sa 2 rada, kliničke toksikologije sa 57 radova, problemi iz oblasti zakonske regu-

lative sa 5 radova, profesionalne toksikologije sa 78 radova, radiotoksikologije sa 7 radova, veterinarske toksikologije sa 5 radova i forenzičke toksikologije sa 11 radova, što ukupno čini 260 radova.

Pored učesnika iz naše zemlje prisutni su bili i toksikolozi iz Švedske, Rusije, Bugarske, Makedonije, Gruzije, Turske, Kanade, Grčke ...

Učesnici iz naše zemlje iz Beograda, Novog Sada, Niša, Leskovca, Prištine, Podgorice, sa različitim naučnim ustanovama prezentovali su najnovija naučna dostignuća iz različitih oblasti toksikologije.

Sa Univerziteta u Prištini radove su prezentovali kolege sa Medicinskog fakulteta (Baščarević S., Bursać M., Mitić R., Baljošević I.), Poljoprivrednog fakulteta (Ilić Z., Đikić A.) i Prirodno-matematičkog fakulteta (Filipović-Trajković R.).

Z. Ilić





UNIVERSITY OF PRISTINA
SERBIA

THE UNIVERSITY THOUGHT
PUBLICATION IN NATURAL SCIENCES

INSTRUCTIONS TO AUTHORS



The "University of Pristina publication in Natural Sciences" periodical, a publication of natural sciences, publishes original scientific papers and review articles as well as book reviews and "in memoriam" type articles from the field of theoretical and applied natural sciences. All articles have not been published before.

It is printed semi annually. All the articles are written in English with brief summaries in Serbian (the translation of summaries is arranged by the Editorial Board).

The length of original articles should not exceed 16 pages per article including illustrations. Written articles are sent to the Editor's address in two copies.

During the work, Latin names of plants and animals are underlined. If the list of species is considered, then it goes with the author's name and year of description, i. e., *Maja squinado* (Herbst, 1788), and the belonging to the system species is indicated in the title (*Crustacea, Decapoda, Brachyura*).

Measurement units should be presented in accordance of current standards (Système International d'Unités — SI).

When quoting feminine references, full name of is given, but with masculine names, the surname is followed by the first name initial. The full title is provided, with no abbreviations, and must be provided in accordance with the List of Serial Publications in the British Museum (Natural History) Library.

Reprints to the number of twenty without cover will be supplied free of charge. Additional reprints may be ordered with returned gallery proofs after acceptance of invoice.



Authors are expected to submit a computer disk (3.5" DOS formatted) with the final, accepted version of their manuscript in two printed copies (on laser printer if available). The manuscript and disk should include the clear indication of the word-processor and other program(s) employed. The preferable program is MS Winword (6.0 or higher), but some other may be also accepted (AmiPro or VenturaPublisher). Disk should also include a copy in an ASCII text-format. Authors are encouraged to submit all the computer graphics (in PCX or TIFF format) and tables, each in separate file. Drawings also can be done in black ink on smooth tracing paper. High contrast black and white photographs are supplied. All text file(s) should be written with one font and one size type throughout (10 pt). In any case of paragraph and table formating, the use of multiple spaces must be avoided. For the details of the file formats, fonts, software, etc. authors may contact the editor.

EDITOR

Predrag Jakšić, Ph. D.
Faculty of Science
Vidovdanska b.b.
38000 Pristina
Yugoslavia